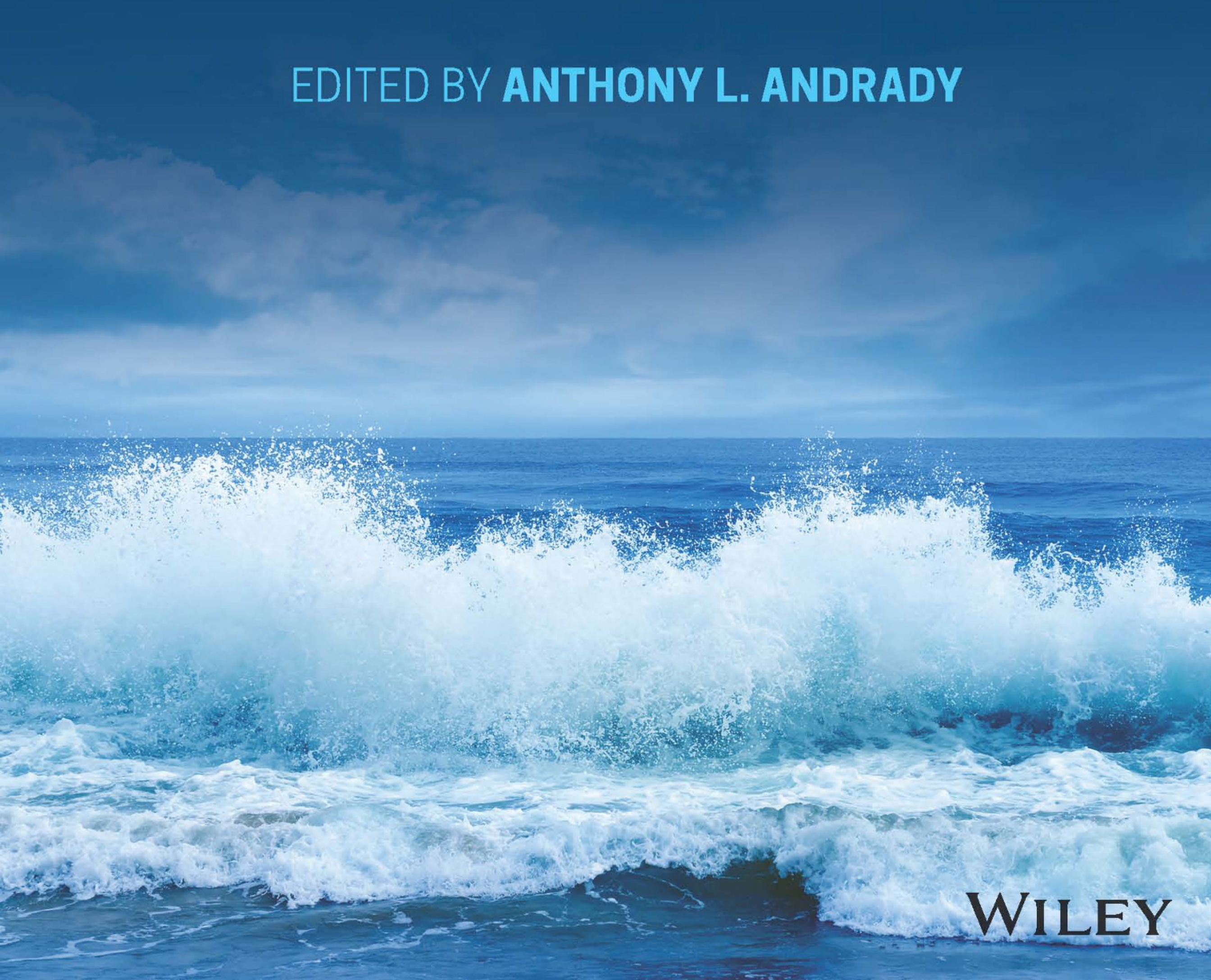
PLASTICS AND THE OCEAN

ORIGIN, CHARACTERIZATION, FATE, AND IMPACTS

EDITED BY **ANTHONY L. ANDRADY**



WILEY

Plastics and the Ocean

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts

Edited by

Anthony L. Andrady
North Carolina, USA

WILEY

This edition first published 2022
© 2022 John Wiley & Sons, Inc.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at http://www.wiley.com/go/permissions.

The right of Anthony L. Andrady to be identified as the author of the editorial material in this work has been asserted in accordance with law.

Registered Office
John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA

Editorial Office
111 River Street, Hoboken, NJ 07030, USA

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Wiley also publishes its books in a variety of electronic formats and by print-on-demand. Some content that appears in standard print versions of this book may not be available in other formats.

Limit of Liability/Disclaimer of Warranty
In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

Library of Congress Cataloging-in-Publication Data applied for

[Hardback: 9781119768401]

Cover Design: Wiley
Cover Image: © Serg64/Shutterstock

Set in 9.5/12.5pt STIXTwoText by Straive, Pondicherry, India

This work is dedicated with gratitude to my two mentors- Dr. R.O.B. Wijesekera (Ceylon Institute for Scientific Research, Colombo, Sri Lanka) and Professor Jim Harwood (University of Akron, Akron, OH, USA), both exceptionally talented teachers as well as accomplished researchers, under whose able guidance I was fortunate enough to receive my own training in scientific research.

Contents

List of Contributors

Linda A. Amaral-Zettler
NIOZ – Royal Netherlands Institute for Sea Research
Den Burg, The Netherlands
and
Institute for Biodiversity and Ecosystem Dynamics
University of Amsterdam
Amsterdam, The Netherlands

Anthony L. Andrady
Department of Chemical and Biomolecular Engineering
North Carolina State University
Raleigh, USA

Nathaniel J. Clark
International Marine Litter Research Unit,
School of Biological and Marine Sciences
University of Plymouth
Plymouth, United Kingdom

Garth A. Covernton
Department of Ecology and Evolutionary Biology
University of Toronto
Ontario, Canada

Lia N. Corbett
NIOZ – Royal Netherlands Institute for Sea Research
Den Burg, The Netherlands
and
Institute for Biodiversity and Ecosystem Dynamics
University of Amsterdam
Amsterdam, The Netherlands

Winnie Courtene-Jones
International Marine Litter Research Unit
School of Biological and Marine Sciences
University of Plymouth
Plymouth, United Kingdom

D. Cracknell
University of Plymouth
Plymouth, UK

Astrid C. Fischer
International Marine Litter Research Unit,
School of Biological and Marine Sciences
University of Plymouth
Plymouth, United Kingdom

Jennifer M. Lynch
Chemical Sciences Division, National Institute of Standards and Technology
Gaithersburg, USA
and
Center for Marine Debris Research, Hawaii Pacific University
Honolulu, USA

Amy L. Lusher
Norwegian Institute for Water Research (NIVA)
Oslo, Norway
and
Department of Biological Science
University of Bergen
Bergen, Norway

Francois Galgani
Institut Français de Recherche pour l'Exploitation de la MER (IFREMER),
Centre Méditerranée
La Seyne-sur-Mer, France

Olivia Gérigny
Institut Français de Recherche pour
l'Exploitation de la MER (IFREMER)
Centre Méditerranée
La Seyne-sur-Mer, France

Aoife A. Gowen
School of Biosystems and Food Engineering
University College Dublin
Dublin, Ireland

Xuan Guo
Laboratory of Environmental Technology
INET, Tsinghua University
Beijing, China

Peter T. Harris
Grid Arendal
Arendal, Norway

M. Kooi
Aquatic Ecology and Water Quality
Management Group
Wageningen University
The Netherlands

Bimali Koongolla
Guangdong Provincial Key Laboratory of
Applied Marine Biology
South China Sea Institute of Oceanology,
Institution of South China
and
Sea Ecology and Environmental Engineering
Chinese Academy of Sciences (CAS)
Guangzhou, China

Katrina Knauer
Novoloop, Inc.
Menlo Park, USA

L. Lebreton
The Ocean Cleanup
Rotterdam, The Netherlands
and
The Modelling House
Raglan, New Zealand

Daoji Li
State Key Laboratory of Estuarine and Coastal
Research
East China Normal University
Shanghai, China

Kai Liu
State Key Laboratory of Estuarine and Coastal
Research
East China Normal University
Shanghai, China

Angiolillo Michela
Istituto Superiore per la Protezione e Ricerca
Ambientale (ISPRA)
Roma, Italy
and
Stazione Zoologica Anton Dohrn (SZN)
Napoli, Italy

Thomas Maes
Grid Arendal
Arendal, Norway

T. Mani
The Ocean Cleanup
Rotterdam, The Netherlands

S. M. Mintenig
Aquatic Ecology and Water Quality
Management Group
Wageningen University
The Netherlands

M. B. Tekman
Deep-Sea Ecology and Technology, Alfred
Wegener Institute
Helmholtz Centre for Polar Research
Germany

Tim van Emmerik
Hydrology and Quantitative Water
Management Group
Wageningen University
The Netherlands

S. Nuojua
University of Plymouth
Plymouth, UK

S. Pahl
University of Plymouth
Plymouth, UK
and
University of Vienna
Vienna, Austria

Karen Raubenheimer
Australian National Centre for Ocean Resources and Security (ANCORS)
University of Wollongong
Wollongong, Australia

Katherine R. Shaw
Chemical Sciences Division,
National Institute of Standards and Technology
and
Center for Marine Debris Research
Hawaii Pacific University

Anna Schwarz
Netherlands Organisation for Applied Scientific Research (TNO)
Utrecht, The Netherlands

Natalie S. Smith
International Marine Litter Research Unit,
School of Biological and Marine Sciences
University of Plymouth
Plymouth, United Kingdom

Eric Tambutté
Centre Scientifique de Monaco
Monaco, Principality of Monaco

Brijesh Kumar Tiwari
Department of Food Chemistry and Technology
Teagasc Food Research Centre
Dublin, Ireland

Richard C. Thompson
International Marine Litter Research Unit,
School of Biological and Marine Sciences
University of Plymouth
Plymouth, United Kingdom

Tim van Emmerik
Hydrology and Quantitative Water Management Group
Wageningen University
Wageningen, The Netherlands

Jun-Li Xu
School of Biosystems and Food Engineering
University College Dublin
Belfield, Ireland

H. Wolter
The Ocean Cleanup
Rotterdam, The Netherlands

Jianlong Wang
Laboratory of Environmental Technology
INET, Tsinghua University
Beijing, China

Ming Zhao
School of Biosystems and Food Engineering
University College Dublin
Belfield, Ireland
and
Department of Food Chemistry and Technology
Teagasc Food Research Centre
Dublin, Ireland

Preface

Interestingly, the invention of the first plastic was closely linked to the conservation of the African elephant. The material was invented as a low-cost replacement for ivory used to make Billiard balls back in the 1800s. With a single elephant tusk yielding just three balls, the expense, difficulty, and perhaps even the brutality of securing ivory, drove Michael Phelan, a star player of the game and an entrepreneur of his day, to announce a prize for anyone with an apt substitute for the unique ivory. That led the US inventor Wesley Hyatt, in 1869, to come up with hardened nitrocellulose (which he called celluloid) as a good substitute. Though he did not receive the prize, his efforts ushered in an era of plastics, a defining feature of the anthropocene epoch. It was soon followed by Bakelite in 1907 and then by a series of other plastics that continue to serve us even today. In fact, all the common plastics in use today were discovered by the early 1950s. An early success was nylon (invented by Carothers at Du Pont) introduced to the consumer at the 1939 World Fair, causing a sensation with 64 million pairs of stockings sold in a year. As nylon was a replacement the natural silk used in hosiery, the discovery of this first synthetic textile fiber saved millions of silkworms from an early demise as the demand for fine natural silk leggings dropped.

Plastics captured the imagination of the public and much was expected of this miraculous material which lived up to public expectations, quickly finding applications in fabric, packaging as well as in numerous other consumer products. The August 1955 issue of the *Life* magazine proudly announced the dawn of a plastic era with “throwaway living,” where housewives would finally be relieved of having to clean utensils after each meal. Not only did this ominous claim come true with every single item in the Life magazine illustration becoming a common household product, but also introducing a host of innovative single-use plastics products widely used today. With nearly half the commodity plastics produced today devoted to disposable products, the unmanaged or carelessly disposed post-use plastics have now ended up in our environment, ironically harming wildlife, especially marine organisms. Today every aquatic system including the Marianna trench, the Arctic ice masses, and rivers on even uninhabited islands around the world are contaminated with post-use plastics. Marine convergence zones, like those in the Northern Pacific, concentrate small fragments of plastics, the microplastics, counted in the trillions in the upper ocean. As some plastics in the ocean sink to the sediment, what is sampled in surface water is only the tip of the proverbial iceberg. Their abundance in the water column, especially the bottom sediment, is reported to be much larger than in either surface water or the dry beach sediment. How much plastic enters the oceans is not precisely known. An estimate places the influx in 2010 at 4.8–12.7 MMT but it keeps growing each year.

An Already Stressed Ocean

The ocean that ends up receiving an annual increment of plastic waste from both land-generated debris *via* riverine transport and also directly from coastal areas, is already under stress. The burning of fossil fuels over the past several hundred years has already increased the acidity of surface waters by 30% threatening the survival of hard-shelled species; it's impact on the global fishery is not reliably known. Rampant unsustainable overfishing depleting the fishery, also leaves behind enormous amounts of derelict plastic gear each year, to continue on wasteful "ghost fishing" into the next generations. Ocean also has to contend with industrial or medical wastes that introduce either pathogens or toxic chemicals into the water, creating dead zones at sea. Over-enriching local patches of the sea by excess nutrients cause eutrophication, toxic algal blooms or fish kills. More than half the coastal and estuarine waters in the contiguous US are already affected by one or more of these phenomena to some extent.

To this already stressed ecosystem, human activity now introduces an annual load of at the very least, 8 MMT of plastic (even not counting ocean-generated plastic debris) with no known mechanism that can remove these plastics even in the long term. All the plastic debris discharged into the ocean, except for what gets washed ashore, accumulates in the bottom sediment, but little is known about how these plastics affect the benthic ecology. Recent studies estimate the floating plastics in the ocean in 2010 at 0.5 MMT; but this is only what can be sampled by plankton nets (mesh size 300 μm) and most of the plastic debris might be smaller, below the threshold size for plankton nets. Also, net-sampling of floating plastics excludes the majority of the plastic debris that resides in the water column or the benthos. Not surprisingly, what is counted is therefore far less than one might expect based on global plastic production.

Is it a Cause for Concern?

In common with all highly visible environmental problems with potential human health impacts, microplastics in the ocean has also been subject to media hype and exaggeration. But beyond the hyperbole, there lies a very real emerging problem that deserves the prompt attention of the research community. Exponentially growing research literature on the topic and many international professional forums addressing microplastics demonstrate some level of public commitment to the quest. Again, as with all environmental issues, some researchers do not agree that a serious problem does exist. Some point out that oceans are rich in natural micro-and nanoparticles in any event and the impact of the small fraction of microplastics would be minimal. Others cite the much higher microplastics concentrations (compared to levels likely to be present in the ocean), used in toxicology studies that show adverse impacts, to justify their stance. However, given that plastic waste will continue to be emptied into the ocean year after year, at the rate of about a garbage truck load a minute, (that will increase to four per minute by 2050), these arguments are not particularly persuasive. In fact, these are reminiscent of the complacency in the days before the Minamata tragedy in Japan in 1950s, where organic mercury was emptied into that river (coincidentally by a plastic manufacturer) on the expectation that the water concentrations would be far too low to cause any adverse health impact. Microplastics unlike the inorganic fines in the ocean are continually fragmenting organic particles that also absorb and concentrate persistent organic pollutants (POPs) dissolved in seawater. At least in some species ingesting them, POPs bio-accumulate and bio-magnify along the marine trophic chain, delivering progressively higher doses of the POPs, pharmaceuticals, metals, and enzyme-mimicking endocrine disruptor compounds to a range of marine organisms. With nanoplastics that can permeate the gut wall, these compounds can be delivered systemically. Microplastics present a threat that is very different from that of common toxicants and may well require criteria and methodologies beyond those in classical toxicology in their study. Even the toxicological data on the effects of microplastics ingestion often pertain to short-term studies and provide limited information. Virtually nothing is known of dose-response curves, long-term effects, embryonic toxicity, and intergenerational effects or their potential synergy with conventional toxic compounds. Not only do they have direct effects on the ingesting organisms but also indirect effects such as changing local marine biota by introducing rafter species, especially antibiotic-resistant bacteria developing on their surface biofilms.

How Much of a Threat do Plastics in the Ocean Pose?

MPs are ubiquitous in aquatic environments with about the same surface concentrations (from 0.01 to 1000 particles/m^3 of surface water) in the ocean and rivers around the globe. Over 50 trillion MPs were estimated as merely the floating stock in the ocean in 2017. Plastics are persistent and do not mineralize in an observable timescale, especially in the ocean. The threat of microplastics in the ocean persists beyond the present generation as their levels will keep increasing in future years and their ecological effects are likely to be irreversible. Available data show bioaccumulation of microplastics in several species and biomagnification by predation, while moving along the marine food web to reach the human consumer. For instance, some bivalves as well as commercial fish species are already reported to be contaminated with microplastics. That only two to three microplastics (discernible by eye or low power microscope) are found in a sample of fish or seafood species is not reassuring, because the fish could have been ingesting that amount of microplastics routinely and potentially bioaccumulating POPs sorbed by these in its tissue.

Their growing abundance indicated by an expanding body of research findings on microplastics in the ocean raises the question of their wider impacts on the ecosystem as a whole. Has the impact of microplatics now evolved beyond that of a mere pollutant, challenging planetary sustainability to exert a systemic influence on Earth's resilience? While they do not satisfy all criteria presently used to qualify as a planetary boundary threat, some have suggested that they would be a serious candidate phenomenon. There are, of course, many unknowns and the research that would address these gaps in knowledge needs to be undertaken without delay. The magnitude of microplastic-related impacts at the population level and how seriously they might impact the functioning of the physical and biological cycles in the ocean, remain unclear. So is the ingestion-related distress across the spectrum of marine organisms. Valid methodologies to allow decisions making despite these limitations need to be developed. Inadequate funding, especially in the US, to study such impacts especially at global hot-spots for plastic pollution, holds back this important task. Of the reviews on the topic published over the last few years, less than half are by scientists in Asia, the prime hotspot for plastic pollution. Also, a great majority of the research reports tend to be qualitative and the scarcity of relevant hard numbers to gauge the impacts, impedes this assessment.

Plastics in the ocean is a serious man-made problem that affects the present as well as future generations. A few decades from now, it may assume proportions that complicate or even defy any reasonable efforts at mitigation or containment. That the threat of plastic pollution of the ocean environment is serious and its effects irreversible are well established. Consistent with the precautionary principle, despite the scientific uncertainty of their full impact, adopting measures to curb the problem is prudent.

Anthony L. Andrady
Apex, NC 27523

Foreword

Charles James Moore

Moore Institute for Plastic Pollution Research, 160 N. Marina Drive, Long Beach, CA, USA

As I began writing this Foreword in the waning days of 2020, the media was replete with reviews of the year soon to be thankfully gone. Besides 2020 being one long battle against COVID-19, the narrator of the Columbia Broadcasting System's (CBS) year in review made the following statement: "2020 was the year the plastic pollution problem got the world's attention." Apparently, the problem was baking in the world oven for a good half-century and finally came out in a form that caught "the world's attention." For those of us working for decades to draw back the plastic curtain of ignorance that has kept the public from a general understanding of the material that characterizes the modern era, this was a belated yet welcome assertion.

The study of marine plastics arose before plastics were acknowledged to be problematic for the ocean. At first, marine scientists were simply noting that plastics had been found in birds and on the sea surface and were unsure of what this meant. The problematic nature of synthetic polymers in our water world could have been inferred from the fact there is no background or natural level of these persistent anthropogenic compounds anywhere. This makes them a priori a pollutant; they do not belong in or to any natural system. Small amounts of synthetic polymers in the environment might have been ignored by science, but the quantities rapidly increased and became impossible to ignore. Sadly, it is because of plastic pollution that we study ocean plastics. In this volume, an esteemed publisher of scientific literature and a world-renowned expert on environmental plastics have teamed up to give you widely varied perspectives that together demonstrate clearly that marine plastic pollution its own field of science. If science can be characterized as a branch of knowledge that provides answers by carefully studying a phenomenon from as many areas of expertise as possible, then the study of plastic pollution of the marine environment has surely become its own field of scientific inquiry. For a deep and broad understanding of the issues surrounding ocean plastics, Wiley could not have found a better editor for this volume than Dr. Anthony Andrady. His 2003 volume *Plastics and the Environment*, was the most comprehensive treatment of the subject ever written with contributions from twenty-two authors.

No scientists are exempt from the world views known as paradigms that reign in their historical milieu. Scientists are slow to acknowledge the need for a completely new field of research, and academic institutions and their funders are slow to divert resources to a new scientific discipline, so it has taken over half a century to create awareness and a consensus so that institutions can seek and give funding that opens wide the doors to plastic pollution research. The production of 1000's of peer-reviewed studies and several textbooks over the last quarter-century is strong evidence that plastics and the ocean are now linked in a novel, though highly undesirable marriage for the foreseeable future; an unhappy union whose dissolution will be messy and unknowably prolonged. A world polluted by plastic is indeed a new world, and its discovery and elucidation could be described as a scientific revolution.

Thomas Kuhn stated in *The Structure of Scientific Revolutions*, "Though the world does not change with a change of paradigm, the scientist afterward works in a different world. . ." May we not take exception to this dictum in the case of plastic pollution? The world has changed, since its water, air and soil, as well as the space around it, are infected with synthetic polymers never before seen in its long history. The contemporary scientific paradigm is an anthropogenic one, and the modern scientist works in a world, in many ways, made by humans.

The field of marine plastic research may conveniently be divided into three chronological phases:

1) The Discovery Phase, 1960–1999, when the phenomenon of ocean plastic was first reported and confirmed.
2) The Consolidation Phase, 2000–2014, when ocean plastic research produced considerable quan- titative data and highlighted areas of concern, mainly entanglement and ingestion. Other areas considered collateral were aesthetics, increasing international production of plastic consumer goods leading to increasing ocean plastics, biofouling, three-dimensional movement in the water column, transport of exotics and effects on the health of marine species.
3) The Rapid Growth Phase, 2015-present, when large institutions and governmental organizations began to see ocean plastics as worthy of high-level research and remedial action, and nongovernmental organizations focusing on plastic pollution worldwide.

The dawn of the Age of Plastic can be traced to its increased development and use in WWII. During the Pax Americana that followed, synthetic polymers spread rapidly from wartime to peacetime consumer and industrial applications. The famous LIFE Magazine article entitled "Throwaway Living," made single-use foodservice "modern" in 1955, but never addressed the after- life of the items thrown away. Away was far, not near. After three decades of this growing single-use lifestyle, the public became aware of problems with finding a faraway place for waste. This was highlighted by the long but circular voyage of the barge *Mobro 4000* from New York to Belize and back, when despite repeated attempts, no U. S. state, territory, or foreign country would accept 3000 tons of New York's garbage. Upon the barge's return to New York, symbolizing a very expensive and failed attempt to find "away," the refuse was burned and the ash buried in a landfill. To this day, many forms of burning and burying continue to dominate plastic disposal, both of which are polluting "solutions" that waste the energy and resources used to make the original products.

The question of what happens to trash in a landfill was explored in the 1970s by William Rathje, a professor of anthropology at the University of Arizona. He found that when buried deep in a landfill, common biodegradable items, such as carrots, hot dogs, and newspapers did not biodegrade. A similar result for the ocean was observed after the sinking of the deep submergence vehicle Alvin, operated by Woods Hole Oceanographic Institution. Carl Wirsen and Holger Jannasch recovered the soup, sandwich, and apple lunch that sank to a depth of 1500 meters when Alvin's lowering cable broke during surface launching. After 11 months of inoculation with seawater, "The apples were in a condition equal to that of conventional careful storage, and the bread, may onnaise, ham, and bouillon appeared to fare considerably better than they would have under normal conditions of refrigeration." Jannasch and Wirsen conducted subsequent experiments, using specially designed vessels lowered to great depths with biodegradable materials inside and then inoculated with seawater. They concluded that, "if the true removal of pollutants is intended, then the slow rates of microbial degradation argue clearly against deep ocean disposal." (Oceanus)

Seventeen years after the end of World War II, Steve Rothstein was studying seabirds and found certain petrel species (collected in 1962) had eaten plastic. As he told an interviewer compiling the early history of plastic pollution: "I didn't quite realize the significance of things. I figured, well, there's probably, maybe some plastic out there in the ocean and the birds are swallowing it. And I assumed that maybe everyone knows this, or it's not that worth reporting that much" (Plastisphere). As it turned out, it was indeed "worth reporting," but it would take two decades of such reports, mostly in journals and reviews characterized by Peter Ryan in "A Brief History of Marine Litter Research" as "not such good places," before the First International Marine Debris Conference was convened by the Southwest Fisheries Science Center in Honolulu in 1984.

Ed Carpenter, the first scholar to characterize floating marine plastics in the "good" peer-reviewed literature, (Science 1972), recognized potential problems associated with plastics in the ocean, such as their ability to sorb PCBs, and then be ingested by marine animals due to their ability to mimic natural prey, but he let the subject lapse after getting pressure from the Society of the Plastics Industry, leading him to wonder if his position as a marine biologist at Woods Hole might be placed in jeopardy by the industry complaining to his superiors. (Plastisphere Interview) Another paper published in a "good" journal, Nature, in 1974 by Wong et al. looked at "Quantitative Tar and Plastic Waste Distributions in the Pacific Ocean." The surface tows done for this study were conducted during the 1972 San Francisco to Honolulu Transpac sail race and would have avoided areas of light winds where debris concentrations may have been higher.

The initial response of the plastic industry to environmental plastic pollution was to consider plastic "litter" merely an aesthetic problem. After Carpenter's papers were published in *Science,* and Wong's in Nature, W.C. Ferguson, a member of the Council of the British Plastics Federation and a fellow of the Plastics Institute stated that "Plastics litter is a very small proportion of all litter and causes no harm to the environment except as an eyesore." This may still be the general public's attitude. Their nearly constant contact with the material, its lack of taste, smell, and obvious physical effects, have led most people to consider consumer plastics inert. If it were harmful in any way, why would it be used for our clothing, our home furnishings, and to serve and contain our food?

The need for a volume on plastics and the ocean before a volume on plastics in the soil or the air, or even in earth orbit, arises from the fact that the land we live on slopes down to the sea and gravity, coupled with wind and rain results in the ocean being the first receiving body to absorb massive amounts of vagrant plastics. The first plastics found by ocean scientists were a mix of discarded plastic consumer objects, but also pre-production plastic resin beads that came to be known as *nurdles*, the form that thermoplastic resin raw material is shipped to "converters," as the fabricators of plastic objects for the marketplace are known. These pellets showed up in the bellies of seabirds and in small mesh nets towed mostly at the ocean surface. In the decade following Carpenter's paper, larger objects came to be noticed and spawned the National Atmospheric and Oceanographic Administration (NOAA) international marine debris conferences. The early conferences focused primarily on derelict fishing gear as indisputable harm was being done to ships by blockage of intake ports and entanglement around propellers and drive shafts. To try to stop derelict nets and lines from being caught in propellers, several companies developed knives that could be attached to driveshafts to cut these lines as they wound around them. This fouling with debris had been a rare problem for vessels before the age of plastic, but as the age progressed, and less expensive and more persistent plastic fishing nets and lines proliferated, entanglement increased, and with its high cost to remedy, interest in tracking concentrations of this material became a new focus. Increasing reports appeared on derelict nets and fishing gear killing thousands of marine mammals through entanglement. This led to an interest in observing and recording the occurrence of floating marine debris. In 1987, two NOAA scientists at the National Marine Fisheries Service

Auke Bay Laboratory, Steve Ignell and James Seger, prepared a paper on methods for observing debris using line transects of vessels in transit. It was apparent to the authors that sunlight reflected by wavelets or "glare" would be "the most important single environmental factor affecting the sighting probability. . ." The paper was never submitted, probably because "Extensive analyses of sighting probabilities relating distance, wave height, and light conditions to type, sizes, and colors of marine debris will be needed to incorporate these data into debris estimation procedures." (Manuscript provided by Steve Ignell). The year before, Ignell had written another paper with Day and Clausen that emanated from the Auke Bay, AK laboratory entitled: "Distribution and Density of Plastic Particulates in the North Pacific Ocean in 1986." This paper preceded a more comprehensive study by Day, Shaw, and Ignell in 1990, "The quantitative distribution and characteristics of neuston plastic in the North Pacific Ocean, 1985–1989," published in the proceedings of the Second International Conference on Marine Debris in 1989. Plastic particulates were becoming more interesting, but the term "microplastics" was not yet used.

Surface drift up to this time had been in large part focused on the transport of fish eggs and larvae, especially those of commercially important species like salmon. James Ingraham Jr. had developed the Ocean Surface Current Simulator (OSCURS) for this purpose while working for NOAA in the Pacific Northwest. Collaborating with oceanographer Curtis Ebbesmeyer, he was able to adapt this simulator to track a container spill of Nike sneakers and predict where they would wash ashore on the West Coast. He expanded on this work to focus on North Pacific accumulation zones and presented his findings in the year 2000 at the 4th International Marine Debris Conference in Honolulu. The results showed two major areas of drifter accumulation: (i) off southern Japan, which has come to be known as the Western Garbage Patch and (ii) the middle of the eastern North Pacific which has come to be known as the Great Pacific Garbage Patch. The work by Day and colleagues never focused on the east-central North Pacific. When I crossed the area in 1997, I was impressed by the abundance of floating plastics. Two years later, I returned and sampled the area, finding three times the abundance and seven times the weight of the highest concentrations per km^2 found by Day a decade earlier in the western Pacific. In order to assess the potential for ingestion of plastics by open ocean filter feeders, we compared the abundance and mass of the zooplankton caught to that of the plastic in our manta trawls. We found the number of zooplankton was five times greater than the number of plastic pieces >0.3mm in diameter, but the weight of the plastic was six times greater than the zooplankton. We published our findings in *Marine Pollution Bulletin* (42,12, 2001). This finding was shocking and controversial, but to have more plastic than life anywhere in the ocean, no matter how you look at it, was explosive. Another important paper linking floating plastics to absorption of persistent organic pollutants was published the same year by Mato and Takada et al., "Plastic resin pellets as a transport medium for toxic chemicals in the marine environment." They found the pellets could sorb hydrophobic pollutants up to one million times their level in the surrounding seawater. This gave credence to the description of small ocean plastics as "poison pills" for marine creatures.

Of course, during these developments, the plastic industry and its professional organizations were becoming aware of calls to label plastic waste in the environment as pollution. I was invited to speak at a meeting of the Southern California Film Extruders and Converters Association and was introduced to an industry response that focused on making plastic waste "disappear" using an "OxoDegradable" plastic additive. There were two benefits promoted by the producer of the OxoDegradable additive. The first was that it would accelerate the breakdown of the polymer chain, minimizing the risk of entanglement, such as was seen to occur with plastic six-pack rings used to hold canned beverages. When discarded into the marine environment, they had been photographed choking several species. The second supposed benefit of the additive was more rapid biodegradation. The idea was that no matter how slowly, plastic polymers will undergo some biodegradation in the environment, and this process could be accelerated by mixing fragmenting agents into plastics to make them smaller. Although oxo additives did not themselves improve biodegradation, the fact that they produced smaller pieces of plastic suggested that they would disappear sooner through greater exposure per unit of mass to biodegradation organisms. A representative of the company was showing a jar of soil with fragmented plastics to make his point. However, when asked to produce proof of final degradation, none was forthcoming. This did not stop the company from telling its customers to label their plastic products biodegradable if they contained oxo-degradable additives. Experiments with the six-pack rings showed OxoDegradable additives to be ineffective in the cold, wet environment of the ocean, making their effectiveness in preventing entanglement questionable.

So, if you are the plastic industry, and you can't show that vagrant plastic waste will go "away," you might find it advantageous to blame consumers of plastic products for their failure to properly dispose of plastic waste. An extremely effective campaign was mounted by an industry- sponsored organization in the US called "Keep America Beautiful." Its focus was the "litterbug," who did not properly dispose of their used products. If only people would not litter, the problem of plastics in the ocean would go away. Even scientists studying the problem of ocean plastics believed this theory. After listing potential (though not actual) solutions in their paper: "Global research priorities to mitigate plastic pollution impacts on marine wildlife," Vegter and 26 co-authors con cluded that, if their potential solutions were implemented ". . .it would be feasible to deal with what is ultimately an entirely avoidable problem." It seems at just this point; the scientists stop being objective, and revert to fantasy. There is no avoiding the problem of ocean plastic pollution in any sense, nor is there any way for it to reach some sort of equilibrium or begin to diminish in any realistic near-term scenario. Plastic use will surge with the conversion of oil for fuel to oil for plastic. 3-D printing of everything imaginable with plastic feedstocks along with plastic packaging for nearly every manufactured product and many fruits and vegetables will contribute to the projected doubling or tripling of plastic production by mid-century. Therefore, it is very important to have a broad view of the resulting issues that you will get from studying the subjects covered in this volume. Plastic pollution and its effects will continue to plague the ocean for many future generations of scientists.

After my discovery or, more accurately, my confirmation of the existence of the "Great Pacific Garbage Patch," and publication of my findings in *Marine Pollution Bulletin* 42:12 (2001), I resolved to work diligently to highlight the issue of ocean plastic pollution, not only with the public but also with industry and the scientific community. I believed the role of "popularizer" of scientific findings to be an important one, and that I had sufficient speaking and writing skills to fill that role successfully. The most widely read article I wrote appeared in *Natural History* magazine. The article titled "Trashed, *Across the Pacific Ocean, plastics, plastics, everywhere*," appeared in November, 2003. After this article, I was besieged with requests for interviews with writers for many different publications from "Best Life, *Our oceans are turning into plastic . . . are we*," to "US News and World Report," and "Rolling Stone." Audio-visual media were also interested and I never turned down a single interview, from a student classroom to Late Night with David Letterman. Documentaries were made by the likes of Academy Award winner Jeremy Irons, who sailed aboard my research vessel to do the film, *Trashed*. Also sailing with me were the crews of Nightline and CBS Sunday Morning, among many others. I even took a public television film crew from the Korean Broadcasting System out to the Great Pacific Garbage Patch to film our research As the media began to produce more content on the issue of ocean plastics, the scientific community also began to show greater interest in the topic. A little-known Italian scientific organization, The World

Federation of Scientists, started by a physicist and scientific advisor to the Pope, had been holding annual conferences to discuss what they considered "planetary emergencies," such as climate change and pollution. For their 2006 meeting at their headquarters in Erice, Sicily, they wanted to include "Pollution of water by plastic" as a new planetary emergency. They reached out to Jean Michele Cousteau, President of the Ocean Futures Society, who had given a keynote address, "Trashing the Sea" at the 3rd International Marine Debris Conference in 2000. The organizers wanted him to present data on ocean plastic pollution, but his group had done no studies of the subject and had no data to present. They then contacted me to see if I would be willing to present my data at the conference, and I agreed. This meeting of top scientists was to become more productive than I could have imagined. There was a small press room, and a past editor of the Transactions of the Royal Society overheard me talking to someone about plas tic pollution. He approached me and offered to create a dedicated issue on the topic in one of the oldest and most prestigious scientific journals. Up to this time, no researcher had published on the transmission of chemicals sorbed to plastic into wildlife. Several papers were presented at the conference in Erice on the endocrine-disrupting effects of compounds in plastics such as BPA and phthalates, but the connection had never been established linking them directly to wildlife through plastic ingestion. The Theme Issue was edited by Richard Thompson, author of the paper "Lost at Sea: Where is all the plastic?," Shanna Swan, a researcher on phthalates at the USEPA and author of Countdown, Fred vom Saal, a pioneering researcher on the effects of BPA, and myself. The theme issue in *Transactions of the Royal Society B*, was titled "Plastics, the environment and human health." It contained the article by Teuten et al., "Transport and release of chemicals from plastics to the environment and to wildlife," which was an important milestone in the field of ocean plastic research. I bring up these personal experiences for two reasons: (i) some of these aspects of the history of plastic pollution research have not before been reported and (ii) to show how scientific progress may in some cases be advanced by individuals who straddle the line between research and activism.

After the Royal Society publication in 2009, research papers on the effects of chemicals associated with plastics became commonplace and we began to enter the rapid growth phase of ocean plastic research. The paper that created the most interest in ocean plastics after my actively promulgated finding that plastic outweighed zooplankton in the central Pacific was Jenna Jambeck's paper published in *Science* in 2015 titled "Plastic waste inputs from land into the ocean." The editor of this volume and the author of chapter 12 were co-authors. Both the scientific community and the public were shocked at the median figure of eight million tons of plastic waste per year enter ing the ocean, and that this amount would be likely to grow into the next century, since "peak waste" would not be reached before 2100. In 2016, based on this paper, the Ellen MacArthur Foundation predicted that there would be more plastic than fish in the ocean by 2050 and that one refuse truck's worth of plastic is dumped into the sea every minute. I would speculate that few major newspapers or online news platforms failed to mention one or both of these estimates. Images that showed the sea surface covered with plastic in near coastal areas became more com mon. Many had requested similar images of the "trash island" because of my work in the Great Pacific Garbage Patch. However, because debris there occurs in Langmuir windrows (long lines) that can stretch for more than 50 miles, and the debris is rarely touching, no areas covered in debris existed in the gyre, even in the areas with the highest concentrations of surface plastic. I have emphasized the point that plastics in the ocean are pollutants, but there is still considerable debate concerning their harmfulness. A milestone 2013 paper linking plastic ingestion in fish to negative physiological outcomes was by Chelsea Rochman and colleagues, "Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress." Consumption of plastic particles that had sorbed pollutants while floating in San Diego Bay resulted in liver abnormalities in fish.

There remained what many considered the most important aspect of plastic pollution, its effect on human health, as papers quantifying the plastics consumed in seafood were becoming common. In 2017, Fred vom Saal and Aly Cohen edited an Oxford University Press Publication titled Integrative Environmental Medicine intended for medical practitioners. Their goal was to mainstream cutting- edge concepts that were not taught in traditional medical courses. Sara Mosko, a physician and I contributed a chapter: "The Plastic Age: Worldwide Contamination, Sources of Exposure and Human Health Consequences." The Key Concepts included this provocative statement: "The list of human health problems that correlate with exposure to chemicals in plastics reads like a catalog of modern Western diseases." Although correlation is not causation, correlations do merit further investigation. We are now in the phase of plastic pollution research where the dividing line between environmental effects and medical research has been breached and medical researchers are looking seriously at potential human health effects. While at first, concerns about eating fish that had consumed plastic were paramount, we now have ample evidence that exposure through respiration is a greater threat, and that plastics at the nanoscale have invaded consumables of all kinds.

An implication of the dictum that the dose makes the poison is that as the dose of a substance increases, so does its potential toxicity. There are certain substances in plastics that contradict this. I imagine a crowd unable to get through a door when an individual could. Binding to receptors can exhibit a U-shaped curve where a very low dose given at the right time binds to a receptor and larger doses have less effect until the system is eventually overwhelmed at very high doses. Future ocean plastic research will examine such questions and others as they relate to population-level effects.

This volume concludes with two chapters on behavior change and legal remedies, which are certainly important in stemming the tide of vagrant plastics invading the ocean and the entire biosphere. However, the economic drivers of plastic pollution are in the ascendant, and until the worldwide growth of infinitely variable plastic products is redirected by a major paradigm shift, scientists will continue to work in a "different" plastic world.

1

Plastics in the Anthropocene

Anthony L. Andrady

Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC, USA

We live in an era where human beings dominate and control most geochemical processes on Earth's surface, including some aspects of the ocean system. It is impressive that *Homo sapiens* accounting for a mere 0.01% of the biomass on Earth, can exert such control; the mass of structures built on Earth by man now exceeds the total biomass on the planet (Elhacham et al. 2020). The present epoch of man deserves to be formalized a distinct period, the Anthropocene, within the geological time scale (Crutzen and Stoermer 2000). This era started in the post-World War II (WWII) years (Steffen et al. 2015; Zalasiewicz et al. 2016) and is ongoing. Plastics, a unique identifier of the Anthropocene, survives as stratigraphic markers in the soil to guide future archeologists exploring our era. Historical origins of plastics, however, can be traced further back in history, perhaps to 1869, when Wesley Hyatt invented nitrocellulose as a potential substitute for elephant ivory that was used to make billiard balls at that time. Even though Wyeth's celluloid billiard balls were a failure (as some of them exploded on impact), this unique product opened the floodgate for synthetic plastic products in to the consumer world. But, the commodity plastics we are familiar with today, came of age much later when the War effort spurned a rapid expansion of the materials industry in the US with public funding allowing new plastic resin plants to be built to produce vital plastics for the military supply chain.

Postwar years saw the enthusiastic acceptance of plastics by consumers worldwide, thanks mostly to the efforts of industry to promote plastics as a unique "wonder material," and much was expected of this novel semi-utopian material that promised a wide range of affordable products. Today, plastics have emerged as the material of choice in a variety of applications ranging from food packaging to spacecraft design. The abundant societal benefits of plastics (Andrady and Neal 2009) are evidenced by the rapid substitution of conventional materials used in packaging, building, transportation, and medicine, with plastics. Plastics have, by now, become indispensable to the modern lifestyle, with their *per capita* consumption governed generally by the affluence of the country. While the US, Canada, and Japan, for instance, use over 100 kg *per capita* of plastics annually, India and some countries in Africa or Central Europe, use less than 50 kg *per capita* (e-Marketer 2021). To meet this steadily increasing global *per capita* demand of an average ~46 kg annually, plastic resin production had grown to 359 million metric tons (MMT); 432 MMT inclusive of the polymer used in synthetic textile fibers) in 2019. China accounted for about 30% of the production, and with ~50% of the global resin demand in Asia, the country is well poised to remain as the leading resin manufacturer in the world. The annual global production of plastics in the year

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

2015 alone, if processed into a thin plastic "cling film," was estimated to be large enough to wrap the entire earth in plastic wrap (Zalasiewicz et al. 2016).

An estimated (Geyer et al. 2017) 7300 MMT of plastic resin and fiber was manufactured globally from just after WWII until the year 2015. By 2020, this figure rose to 8717 MMT. More than half of this was either PE (~36%) or PP (~21%). In addition, the thermoplastic polyester (e.g., poly(ethylene terephthalate) [PET]) used in beverage bottles, polystyrene (PS) in packaging, and poly(vinyl chloride) (PVC) as a building material, were also produced. Reflecting their high-volume use, these same 4–5 classes of plastics typically dominate the plastic content in the municipal solid waste stream (MSW), in urban litter, as well as plastic debris in the marine environment. The current discussion is therefore focused on this limited set of plastic types: PE, PP, and PS foam that dominates floating plastic debris in surface waters of the ocean and nylons or polyamide (PA). PET, PS, and PVC, mostly found in the deep sediment. Deep-sea sediment is the most important sink or repository of waste plastics that enter the ocean every year. While no systematic quantitative assessment is available, there is little doubt that plastics accumulate in the benthic sediment and a recent estimate places it conservatively at about 14 MMT (Barett et al. 2020).

1.1 What Are Plastics?

The term "plastic" is used in common parlance as if it is a single material. But it is, in fact a broad category of materials that include hundreds of different types. Plastics are a sub-class of an even larger group of materials called the polymers, characterized by their unique long chain-like molecular architecture, made up of repeating structural units. They tend to be giant molecules with average molecular weights (g/mol) in the range of 10^5–10^6 (g/mol). Being a subset of polymers that can be melted and re-formed into different shapes repeatedly, they are therefore called thermoplastics. The word "plastic" is derived from 'thermoplastic [See Box 1.1]. Hundreds of chemically distinct types of thermoplastics exist, even though only a few are used in most consumer plastic products.

This is somewhat analogous to the about 95 elemental examples in the group 'metals' and their numerous commercially available blends, even though only a few common ones such as copper or aluminum are extensively used. The same is true of plastics, but even within a single type of plastic such as polyethylene (PE)[1] several different varieties of resins with different characteristics are available. For instance, the common varieties of PE are low-density polyethylene (LDPE), high-density polyethylene (HDPE), medium-density polyethylene (MDPE), and linear low-density polyethylene (LLDPE) resins. Each of these varieties includes different grades of that plastic with range of properties despite their identical repeat-unit chemical structure. For instance, one grade of LDPE (low molecular weight grade) is a soft wax used as a lubricant, while another (ultra-high molecular weight grade) of PE, is spun into fibers so strong that they are used as an antiballistic material in military hardware. Therefore, in research reports, identifying a material just as a "plastic" or even as "polyethylene" is not particularly informative; details of at least the type, if available the grade, and its basic properties should be mentioned in order to compare data across publications.

---

[1] The term should really be "polyethylenes" because any given class of plastic such as PE includes many different grades of the same polymer that differ in their average molecular weight, molecular weight distribution, and polymer chain architecture such as the degree of branching. Despite the identical chemical structure, their key properties including strength, melting point and levels of crystallinity are very different.

Box 1.1 Thermoplastics and Thermosets

All plastics are polymers but not *vice versa*; plastics or thermoplastics include only those types of polymer that can be melted and re-formed into different shapes repeatedly. Therefore, polymers such as tire rubber, polyurethane foam, or epoxy resin as well as cellulose or proteins, that do not melt on heating by virtue of their molecular architecture, are not thermoplastics but are thermosets. What is commonly described under "plastic debris" or "microplastics" in marine debris literature, however, often includes some thermosets such as epoxy resin, reinforced polyester (e.g., glass-reinforced plastic (GRP)) and tire rubber particles. In this chapter, we will use the term "polymer" interchangeably with "plastic" for convenience of discussion.

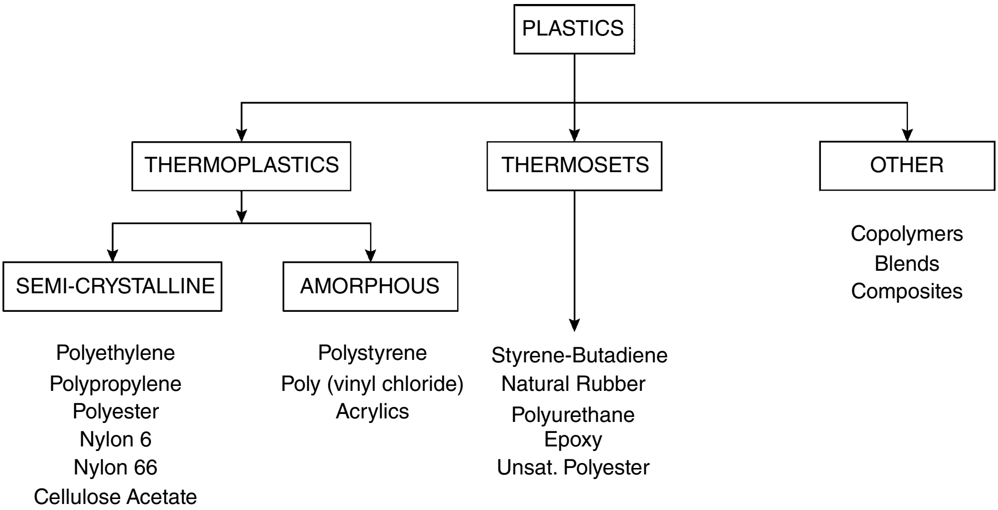


Figure 1.1 Classification of plastic types commonly found in the marine environment.

Plastics owe their impressive success as a material to their unusual molecular structure that obtains a unique combination of advantages (Singh and Sharma 2008). Very long, chain-like molecules in polymers result in strong attractive forces between them that allow for the development of unusual strength in the material. If the long-chain molecules are flexible enough, they can also profusely entangle with each other, resulting in resistance to deformation, contributing to the strength of plastics. Thermoplastics can easily be formed into different shapes at relatively low temperatures to obtain lightweight (low density) products that are strong, transparent, bio-inert, and gas-impermeable, thereby making them ideal as packaging materials. Thermosets, especially polymer composites reinforced with fillers or carbon fibers, serve as a durable, high-strength, and corrosion-resistant material that allows a new degree of design freedom that is exploited in building design and transport applications. It is this combination of characteristics that impart the versatility of plastics in numerous applications. No wonder we now annually produce enough plastics that exceed the global biomass of human beings. Figure 1.1 shows the classification of common plastics in the marine environment.

Figure 1.2 shows a breakdown of the mix of plastic resins manufactured worldwide along with the main application sectors for different resin types. PE is the resin produced in the highest volume(~50%) followed by PP and PET. The figure shows that over 35% of resins produced are

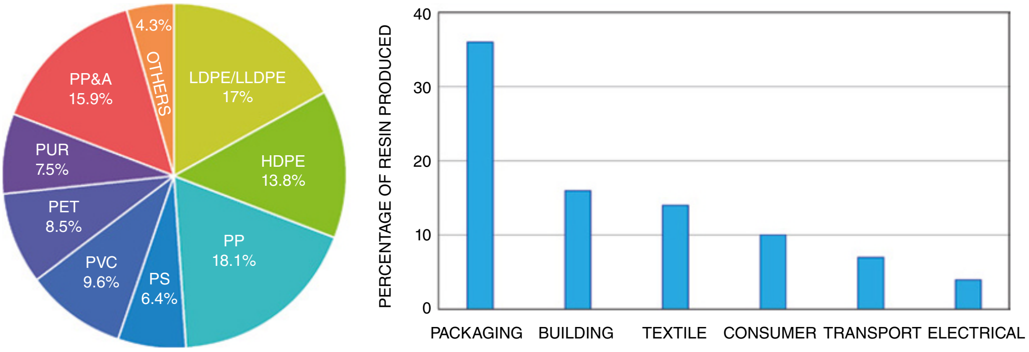


Figure 1.2 Left: Global plastic resin production (2015 data), Right: Percentage use of the production in different application sectors (miscellaneous categories not shown). *Source:* Redrawn from data in Geyer et al. (2017)

used in packaging where products are expected to have the shortest service life and are particularly likely to end up as urban or beach litter.

1.2 Plastics at Present and in the Future

At present, plastic production is a relatively energy-efficient operation supporting a vast global manufacturing industry providing an array of useful products at a resource cost of only about 4–6% of the annual global petrochemical demand (compared to the ~50% used for transportation). The embodied energy[2] EE (MJ/kg) of a material is a useful measure of how "energy-expensive" a given material might be and is the sum of all energy expenditure associated with producing a unit mass of the material or a functional unit of a product. This energy is not "embodied" in a product in the sense that all such energy can be recovered from the material. Market cost, however, is an unreliable guide to the EE of a material or product. Common plastics generally have a lower EE compared to metal, close to that of glass, but higher than that of wood. Most of this energy is typically derived from fossil fuel, a dwindling non-renewable resource that should invariably constrain global plastics production. But, a shortage of feedstock is not expected, especially in the US, at least in the foreseeable future; the boom in natural gas in the US (with about 500 trillion ft^3 of proven gas reserves) guarantees the availability of low-cost feedstock for plastics at least the next couple of centuries. Also widely anticipated is the freeing up of about 45% of the demand on global crude oil for gasoline production because of the expected growth in electric vehicles worldwide (CIEL 2021). The petrochemicals sector, including plastics, will then become the major driver for the petroleum industry, accounting for about a third of the future oil demand (IEA 2020).

As shown in Figure 1.3, manufacturing plastic resin requires a regular supply of fossil-fuel feedstock, a source of processing energy, as well as commons resources such as air or water, a category often either overlooked or incompletely accounted for in calculating the cost of the product, shown on the left side of the figure. In the process, the carbon in the feedstock is sequestered in the plastic resin, while that used as fuel to generate energy for the operation is released as CO_2. A suite of externalities that impact air, water, and the generation of solid waste accompany the manufacturing process. The result of this

---

[2] Embodied Energy (EE) is the energy expended in making a unit mass of the material from feedstock or the ore and includes energy used in raw material extraction, product processing, transportation, construction, use/maintenance, and disposal or reuse.

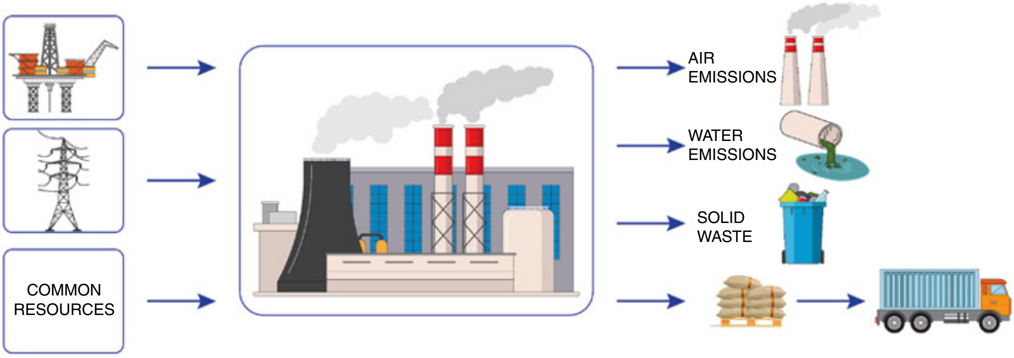


Figure 1.3 Schematic representation of the manufacturing process for plastics resin.

operation are plastic resin pellets. These resin pellets must be transported and further processed thermally to be shaped into useful consumer products that we are familiar with. This also requires additional energy and results in emissions, though to a relatively lesser extent compared to in manufacturing. It is the combination of these externalities, referred to as "embodied impacts," from manufacturing, use, and disposal, that is a major concern given the already-apparent signs of man-made climate change.

Global plastic production will keep increasing in the foreseeable future, especially given the availability of low-cost feedstock and the growing demand for resin. Even at present, the plant capacity for resin production both in the US and globally exceeds the current demand for resin. But, producers are already investing in additional plant capacity[3] anticipating a higher resin demand in future years. By 2050, the consumption of oil used to manufacture plastics is expected to outpace that by automobiles (IEA 2018). As production volumes invariably determine future environmental impacts of the industry, estimating resin production in the medium term is of special interest. An approximate estimate of future demand for plastics might be based on the analysis given in Figure 1.4 that plots the global resin production (MMT) with the world population (in Billions), with the trend therein extrapolated into future decades. Historic data fit a second-order polynomial model ($R^2 > 0.99$) and when extrapolated using projected future global population, the plot suggests an annual resin production of about 1040 MMT in 2050 and 2410 MMT in 2100. However, implicit in the extrapolation is the assumption that current *per capita* consumption of plastics will hold in the future generations, that likely underestimate future plastic production; the *per capita* use of plastics in high-income countries such as the US are expected to increase by 19% by 2050 (Kaza et al. 2018). More sophisticated predictive models estimate even a higher volume of future production of 1100 MMT (World Economic Forum 2016), 1800 MMT (Ryan 2015), or 4000 MMT (Rochman et al. 2013) by 2050. While accurate projections of production volumes are always difficult to estimate, it is reasonable to expect this volume to be at least 1000 MMT by 2050.

Manufacturing plastic resin at this unprecedented scale will entail a set of unique global environmental challenges. Instead of the current demand of 4% of annual fossil fuel production, plastics will then require 20% of the production, and result in 15% of the global carbon emissions (World Economic Forum 2016). Particularly worrisome are the estimated unmanageable increases in global CO_2 emissions in that scenario. This carbon footprint is primarily associated with manufacturing, use, and disposal of plastics and is referred to as "embodied carbon" or "aggregate emissions". Zheng

---

[3] The multibillion-dollar plastic resin manufacturing plant coming up in Beaver County, Pennsylvania, is expected to produce 1.6 million metric tons of plastic pellets annually when it opens in 2022.

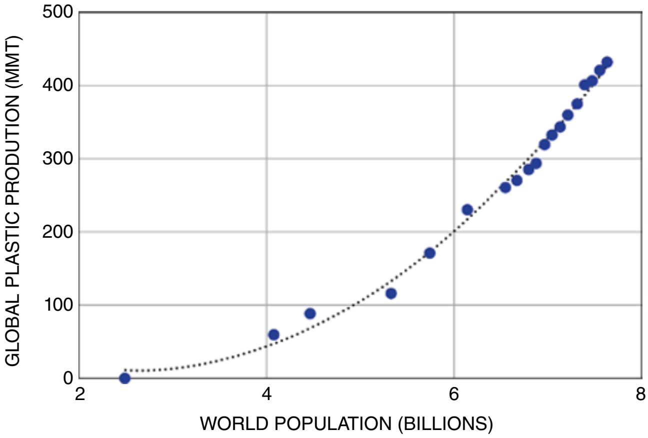


Figure 1.4 Global plastic resin production versus the population.

and Suh (2019), based on 2015 production data, reported annual lifecycle emissions of 1.8 GTCO$_2$-e from plastics, that amounted to only 3.8% of the global emissions in 2015. With the entire chemical industry accounting for only about 15% (Edenhofer et al., 2014) share of global emissions, this is a reasonable figure considering the societal value of plastics. The future forecast, however, is bleak, with an estimated 6.5 GTCO$_2$-e annually emitted by 2050 or nearly three times the present value attributed to plastics (Zheng and Suh 2019). This could even reach 8.0 GTCO$_2$-e if all post-use plastics are incinerated for energy recovery. That much of carbon emissions will not only be challenging to manage but will certainly make it difficult for the world to abide by the legally binding treaty agreed to by 197 parties (including the US) at the 2015 Paris Agreement, to hold global warming well below 2.0 °C (preferably to 1.5 °C) over the pre-industrial levels. With the global average temperature being only 0.8 °C short of this limit in 2020, achieving this goal will be a challenge in any event. Dire effects consequent to human failure at controlling climate change, including heat waves, ice-free Arctic summers, sea-level rise, declining coral reefs, loss of biodiversity, and lower crop yields, are already evident (IPCC 2018).

While the above discussion centered around CO$_2$, it is by no means the worst greenhouse gas responsible for warming; methane, nitrous oxide, and fluorocarbons are much more efficient as greenhouse gases.[4] Offsetting combustive CO$_2$ emissions by potentially better controlling the emission of greenhouse gases in other application areas may be of some help. With plastics, over 60% of the emissions arise from feedstock extraction or the resin production stage (either from oil extraction or fracking[5] for natural gas extraction), making material recycling an attractive strategy to reduce CO$_2$ emissions. While carbon emissions were used here to illustrate the problems of embedded impacts, it is certainly not the only negative environmental impact of plastic manufacturing. Externalities include acidification of water, water pollution, marine aquatic toxicity,

---

[4] Taking the global warming potential of CO$_2$ to be unity, that of methane is 28–36, nitrous oxide 265–298 and fluorocarbons is 10^4 or 10^5!

[5] Fracking is a technology used to recover natural gas (or even oil reserves) from shale, sandstone, limestone, and carbonite. The fracking liquid (water with dissolved chemicals) pumped under high pressure into the deep vertical fracking wells can contaminate the water table as well as streams or lakes from the invariable leaks and spills. Air pollution due to release of gas (venting or flaring) during the process is also a serious problem. With a majority of the producing wells using hydraulic fracking the cumulative effect on the environment is believed to be very significant. But, it is the boom in fracking that guarantees low-cost natural gas in the US.

photochemical oxidants, eutrophication potential, human toxicity, and ozone depletion potential (Stefanini et al. 2020).

A major consequence of higher production of plastics will be the increase in the post-consumer plastic waste stream, already ineffectively managed worldwide (Jambek et al. 2015; Lebreton and Andrady 2019). This burgeoning plastic waste not only impacts the municipal solid waste (MSW) stream that we poorly manage but also contributes to the unsightly urban litter. Unlike paperboard or wood, plastics do not biodegrade in any appreciable timeframe (see Chapter 11) and will persist as urban litter over an extended period of time. Cities with a high population density, such as Mumbai in India (76 800 persons/sq. mile), Karachi in Pakistan (49 000 persons /sq. mile), and Seoul in Korea (45 000 persons /sq. mile), will be particularly affected by the future plastic litter problem. A recent model based on population density (LandScan data), the GDP, and country-level plastic consumption data, identified future global "hot spots" for plastic waste generation, assuming a "business as usual" scenario (Lebreton and Andrady 2017). Worst affected regions in the next decades were identified as South Asia, East Asia, and South East Asia on a regional basis and China, India, and the Philippines on a country basis.

Geyer et al. (2017) estimated 42% of the plastics entering the waste stream at present to be packaging-related. The MSW in affluent countries is already rich in plastic packaging waste (Kaza et al. 2018). The fraction of all plastics in the MSW stream in the US has grown from negligible levels in 1970 to 16.3% by weight (357 MMT) by 2018, with PET, PE, and PP making up 32% of the total plastic waste. Plastic waste generation (PWG) *per capita* varies with the affluence of the country. Compared with the PWG of 88- 98 kg/year *per capita* for affluent countries such as Korea and the UK, less wealthy countries like India, China, and Pakistan generate only 13–19 kg/year *per capita*. The US has the highest PWG of 130 kg/year *per capita* (Law et al. 2020).

Proliferation of single-use plastic packaging, including beverage bottles, single-serve sachets, dessert cups, and disposable bags, has exacerbated the situation, especially in the more affluent countries (Geyer et al. 2017). How the generated plastic waste is managed also varies geographically, depending on the availability of adequate infrastructure. In affluent countries, a combination of landfilling and incineration is used, with the US relying heavily on landfilling.

1.2.1 Plastics in the Ocean Environment

In the 1970s, yet another dimension of plastic waste came to light with the discovery of plastic litter in the marine environment. The very first observations of plastics in the ocean dates back to 1972 (Carpenter and Smith 1972) and was followed by reports in the 1970s and 1980s on the high concentrations of plastics in the North Pacific (Day et al. 1990; Merrell 1980), North west Atlantic Ocean (Coltonet al. 1974), Mediterranean Sea (Morris 1980), and the Spanish Costa del Sol (Shiber 1982). A study of the ocean influx of plastics for the year 2010 (Jambeck et al. 2015) estimated that of the 270 MMT of plastics produced that year, about 32 MMT that ended up mismanaged waste was generated in coastal regions (constituting 50 km from the coastline). And assuming 3% of this waste to reach the ocean, the global marine influx was calculated to be between 4.8 and 12.7 MMT. The fraction of mismanaged waste plastics would not only be much higher today, compared to that in 2010 but the original estimate excluded plastics influx from marine activity such as fishing and riverine transport. Riverine transport of plastics from land into the ocean was identified as an important route in accumulating plastics waste (Leberton et al. 2017; Leberton and Andrady 2017; Schwarz et al. 2019), with the 20 top-polluting rivers accounting for as much as 67% of the annual input of plastic debris (i.e., 1.15–2.41 MMT annually) into the ocean (Lebreton et al. 2017). Plastic debris from commercial fishing activity also contributes a significant

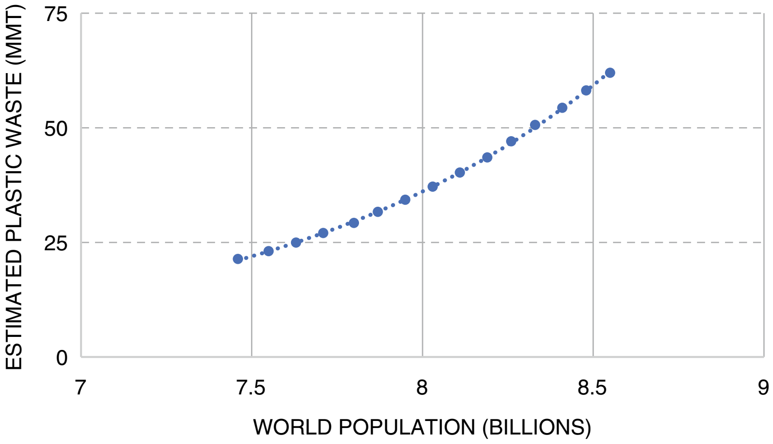


Figure 1.5 Estimated plastic waste in the aquatic system versus projected population growth (2016–2030). *Source:* Waste estimates from Borelle et al. (2020).

amount of gear-related debris (dolly ropes, net fragments, or floats) into the ocean, estimated at 0.6 MMT per year (Boucher and Friot 2017). Gear-related plastics are mostly PE and PP that are positively buoyant, as well as nylons (PA) used, for instance, in gill netting, that sinks in seawater. Also included in this category are the crab pots deployed in large numbers each season. With a significant fraction of 12–20% of them lost each season, ending up as ghost-fishing gear in the ocean. Ten thousand such pots are lost annually in Puget Sound alone.

In 1997, Moore et al. (2001) reported an unusually high incidence of plastic micro-debris in the North Pacific Gyre, a swirling vortex of water in the ocean, a couple of hundred miles North of Hawaii. In this 1.6 million sq. km. area (approximately 135°W to 155°W and 35°N to 42°N), the abundance of floating plastic fragments (some too small to be visible) was statistically higher than elsewhere at sea. A 2018 study estimated this garbage patch to carry 80 TMT of plastic, including ~1.8 trillion pieces of MPs (Lebreton et al. 2018). Misleadingly called the “Pacific Garbage Patch” in the media, the area is not a visible “patch” with obvious plastic floating debris, nor is it a floating island of dense plastic litter. The swirling water collects the micro-plastic fragments at a statistically higher abundance and its center is calm and nonturbulent. Oceanographic modeling of particles subject to water currents predicts the formation of five such gyres, of which the North Pacific Gyre would be the largest (Eriksen et al. 2014; Van Sebille et al. 2015). How much plastic has accumulated in the deep water or the sediment at the gyre location, is not known. But, the floating stock of plastic debris is known to be a minuscule fraction (Eriksen et al. 2014) of what is estimated to reach the ocean each year, and a majority of ocean plastics are not visible at the surface. What is especially worrisome is that no mechanism in nature is able to remove the plastics from the ocean at a significant rate. With little or no degradation in the low-temperature, anoxic sediment where the plastic debris ends up (Andrady 2011; Hurley et al. 2018), it is safe to assume that nearly all the plastic that ever entered the ocean still persists there in the sediment.

Plastics are now known to be present in all ocean basins (Andrady 2011; Cole et al. 2011; Derraik 2002; Peng et al. 2020; Law and Thompson, 2014), shorelines the world over (Li et al. 2016), in Antarctica (Ivar do Sul and Costa 2014; Waller et al. 2017), in the frozen polar ice masses (Peeken et al. 2018) (with the possibility of global warming releasing them gradually into the ocean) (Obbard et al. 2014), in remote alpine lakes (Gateuille et al. 2020), and even karst groundwater. Figure 1.5 shows the trend in plastics debris in aquatic environments.

Plastic waste in the ocean poses a variety of well-known environmental problems and most of these are discussed throughout this volume. The main concerns might be summarized under the following eight categories.

a) Aesthetic damage to shorelines by beach plastic litter. Entanglement (Ryan 2018; Reinert et al. 2017) of marine life in plastic netting, rope, six-pack rings, containers, and "ghost fishing" by lost and abandoned fishing gear (Richardson et al. 2019).
b) Sorption and adsorption of chemical species in seawater, river water, and wastewater by plastic debris. Some hydrophobic chemicals in seawater may concentrate in the plastic fragments and be transported elsewhere (see Chapter 9).
c) Ingestion of plastics (Reynolds and Ryan 2018; Santos et al. 2015), especially microplastics by a wide range of marine animals. Any chemicals the plastic carries may be bioavailable and lead to toxicity (Avio et al. 2015; Guo and Wang 2019; Rochman 2013; see Chapter 12).
d) Accumulation of waste plastic debris in the bottom sediment affecting its ecology (Barett et al. 2020; see Chapter 6).
e) Introduction of alien species to new ecosystems by "rafters" or foulant species on the surface of floating plastic debris (Kiessling et al. 2015; Rech et al. 2018).
f) Possible development of antibiotic- and metal-resistant microorganisms on foulant layers on plastics that have sorbed antibiotics through exposure to wastewater (Yang et al. 2019).
g) Interference with the operation of seagoing vessels by derelict fishing gear (Hong et al. 2017).
h) Potential contamination of fish and seafood leading to the increased human intake of MPs and NPs (Cox et al. 2019; see Chapter 13).

Of these problems, their ingestion by organisms, especially seafood species, is widely discussed because of the potential threat it poses to human health, in addition to the ocean ecosystem.

1.2.2 Microplastics in the Ocean

While the entanglement hazard of plastic macro-debris such as derelict net fragments or six-pack rings on large marine animals is easier to observe, it is the small-sized debris not discernible visually that will have the more significant impact as they can interact with a much wider range of marine species. Particularly significant are fragments of plastics (<5 mm to 250 μm) generally referred to as "microplastics" (MPs) (Arthur et al. 2009). The term, however, is a misnomer as reports of "microplastics" in the ocean invariably include fragments with dimensions that are orders of magnitude larger than a micron. MPs constitute a very small weight fraction of the plastic debris in the ocean but are predominant in terms of their numerical abundance. It is their abundance rather than their mass per unit volume of water/sediment, that is directly related to potential threats to marine life.

There is obvious merit in subdividing the size range encompassed by microplastics into several narrow subranges, for instance, as in the classification proposed by the GESAMP (2016). Consistent with the nomenclature used by some researchers (Andrady 2011; Lusher 2015; Nelms et al. 2019), it is reasonable to specify the narrower size range of 1 mm to 1 μm as "true" microplastics (with those smaller, as nano plastics (NPs), and larger as mesoplastics). MPs also occur in different geometries, including microfibers, plastic fragments, films, pieces of foam (such as PS foam and polyurethane), and virgin resin pellets that are believed to "leak" into the environment from plastic processing operations as well as during the transportation of resin (Karlsson et al. 2018). Geometry-specific physiological impacts are possible with the ingestion of MPs, especially the NPs (Danopoulos et al. 2021). Nanoplastics derived from MPs or larger debris are an especially important category because their size allows a very large range of marine animals to ingest these.

Secondary MPs derived from mesoplastics by fragmentation may degrade further yielding NPs (Andrady 2017; Chapter 8). Some data suggests the NPs that are extensively weathered contribute to the pool of dissolved organic carbon (DOC in seawater (Zhu et al. 2020; Romera-Castillo et al. 2018).

Plastic micro-debris is further categorized as primary and secondary, based on their origin.

a) Primary MPs are intentionally manufactured in that size scale for use in a specific application; and
b) Secondary MPs result from the fragmentation of plastic macro litter in the ocean environment, often assisted by their weathering degradation as discussed in Chapter 8 (Andrady 2017; Barnes et al. 2009). Though fragmentation may also occur with virgin material, plastics that have undergone extensive weathering under exposure to solar UVR, and therefore weakened or embrittled, tend to fragment far more easily in the environment (see Chapter 8.)

Examples of primary MPs include manufactured microbeads used as exfoliant additives in personal care products such as facial creams and toothpaste (Fendall and Sewell 2009). These microbeads typically have a size range of 164–327 μm (Napper et al. 2015) and are predominantly made of polyethylene (Gouin et al. 2015); therefore, at least initially, float in seawater (Van Cauwenberghe et al. 2015). They are accessible for ingestion by a range of smaller marine organisms that populate the photic upper layer in the ocean. However, the use of microbeads in rinse-off type cosmetics has been phased out in 2019–2020 in both the US and the EU, preventing 1500 tons per year of these from entering the aquatic environment (Sun et al. 2020). But noncosmetic uses of microbeads that include plastic-blasting media, textile printing, and biomedical applications (Leslie 2014) continue worldwide.

Microfibers (MF) in the environment can originate from either textile manufacturing or fabric laundering (Cesa et al. 2020), especially when using top-loading washing machines. A single wash cycle of a garment (a fleece jacket) in detergent-free water in a household washing machine releases about 0.3% of its weight as MFs (Hartline et al. 2016) while studies have found 1079 to 10^6 fibers per kg fabric in five repeated washes to be released into wastewater (Zambrano et al. 2019; Falco et al. 2019). Furthermore, textile fibers such as nylon or polyester can undergo fragmentation consequent to weathering on exposure to solar UVR (Sait et al. 2021). These microfibers can be micro- (<100 μm) as well as nanoscale (<100 nm) (Mintenig et al. 2017) and pose a similar threat to marine biota as MPs (Henry et al. 2019). How much fiber exists as debris in the ocean, is difficult to assess, especially because textile fibers are denser than seawater. A recent estimate places it at ~0.2 MMT released annually; as with MPs, the ecological significance of MFs does not scale with the tonnage but with the particle abundance of these in seawater. However, fibers found in seawater collected from six ocean basins turned out to be predominantly (79.5%) cellulosic with synthetic fibers constituting only 8.2% of the microfibers (Cesa et al. 2017). This observation is inconsistent with >50% volume production being synthetic recalcitrant fibers; but the denser synthetics fibers are more likely to be in the sediment. The high percentage of inherently biodegradable cellulosic fiber in the ocean is yet to be explained.

A summary compilation of available datasets on the abundance of MPs in the ocean (particles/m^3) is shown in Figure 1.6 for particles in the size scale of 100–5000 μm. But floating-stock assessments are invariably underestimates because of the size limit imposed by the mesh size of the sampling nets and the collecting effectiveness of different sampling gear (Zheng et al. 2021). Lindeque et al. (2020) found the MPs concentrations to be an order of magnitude larger when sampling with a 10 μm mesh as opposed to a 500 μm mesh net. For instance, N. Atlantic surface water sampled at 23 sites using a 10 μm mesh net (Enders et al. 2015) yielded MPs in the size range of 10–150 μm,while using a 200 μm mesh net to collect samples at 141 sites during a global circumnavigation cruise (Cozar et al. 2014), yielded MPs in the size range of 0.4–15 mm. Even taking into account the differences in

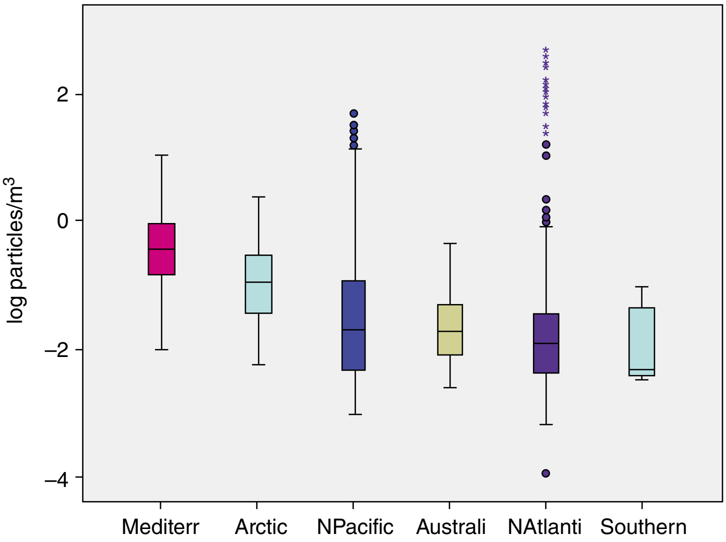


Figure 1.6 Density (log particles/m^3) of MPs (100–5000 μm) in the different oceans. Horizontal line: median; box boundaries: 25th and 75th percentiles; bars: range of observed values; dots and asterisks: potential outliers. *Source:* Courtesy Beiras and Schönemann (2020).

location and identification, these samples likely belong to statistically different populations. Regardless of such drawbacks, however, all efforts at quantifying sea-surface plastics will still capture only ~1% of the total influx of plastics into the ocean as most would have sunk into the sediment.

Because 1.5–4.1% of the annual production can end up in the ocean (Jambeck et al. 2015), 7800 MMT of plastics hitherto produced should have resulted in at least 57–160 MMT of plastics in the ocean. However, inventories find less than 0.25 MMT of plastics in surface waters (Eriksen et al. 2014; Van Sebille et al. 2015) and their abundance does not correlate with production volumes over the recent years (Thompson 2004). This disparity has led to the notion of a "missing fraction" of MPs, especially the smaller fragments in the ocean (Kvale et al. 2020; Woodall et al. 2014). However, floating plastics essentially represent a "snapshot" view of the MPs in the short window of time they float before extensive fouling sink them into the water column. Also, the search for a missing fraction assumes that all floating MPs will be larger than the mesh size of collecting gear (around 330 μm) excluding most of the small MPs and NPs from the count. The missing fraction reflects limitations of the sampling gear and not taking into account the MPs below the surface water level, especially in the sediment (Kanhai et al. 2019; Nakki et al. 2019; Ramirez-Llodra et al. 2011). A recent estimate (though based on only six sampling sites) estimates 14 MMTs of MPs that are >50 μm in the sediment (Barrett et al. 2020).

Beaches worldwide routinely accumulate plastic debris, including large amounts of microplastics (Kako et al. 2020; Koongolla et al. 2018; Tavares et al. 2020). Unlike larger plastic litter, the MPs are not removed during beach clean operations, or routinely collected on managed beaches. Worldwide beach clean exercises (Ocean Conservancy 2019) annually covering 36,000 miles of coastline yield a consistent list of highly abundant plastic litter items, with cigarette filters topping the list with 5.7 million collected. Plasticized cellulose acetate fibers used in cigarette filters are recalcitrant in the ocean environment, explaining their ubiquity in coastlines around the world. All of the top seven beach litter items reported are made of plastic; if MPs and NPs could also be somehow included in the count, the abundance of beach plastic debris would be higher by several

Table 1.1 Abundance of the top seven items found in global coastal cleanup by Ocean Conservancy (Washington DC) and types of plastics commonly used in them.

Litter item	Count in millions	Plastics typically used
1) Candy wrappers	5.72	PE, PP, PET
2) Cigarette filters	3.73	Cellulose acetate
3) Beverage bottles	3.67	PET
4) Bottle caps	1.97	PP
5) Straws and stirrers	1.75	PE
6) Cups and plates	1.39	PE, PS, EPS
7) Bags	0.94	PE

Data pertain to 36 000 miles of coastline in different global locations. Based on data by Ocean Conservancy on the 2018 Coastal Cleanup.

orders of magnitude. Table 1.1 summaries the seven most abundant plastic debris items found in beach cleaning operations in different parts of the world by the Ocean Conservancy, Washington DC, in 2018. Their global beach cleaning operation is an annual event.

1.2.3 Chemicals in Plastic Debris

Plastics used in products typically include a suite of chemicals intimately mixed with the base resin. These include (i) intentionally added chemicals or additives to modify the properties of the base resin to suit the needs of the product (Groh et al. 2019; see Chapter 2); (ii) low levels of the relevant residual monomer trapped in the plastic (not an issue with PE or PP with gaseous monomers, but relevant with PS, PVC or polycarbonate [PC]); and (iii) unintended compounds sorbed from seawater and concentrated by partition (Hüffer and Hofmann, 2016; Pascall et al. 2005; Rochman et al. 2013; see Chapter 9). Some of these sorbed chemicals are persistent organic pollutants (POPs) that are toxic compounds as well, and remain in the environment for extended durations, allowing them to be widely distributed via water, soil, and air. These tend to accumulate in the fatty tissue of animals that ingest them and may bio-magnify as they move to higher trophic levels. Any POPs in seafood are of special interest to human consumers. Despite their very low dissolved concentration in seawater, the equilibrium concentration of POPs in the MPs and NPs tends to be very high, reaching concentrations that are ~2 to 6 orders of magnitude higher than in sediment (Mato et al. 2001) or seawater (Wright et al. 2013). Sorption cleans the water of these pollutants but in the process, also generates MPs loaded with POPs, heavy metal compounds, and pharmaceuticals, ingestible by marine biota.

1.3 Ingestion of Microplastics Marine Organisms

That the marine environment contains numerous natural particles in the same size range as MPs/NPs that in any event constitute only a small fraction of all particles, is often pointed out. Marine organisms having evolved in this particle-rich environment are reasonably expected to be not particularly affected by them. However, it is the high level of both sorbed or adsorbed chemicals in MPs that set them apart from the many inorganic “fines” abundantly found in seawater that may carry only surface-adsorbed pollutants. The MPs and NPs with sorbed POPs are well known to be

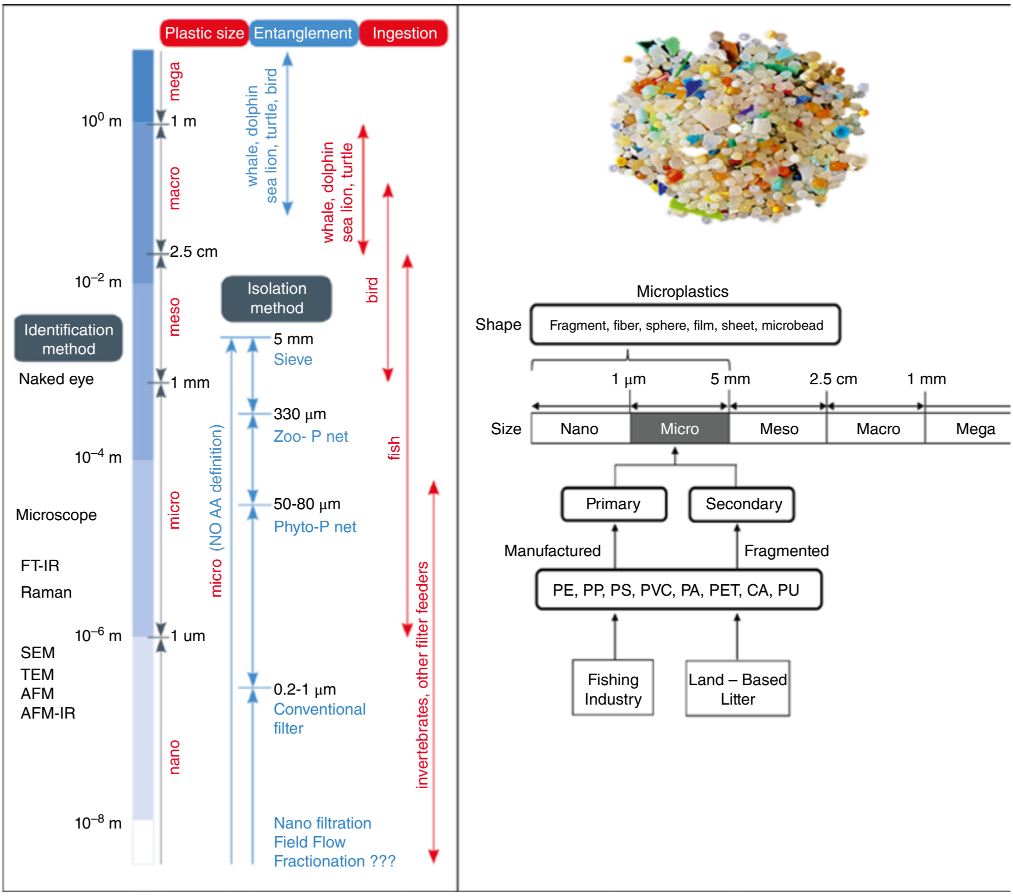


Figure 1.7 Left: Categories of marine plastic debris developed by GESAMP (2015) indicating the size ranges for potential ingestion, and the techniques for their analysis. Right: A schematic showing the origin of plastic micro-debris. *Source:* Adapted from the same report. SEM - Sacnning Electron Microscopy; TEM - Transmission Electron Microscopy; AFM - Atomic Force Microscopy; and AFM-IR - AFM with infra-red Spectroscopy.

ingested by organisms ranging from zooplankton (Cole et al. 2013; Sun et al. 2017) to whales (Fossi et al. 2014; see Chapter 12), providing a pathway for these chemicals into biota (Hartmann et al. 2017). Particular attention has been paid to marine birds (Fry et al. 1987), where over 25% of the species (Pham et al. 2017), and sea turtles, where all species, are reported to ingest plastics (Kühn and van Franeker 2020). A particular concern is the ingestion of MPs and NPs by commercially important fish and seafood species (see Chapter 13). How the entanglement and ingestion risk of MPs relate to their particle size is illustrated in figure 1.7.)

But, presently, there is no consensus on whether the POPs in ingested MPs do adversely affect the organism. Such effects would be compound- and species-specific, but only a limited combination of POPs/species have been investigated as yet. Relevant data are therefore, quite variable even on species ingesting virgin plastics. For instance, adverse outcomes of ingesting virgin "clean" MPs have been reported for fish species (Jovanović et al. 2018) but were ruled out with sea urchins (Kaposi et al. 2014). An important focus of ingestion studies should also be to asses if the relevant POPs are bioavailable (Avio et al. 2015) to ingesting organisms at a high enough dosage to result in any physiological impacts. Bioavailability (Avio et al. 2015) of POPs is determined by (i) the residence time of MPs in the gut environment, (ii) hydrophobic gut contents that encourage release, and (iii) if POPs molecules can permeate the gut wall to enter systemic circulation (as opposed to being egested). However, data supporting the bioavailability of POPs are available only for several marine species (Bakir et al. 2016; Chua et al. 2014; Schrank et al. 2019), including mussels (Browne et al. 2008) and zebrafish embryos (Batel et al. 2018; Pitt et al. 2018). Bioaccumulation and biomagnification are introduced in Box 1.2.

Box 1.2 Bioaccumulation and Biomagnification

Bioaccumulation is the gradual build-up of the concentration of a compound in an organism relative to that in its environment, due to ingestion or other modes of intake. **Biomagnification** is an increased concentration of the compound in the predator relative to that in its prey (Miller et al. 2020). A compound that is ingested, but neither metabolized nor excreted at a rate faster than it is consumed by the organism bioaccumulates in its tissue. This is especially true of compounds with a high partition coefficient, (see Chapters 2 and 9). Where the compound is toxic, as with organic mercury, this is a serious concern. Biomagnification results when a predator organism ingests multiple prey organisms, each with a high bioaccumulation of the compound or pollutant (Drollliard 2008; Mizukawa et al. 2009). This leads to a faster build-up of the chemical compound in predator tissue compared to that in the prey. For instance, when DDT was used liberally, it ended up in the water and invariably in fish. The insecticide was biomagnified in predatory birds such as Ospreys feeding on the fish, resulting in an abnormal thinning of the shells of their eggs.

A highly bioavailable compound is readily transported from the gut into the systemic circulation. When a contaminated plastic fragment is ingested, the contaminant must leach out in the gut and permeate through the gut wall, for it to be bioavailable to the organisms. Otherwise, it is egested and has a little physiological effect. Bioavailability can therefore also, depend on lipid levels in the diet, the presence of gut surfactants, and the gut pH (Koelmans et al. 2014; Kwon et al. 2017).

The bioavailability and toxicity associated with MPs in fish have been recently reviewed (Wang et al. 2020). But, the kinetics of leaching and the mechanism of bioaccumulation remains undefined (Qu et al. 2020). It is also reasonable to expect the bioavailability of POPs in the MPs to ingesting animals to be low (Koelmans et al. 2016; Ziccardi et al. 2016), and the MPs may instead even “clean” the gut environment by removing any existing hydrophobic pollutants (Lee et al. 2019; Scopetani et al. 2018). Black Sea Bass (*Centropristis striata)* presented with PVC pellets loaded with 10 wt% of dioctyl phthalate (DOP) plasticizer, ingested them at the same rate as “clean” or virgin PVC pellets, but the egested pellets showed no change in the DOP level (Joseph et al. 2020). Ingestion of MPs of PE spiked with benzophenone by rotifers, copepods, bivalves, echinoderms also did not result in any toxic outcomes (Beiras et al. 2018). The level of POPs delivered to organisms may be low as the fraction of MPs in the diet has to be minuscule. But, pollutants such as endocrine disruptor chemicals or antibiotics, act at very low concentrations, some displaying a non-linear dose-response curves, allowing them to elicit adverse physiological responses at unexpectedly low doses. Also, the physiological effects in these studies were monitored only over the short term. The data taken together do not rule out the possibility of MPs transferring POPs to biota via ingestion, at least in some species.

Pathways that potentially contribute to the dietary intake of MPs, and especially NPs, in humans are now receiving the focused research attention they deserve (see Chapter 13). While the presence of MPs/NPs in food (Kosuth et al. 2018) and beverages (Schymanski et al. 2018; Shruti et al. 2020), and especially seafood (Smith et al. 2018), is well established, no adverse effects on human health have yet been linked to them (see Chapter 13). But, the relevant data, when considered together, suggest the accumulation of NPs and small MPs may have adverse long-term effects (Yong et al. 2020). An interesting and worrisome development are the findings that show NPs enter systemic circulation *via* the gut (Revel et al. 2018); some report (Hussain et al. (2001) unexpectedly find MPs as large as 100 μm to translocate into lymphatic circulation from the gut in humans. Ragusa et al. (2021) recently reported 5–10 μm MPs in the human placenta; 5 particles were isolated from 4 placentae, with less than 5% of the placental mass being analyzed. At this size range, however, MPs may even compromise the blood-brain barrier (Barboza et al. 2018), and those <20 μm have been shown to access all internal organs (Campanale et al. 2020). A few *in vivo* studies (Deng et al. 2017; Jin et al. 2019) on mice, including one on effects on offspring (Luo et al. 2019), show physiological effects of ingesting particles ~5 μm in size. However, an *in vitro* study on human cell lines (human colon epithelial cell) co-cultured with BeWo b30 (human placental trophoblast cell) did not show the same (Hesler et al. 2019). The study found that 0.5-μm PS NPs did not significantly compromise the *in vitro* placental and intestinal barriers. This is a topic with profound implications that deserves focused research attention.

1.4 Sustainability of Plastics

The notion of environmental sustainability is a complex one (well outside the scope of this chapter) and according to its original definition, refers to a mode of development that "meets the needs of the present generation without compromising the ability of future generations to meet their own needs." It is a laudable, qualitative statement, but the strategy to achieve this objective is not clear, especially where development involves depleting a fixed reserve of a natural resource such as rare earth elements or oil. Not only is the number of future generations not specified, but they are also assumed to have the same set of needs as the present generation does. A tempting approach is to "decouple" growth in GDP from environmental impacts (Luo et al. 2019), allowing sustainable development to proceed unhindered. This, however, is not realistic (Ward et al. 2016), especially in the future plastics industry.

But what can be realistically implemented to improve the sustainability of plastics in the near or medium term? The goal should be to ensure that the rapidly depleting resource base for resin production lasts long enough for technological advances to perhaps make those resources obsolete by discovering substitutes. Finding ways to minimize the environmental impact of plastics, given the future increase in production levels, is also critical to ensure sustainability. Specifically, three strategies towards sustainability deserve close attention.

a) *Energy economy*: Plastic resin manufacture and processing into consumer products needs to be more energy-efficient and, wherever possible, rely on renewable energy instead of conventional fossil-fuel derived energy. Innovations to capture process waste energy such as low-grade heat for reuse needs to be enabled.
b) *Feedstock economy*: Using the minimum amount of plastic materials to deliver the necessary functionality for the performance of the product, needs to be implemented. Conserving fossil-fuel feedstock by material recycling (as well as chemical or energy recycling) of post-use plastics and where feasible, by substituting bio-based plastics in place of fossil-fuel-derived resins should be incentivized.
c) *Minimizing toxicity*: Minimizing the release of toxic chemical by-products from resin production, processing, use, and waste disposal of plastics especially into the ocean environment, is a priority. This requires urgently substituting some of the toxic legacy additives with known

adverse ecological impacts, with non-toxic alternatives. Also, capturing CO_2 and process gaseous emissions for conversion into useful products to reduce the environmental footprint of the material should be encouraged.

In 2020 with the COVID-19 pandemic slowing down economic activity, the energy demand also decreased, with that for oil and coal dropping by 7–8% each, accompanied by a consequent decrease in the global carbon emissions. Despite this respite, the world energy demand is still expected to grow by nearly 50% by 2050 to reach 240 Quads (quadrillion BTU; EIA 2020), led primarily by industrial growth in Asia. While more renewable energy will be available in the future, their percent contribution to the overall energy supply will still be only about 16%, as opposed to the present 11%. Therefore, conserving energy, along with using more renewable energy and improving efficiency in plastic processing (for instance, with all-electric molding technology) will be important in making plastics more sustainable in the future.

Moves to encourage economy in using energy and material, conveniently align well with good business practices, and should therefore be driven to some extent by future market competitiveness. There are many examples, such as the down-gauging of plastics film or improved plastic bottles; with the 0.5L PET soda bottle, a 48% decrease in weight was achieved over the last decade, without compromising neither the functionality nor consumer appeal, saving valuable resin material resources. Similarly, reductions in secondary packaging of goods with minimal impact on the level of protection afforded by the package, have contributed to conserving material.

Two major strategies that conserve valuable fossil-fuel resources and reduce the embedded environmental impacts are worth emphasizing: (i) extending the service life of plastic products; and (ii) increasing the use of bio-based plastics, reducing the dependence on fossil fuel in manufacture.

1.4.1 Recycling of Post-Use Plastics

Material recycling saves the energy expended for producing consumer plastic goods because it is the resin production (extraction, refining, and polymerization into resin) step, as opposed to the processing step, that has the higher embodied energy, EE (Schyns and Shaver 2020). Especially with single-use products such as plastic cups, straws, or bags, the item is used only for a short duration and the quality of the plastic resin is barely affected by use. Being thermoplastic materials, the post-use products can be collected and re-melted for use in another generation of products. With most of the EE and embodied impacts associated with the manufacturing phase avoided, the strategy yields significant advantages (see Table 1.2). As seen from the table, savings in energy and in carbon emissions associated with recycling are substantial for plastics generally met with in the marine environment.

Even the leading type of plastic to be recycled in the US, PET bottles, are only recycled at a rate of ~28% presently. Even with bottles, the common use of the recyclate (r-PET) resin is to "downcycle" into other products (products of lower market value relative to the original high-value bottle.) Alternatively, the r-PET may be mixed with virgin PET (or used as a layer in multilayer extrusions) in fabricating original high-value products. For instance, PET resin from plastic soda bottles might be downycled into textile or carpet fiber (Leonas 2017) and then downcycled again (mixed with other plastics) into lower value "plastic lumber" (Wan et al. 2019). Downcycling, however, is not the only recycling option available, as illustrated by the bottle-to-bottle recycling of PET, consistent with the paradigm of "circular economy." To be sustainable, however, the US plastic industry also must join the ranks of high-recyclers of the Word such as Norway, Sweden and South Korea, to recycle much higher fractions of at least the post-consumer PET and HDPE, and encourage the recycling of other plastic resins as well.

Table 1.2 Comparison of the embodied energy (GJ/kg) and carbon footprint (kgCO$_2$-e) for virgin and recycled resin.

Plastic	Embodied energy Virgin (GJ/kg)	Embodied energy Recycled (GJ/kg)	Carbon footprint Virgin (kgCO$_2$-e /kg)	Carbon footprint Recycled (kgCO$_2$-e /kg)
Polyethylene	77–85	45–55	2.6–2.9	2.7–3.0
Polypropylene	75–83	45–55	2.9–3.2	2.0–2.2
Polyester (PET)	81–89	35–43	5.7–4.1	2.1–2.6
Polystyrene	92–102	43–52	3.6–4.0	2.6–3.1
Poly(vinyl chloride)	56–62	32–40	2.4–2.6	1.9–2.4
Nylon 6	116–129	38–47	7.6–8.3	2.3–2.8
Poly(lactic acid)	49–54	3.4–3.8	3.4–3.8	2.9–2.4

Based on data from Ashby (2013).

Low recycling rates in the US and elsewhere often result from the lack of readily-accessible recycling infrastructure at the local level and the minimal market cost differential between virgin and recycled resin. Also, it is not always practical to mechanically recycle a mixed stream of plastic waste. For example, producing high-quality recyclate is simply not possible with blends or multilayer laminated plastic products (Kaiser et al. 2018) or with products that are rendered photodegradable or enhanced biodegradable (a 0.5 wt% of biodegradable PLA contaminating a PET recycling stream discolors the rPET) (Alaerts et al. 2018). Some of waste plastics, however, may be amenable to recycling into chemical feedstock and energy *via* either pyrolysis or incineration. Recycling of waste fishing gear into plastic resin pellets, and their conversion to energy by incineration, are practiced at a small scale in the US, but much progress needs to be made.

Recycling does involve significant costs for collection, sorting, classifying, and cleaning of waste plastics, and there are incidental losses of material during the process that preclude a 100% mass recovery as the recyclate. Even with such losses, the savings in energy are substantial. There are, however, embedded impacts associated with the recycling process as well, and LCA must be carried out to make sure that most of what is saved in energy is not negated by increased environmental impacts. Also, each time a resin is recycled its mechanical characteristics detriorate; with PET, 3–5 repeated recycling results in ~50% decrease in tensile strength and extensibility of the resin (La Mantia and Vinci 1994).

1.4.2 Using Bio-Based Feedstocks for Plastics.

Plastics can be classified based on the feedstock used in their synthesis, into those that are fossil fuel-based and those derived from biological resources. Conventional plastics are mostly synthesized using feedstock derived from fossil fuel while the second category of plastics is synthesized using plant biomass as feedstock, and ISO, as well as the ASTM, refer to these as “bio-based” plastics. The carbon in the plant biomass is derived from the present-day atmosphere or the carbon cycle. However, it is important to recognize that “bio-based” plastics defined in this manner include two distinct categories of plastics; those made from monomers derived from biomass and polymers synthesized by living organisms (or biopolymers) that are modified by man. Thus, three broad classes of biologically derives plastics might be identified.

a) *Biopolymers* that are synthesized by living organisms and exist as polymers in the biomass, including cellulose and poly (hydroxyl alkanoates) [PHAs]. These are extracted and used with no further chemical modification of the polymer.

b) *Modified biopolymers* where a biopolymer is extracted from biomass and chemically changed prior to use, as in the case of cellophane. Dissolving plant cellulose in carbon disulfide (in the xanthate process) or copper salt/ammonia (in viscose process), and re-precipitating the solution in dilute acid yields cellophane and rayon. The material is still plant-derived cellulose but with an altered secondary and tertiary structure of the cellulose molecule. Similarly, in the alkaline de-amidation of chitin from crab shells to obtain chitosan, the primary structure of the polymer is changed with the substitution of the amide with an amine group.

c) *Bio-based* plastics use plant-based biomass feedstock to synthesize monomers that are polymerized into plastics such as PE or PP. For instance, the sugars in waste sugarcane or sugar-beet residue are fermented into alcohol that is easily converted into ethylene, a monomer used to synthesize Bio-PE or PLA. Using renewable bio-based feedstocks can help conserve fossil fuel reserves.

The Bio-PE for instance, is identical in its properties to the conventional PE made from fossil fuel, except that it is "bio-based." Bio-PE, Bio-PP, and Bio-PET all have processing characteristics identical to their conventional counterparts, allowing easy substitution (or drop-in) in standard processing operations practiced in the plastics industry. Bio-based resin and conventioniral resin (from fossil fuel) are chemically indistinguishable except for the isotopic ratio of the carbon in the molecules or the (^{13}C:^{12}C) or ($\partial^{13}C$) (Suzuki et al. 2010). Measured ($\partial^{13}C$) values of a polymer reveal the lineage of its carbon atoms, distinguishing between those derived from renewable biomass and those from fossil-fuel resources. The carbon in the latter is ancient, having formed millions of years back in time, while that in biomass carbon is derived recently from the CO_2 in today's atmosphere, accounting for this difference in their isotopic ratio. Most of the carbon in chemically modified biopolymers is also derived from the atmosphere.

With polymers synthesized by polycondensation of two monomers, one monomer can be bio-based while the other is derived from fossil-fuel feedstock, leading to a hybrid or a partially bio-based plastic. This is the case with hybrid poly(ethylene terephthalate) (PET) resin that is popularly used in "green" beverage bottles in the market, that are only about 22% bio-based; the ethylene glycol monomer is bio-based while terephthalic acid is derived from fossil fuel (Figure 1.8).

There is confusion in the literature as to how the environmental biodegradability of plastics might relate to the above categorization. The biodegradability of plastics in a biotic environment is determined by their chemical structure; the polymer molecule must have main-chain bonds that are hydrolyzable by enzymes secreted by the microorganisms in the relevant environment. There

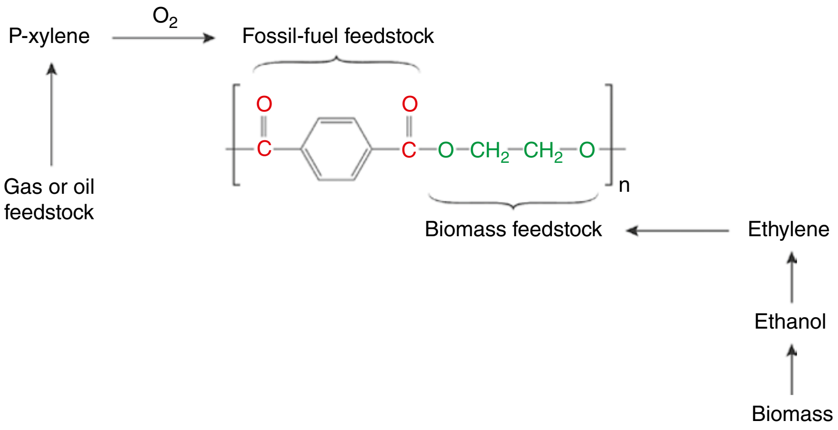


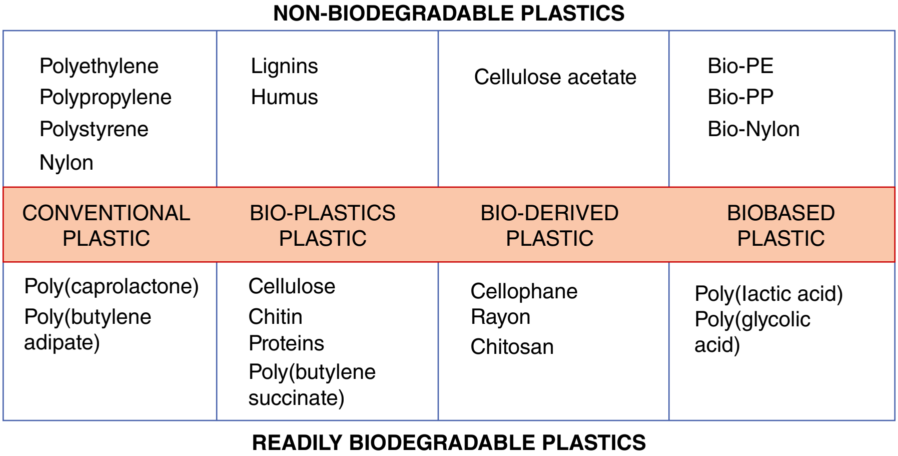
Figure 1.8 Hybrid PET with ~23% of bio-based content (a fifth of carbon atoms is from biomass).

Table 1.3 A simple classification of plastics based on their feedstock.

Category	Criterion	Example
Fossil-fuel based polymers	Man-made polymers made from monomers derived from fossil-fuels	PE, PP, PS
Biomass-based polymers	Man-made polymers are derived from monomers derived from biomass.	PE, polyurethane, PLA
Biopolymers synthesized by a living organism	Polymers are synthesized by a living organism.	Cellulose, Chitin
Structurally modified biopolymers	Biopolymers that are chemically altered to improve properties	Rayon, cellulose acetate, chitosan

is no relationship between the source of feedstock and the biodegradability of the resin, as seen from Table 1.3 and Figure 1.9. Biopolymers such as cellulose or chitin have been in the environment for a very long time allowing biochemical pathways that degrade these to evolve and therefore they tend to be biodegradable. This is not the case with synthetic man-nade plastics that have existed in the environment only since the beginning of the anthropocene. Some authors (Brizga et al. 2020) confusingly include blends of a synthetic polymer with a degradable additive such as starch under "biodegradable" plastics. In these materials such as blends of starch/PE, the polymer component does not biodegrade appreciably.

As already pointed out, increases in plastic production will further deplete fossil fuel reserves and be accompanied by significant emissions, especially CO_2, into the atmosphere (Spierling et al. 2018). Both these negative environmental impacts might be reduced to some extent by using more bio-based plastics (Narancic et al. 2020; Zhu et al. 2016). Using biodegradable plastics made of bio-feedstocks will also help in waste management (Calabrò and Grosso 2018), especially in the marine environment. Presently, their annual supply is limited with only 2.1 MMT (2019 data) of bio-based resins accounting for only ~1% of total global plastic production. Over 57% of their production was PLA and PBAT (poly [butylene adipate-co-terephthalate]), the highest volume biodegradable resin manufactured. In the bio-based category, PE, Nylon, and PET were the highest-volume resins manufactured.[6]



	CONVENTIONAL PLASTIC	BIO-PLASTICS PLASTIC	BIO-DERIVED PLASTIC	BIOBASED PLASTIC
NON-BIODEGRADABLE PLASTICS	Polyethylene Polypropylene Polystyrene Nylon	Lignins Humus	Cellulose acetate	Bio-PE Bio-PP Bio-Nylon
READILY BIODEGRADABLE PLASTICS	Poly(caprolactone) Poly(butylene adipate)	Cellulose Chitin Proteins Poly(butylene succinate)	Cellophane Rayon Chitosan	Poly(lactic acid) Poly(glycolic acid)

Figure 1.9 Classification of plastics according to inherent biodegradability.

---

[6] Bioplastics market data. https://www.european-bioplastics.org/ market/. Accessed March 1, 2021.

In evaluating the merits of substituting conventional petrochemicals with bio-based feedstocks, close attention must be paid to the scope of the relevant life-cycle analyses (LCA). Bishop (2020), in a review of 44 studies comparing bio-based with conventional feedstock for plastics, found that 84% of them did not account for additives in the inventories used in their analyses and most did not adopt a broad enough domain of impacts. For instance, using either sugar beet or wheat, yields a biomass yield of 73 T/ha and 8.6 T/ha, respectively, but the crop needed per ton of PE was 23.9 T and 6.84 T, respectively. On an area cultivated basis, sugar beet yielded a benefit in reducing climate change, that was at least two times greater than that by wheat bran biomass, underling the complexities of selecting the proper biomass source for feedstock (Belboom and Léonard 2016). The bio-based and biodegradable plastic PLA, is often used in food-service items. A "cradle-to-grave" comparison of PLA, PP, and PET for the fabrication of beverage cups found that PLA was superior (by 40–50%) to PP and PET, both in terms of climate change impacts as well as fossil fuel conservation (Moretti et al. 2021). But, in other impact categories such as eutrophication, acidification, particulates, and photochemical ozone formation, PLA was found to be worse than both conventional plastics. Mainly due to the lack of harmonization, it is difficult to compare different LCA studies on biobased resins (Cheroennet et al. 2017; Papong et al. 2014; Simon et al. 2016) with each other. Spierling et al. (2018), in their review of LCA on bio-based plastics, concluded them to significantly contribute to environmental sustainability, potentially eliminating the emission of 240–315 MMT of carbon equivalents at a 65.8% substitution of conventional plastics in use. As with using any material in a given application, there are environmental and economic trade-offs to be considered when using bio-based resins as well. A full environmental assessment of the candidate bio-plastic, based on LCA for the particular application, is a prerequisite for their adoption.

1.5 Plastic Manufacturing

Plastics manufacturing is too broad a subject to be discussed in any detail here, and the following is a minimal introduction to allow readers who are not familiar with plastics to better appreciate the following chapters. Feedstock for polyolefin production are gaseous chemicals, called monomers, that are derived from oil, natural gas, or coal. Generally, a distilled fraction of oil, such as naphtha, is thermally cracked into these olefin monomers. Hydrocarbons in natural gas can also be converted to olefins; alternatively, biomass-derived ethanol can also be converted into ethylene for use as a monomer. The ethylene made by any of these processes is polymerized using specialized catalyst systems,such as the Ziegler-Natta or metallocene catalysts, to obtain olefin polymers with closely controlled molecular weight, chain geometry, and crystallinity. Pressure and temperature are the key variables that determine the structure and properties of the resin formed. The reaction is a catalyzed free-radical polymerization, but several different reactor technologies, such as autoclaves, tubular reactors, stirred tanks, and fluidized bed reactors, are generally used in the manufacture of polyolefin resins. Mostly the same types of reactors are used in the manufacture of PP as well. Styrene monomer used in the manufacture of PS by free-radical polymerization is a liquid, allowing emulsion polymerization in the liquid phase. The result of this resin manufacturing process are the virgin plastic pellets used by processors who convert these into useful plastic products.

An important part of this latter operation is 'compounding', where the plastic is melted and intimately mixed with chemical compounds called additives, meant to improve the properties of the plastics to obtain their best performance in the intended product (see Chapter 2). Mixing can be conveniently carried out in a compounding extruder at a temperature high enough to melt the plastic. The compounded plastic is then used to mold products by one of many techniques, the ones popular with thermoplastics being injection molding, extrusion, and blow molding. These approaches do not work well with thermoset plastics that need to be compression molded.

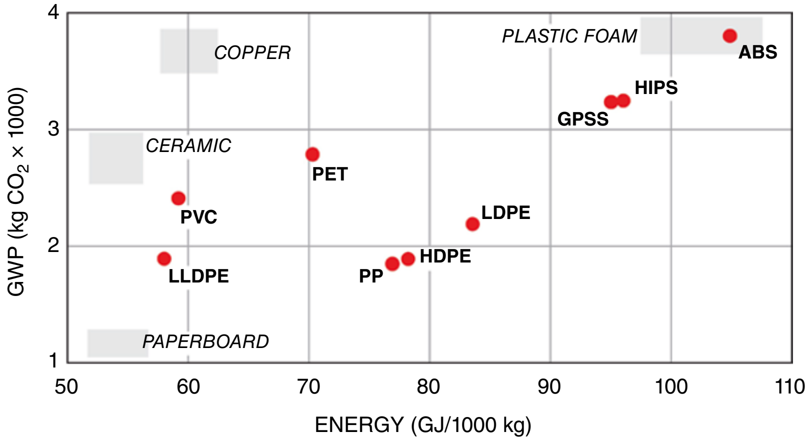


Figure 1.10 A plot of the GWP (kg CO_2-e) versus Embodied Energy (GJ) per 1000 kg of common plastics. Ranges of values for non-plastic materials are indicated by shaded rectangles, for comparison.

The energy expended and the greenhouse gases such as CO_2 emitted (expressed as the global warming potential, GWP (kgCO_2-e)) in producing common plastics, estimated in 2011 by Franklin Associates (for the American Chemical Council), is given in Figure 1.10 and compared with that for copper, alumina ceramic, paperboard, and thermoplastic rigid foams. Similar data for other plastics such as composites, metals such as nickel or aluminum, and for materials such as wood, clay, and stone lie outside the scale of this diagram. These estimates depend on several variables, including the feedstock used, the mix of energy employed in the process, the reaction engineering employed, and the specific grade of the resin produced. Estimates will therefore vary from location to location and even temporally. Still, the figure provides a general appreciation for the magnitude of energy and emissions associated with manufacturing different materials. Most of this energy is expended in extracting and purifying the feedstock rather than in polymerizing the monomer.

Individual plastics cannot be "ranked" for environmental desirability based on the figure, as many other externalities are associated with manufacturing resins. Acidic emissions that potentially acidify the oceans, nitrogen release that can result in eutrophication, ozone-depleting gases that affect the stratospheric ozone layer, and ground-level smog-forming emissions are some of these. A detailed life cycle (LCA) analysis based on reliable inventory data is needed to evaluate the impact of these on the environment. Estimated impacts were recently reported for three classes of polyethylenes (Table 1.4). Again, the impacts will vary with the location as well as the process employed in the manufacture.

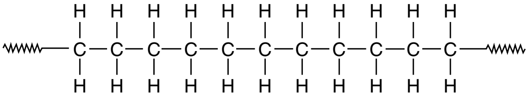
Table 1.4 Estimated environmental impacts of plastic manufacture (per 1000 kg) of plastic.

Plastic	Water (L)	Acidification (kg SO_2-e)	Eutrophication (kg N-e)	Ozone Depletn. (kg CFC-11-e)	Smog (kgO_3-e)
HDPE	8143	5.22	0.26	12×10^6	129
LDPE	11553	6.54	0.30	1.3×10^6	148
LLDPE	7383	4.69	0.25	1.2×10^6	125

Based on American Chemical Council/Franklin Associates.

1.6 Polymers: A Basic Introduction

Structurally, all polymers have very long chain-like molecules but their chemical formulae are relatively simple because often, the same structural unit repeats throughout the long molecular chain. For instance, polyethylene (PE), the plastic manufactured in the highest volume globally, has a long structural formula, a part of which may looks like the following:



$$\sim\!\sim\!\sim\!-\mathrm{CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2}-\!\sim\!\sim\!\sim$$

It is merely a repetition of ($-\mathrm{CH_2}$-$\mathrm{CH_2}$-) units placed end to end. Its structural formula is therefore, conveniently written as $(\text{-}\mathrm{CH_2}\text{-}\mathrm{CH_2})_n$, where n is the number of repeat units in the chain molecule, that can run into hundreds or thousands. As each repeat unit has a molecular weight of 28 (g/mol), that of the entire molecule is $(28 \times n)$ g/mol. Regardless of the length of the chain molecule, chemically, it is still a polyethylene. Since all PE molecules will not have identical chain lengths but different values of n, there is no unique molecular weight for polyethylene or for any other polymer (in contrast with simple organic molecule that have fixed molecular weights). Typically, a sample of a polymer is a mixture of structurally similar chains of different lengths and one can only refer to an *average* molecular weight for the entire distribution of molecules in the sample. Generally, two types of such averages, namely number-average (M_n in g/mol) and weight-average (M_W in g/mol), are used to express the molecular weights of plastics.

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

where N_i is the number of chain molecules having a molecular weight, M_i, and N is the total number of molecules in the sample ($N = \sum N_i$). Note that $(N_i M_i)/M_n$) is the weight fraction of molecules with a molecular weight M_i.

However, the average molecular weight (M_n) is generally insufficient to fully describe the polymer as one can have the same average value of (M_n) for two samples of the same polymer with two very different distributions of chain lengths, as illustrated in Figure 1.11. The broadness of the distribution (called the polydispersity index D) is quantified as the ratio (M_W/M_N). The value of D can vary from sample to sample, but the most probable value is $D = 2$. In addition to the average molecular weight and D, other variables such as branching of the linear chain or the amount of crystallinity contribute to the properties of the polymer.

1.6.1 Crystallinity in Plastics

Polymer chains are not only attracted to each other by Van der Waals forces but are also copiously entangled with each other (as in a serving of cooked spaghetti). It is difficult to pull out a single strand from the mass of entangled chains and that contributes to the strength of the polymer. This is particularly true at low temperatures where chains are less flexible.

When the mass of plastic is heated, however, the energy gained by the chain molecules makes them flexible enough for partial mobility and the material becomes softer and pliable. The molecular structure of plastics such as PE is more complicated than illustrated by this simple

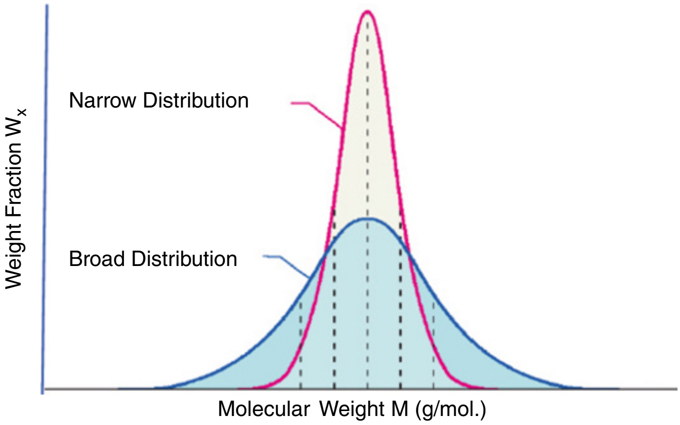


Figure 1.11 A schematic of the molecular weight distribution of two samples of polyethylene.

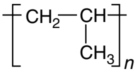
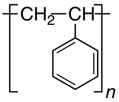
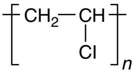
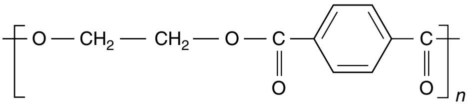
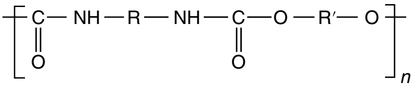
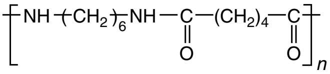
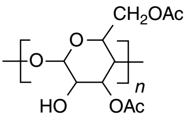
homogeneous model. In these polymers, short sections of several neighboring long molecular chains, rather than being randomly oriented as elsewhere in the mass, show a regular arrangement somewhat resembling the ordering of molecules in a crystal. These domains are therefore called “crystalline domains” as opposed to the “amorphous” regions of the bulk polymer where the chain molecules are randomly arranged (see illustration in Figure 1.12). Plastics that show crystalline domains in their structure are “semi-crystalline” plastics. With these plastics, one can assess a fraction of the mass as being crystalline; for instance, a given HDPE sample may be 80% crystalline. Though these are not true crystals, they still melt or undergo a phase transition on heating but only to reform on cooling. Individual crystallites of PE have dimensions in the tens of nm, but their agglomerates in crystalline domains are large enough to be seen by light microscopy. Because of the higher packing densities of chains, the density $\rho(g/cm^3)$ of crystalline regions is higher than that of amorphous regions in the polymer. That of the bulk plastic, therefore, depends on its percent crystallinity $F(\%)$. In PE, for example, crystalline and amorphous regions have densities, $\rho_C =$ 1.004 and $\rho_A = 0.853$ g/cm^3, respectively.

Values of F (%) can be experimentally determined for a given plastic sample using either pycnometry, differential scanning calorimetry (DSC), or X-ray diffraction methods (Kong et al. 2002; Seidlitz et al. 2016), allowing the average density to be calculated. But, the crystallinity F of a plastic is not an inherent property and thermal treatment or mechanical stress can often increase crystallinity while crosslinking or the presence of solvents can decrease its value. But, the maximum crystallinity achievable by a plastic still depends on its structure, with the highest levels reached in textile fibers as a result of the high levels of the orientation of molecules obtained in spinning and drawing.

Most of the thermoplastic debris commonly found in the marine environment are semi-crystalline plastics. There are exceptions; for instance, PS and expanded foam as well as PVC debris found in bottom sediment are nearly 100% amorphous. Percentage crystallinity, in turn, determines density, sorption capacity and permeability of the plastic. The solubility of organic pollutants picked up from seawater, as well as oxygen essential for abiotic degradation (that are generally oxidative reactions) are reduced as the fractional crystallinity increases.

The chemical structures of common plastics encountered in marine debris are summarized in Table 1.5. The density of the plastic determines if the debris will float in seawater and therefore degrade to some extent by exposure to sunlight, the main mode of degradation of plastics in the marine environment (see Chapter 10.) However, the densities of the base resins can easily change when additives, especially fillers, are used in high volume fractions, are compounded into plastic

Table 1.5 Common plastics litter found in the marine environment.

Polymer	Symbol	Structure	Density ρ (g/cm^3)	Tg (°C)[a]
Polyethylene	PE	$-\!\left(\mathrm{CH_2{-}CH_2}\right)_n\!-$		-125
-Low-density PE	LDPE	Chain structure with long branches	0.89–0.93 85–125	
-High density PE	HDPE	Chain structure with minimal branches	0.94–0.98 130–140	
Polypropylene	PP	 $\left[\mathrm{CH_2{-}CH(CH_3)}\right]_n$	0.83–0.92	-20 to -5
Polystyrene	PS		1.04–1.1 0.05 (Foam)[b]	90–100
Poly(vinyl chloride)	PVC	 $\left[\mathrm{CH_2{-}CH(Cl)}\right]_n$	1.16–1.58	87
Poly(ethylene terephthalate)	PET		1.37–1.45	67–80
Polyurethane	PU	 $\left[\mathrm{C(=O){-}NH{-}R{-}NH{-}C(=O){-}O{-}R'{-}O}\right]_n$	1.2 0.05–0.96 (Foam)[b]	-20
Polyamide (Nylon 66)	PA	 $\left[\mathrm{NH{-}(CH_2)_6{-}NH{-}C(=O){-}(CH_2)_4{-}C(=O)}\right]_n$	1.31	50–60
Cellulose acetate	CA	 D.S ~ 2.45[c]	1.29–1.31	~187

[a] Glass transition temperature
[b] Density of foamed plastics depends on the fraction of air or other gas in the plastic
[c] D.S, the degree of substitution for CA used in cigarette filters (a the predominant constituent of marine beach debris), is about 2.45 but CA is available different values of D.S from 0–3.0 for various applications.

products. Also, products such as foams of PS or bottles of PET may float because of entrapped air, even though the density of the plastic is greater than that of seawater.

1.6.2 Thermal Transitions

When the temperature of an amorphous polymer is increased, the heat energy acquired by the polymer allows increasing degrees of mobility to the polymer chains. At a specific temperature, depending on the plastic, the mobility of chain molecules becomes high enough to make the plastic transition from a "glassy" material to a "rubbery" one. This critical temperature is the Glass Transition temperature, Tg (°C) (Milles et al. 2020). Glassy materials are hard and brittle as

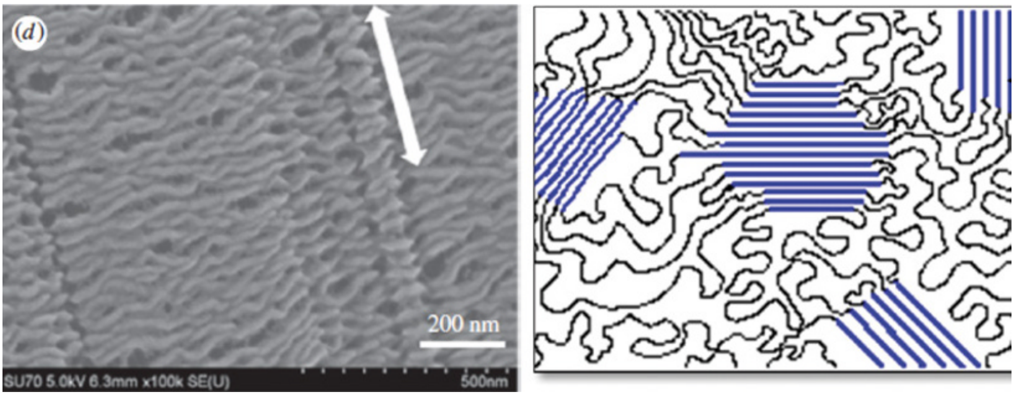


Figure 1.12 Left: Scanning Electron Micrograph of an ultra-high molecular weight HDPE fiber heated at 110 °C for one hour. The crystallites oriented in the direction of the fiber axis (indicated by the arrow) can be seen. Right: Schematic of a semi-crystalline polymer showing oriented chains in “crystalline” regions. *Source:* Left: Courtesy of Miao et al., (2018).

polymer chains are not free to move in response to stress imposed on the material, but heated above this critical temperature, they become more flexible. Above the TG (°C), the polymer chains still remain entangled, unable to move about freely, with only some local movement of chain segments possible. This is, however, a reversible change, and cooling the plastic reverts it back to the glassy state. Chewing gum is usually a polymer below its Tg (°C) at ambient temperatures, but when warmed to body temperature in the oral cavity (to a temperature >Tg [°C]) it becomes rubbery and flexible. Alternatively, soft polymers such as rubber, polyethylene, or protein, that are all above their Tg (°C) at ambient temperature, become glassy, hard, and brittle when cooled to below their Tg (°C) (by dipping in liquid nitrogen [-195.8 °C]).

With semi-crystalline plastics, however, the thermal behavior is somewhat different. The amorphous fraction of the plastic behaves the same as described above and soften above its Tg (°C), but this temperature has no impact at all on the crystalline domains. But, when the plastic is heated to even higher temperatures well above the Tg, the melting temperature of the crystallites, Tm (°C) is reached, when the material changes into a fully amorphous polymer. Further heating above the Tm (°C) (and therefore >Tg [°C]), converts the polymer into a viscous liquid. Neither the Tm (°C) nor Tg (°C) are inherent properties of polymers but can be changed by its thermal and stress history.

The structure of PE was given above simply as $(\text{-CH}_2\text{-CH}_2\text{-})_n$, a linear chain molecule. Commercial grades of polyethylene, however, are generally manufactured with a controlled amount of chain branching in their molecules and therefore have a range of different densities. The type of catalyst used to polymerize ethylene as well as co-monomers (short-chain olefins) mixed with ethylene, determine the stereo-specificity and the chain-branching in the polymer. Chain branching in PE interferes with the development of crystallinity and results in a polyethylene lower density. The density of the polymer is controlled by how much (the percentage) of branching is introduced, and whether these are long (>20 carbon chain) or short (5–10 carbon chain) branches. Nearly-linear PE chains with virtually no branching can crystallize easily and results in a high-density grade of PE called HDPE. Where significant branching is introduced, a relatively low-density and low-crystallinity grade of LDPE (or low-density PE) results. A grade with branching, but mostly with shorter lengths relative to branch chains in LDPE, is the linear-low density grade, LLDPE. Table 1.6 below summarizes the properties of common plastics encountered in the marine environment. The more crystalline HDPE is stronger than LDPE and is used, for instance, in fabricating milk-jugs.

Table 1.6 Characteristics of plastics typically encountered in marine debris.

	Crystallinity (%)	Melting point (°C)	Extensibility (%)	Young's Modulus, *G* (Pa)
LDPE	50–60	105	200–600	0.13–0.3
HDPE	60–80	125	500–700	0.266–0.525
LLDPE	40–60	125	300–900	0.5–1.1
PP	40–60	150–175	100–600	0.9–1.55
PS (GPPS)	—	—	1.2–2.6	1.2–2.6
PS (HIPS)	—	—	15–65	
PVC	10–30	—	11.9–80.0	2.14–4.14
PET	30–40	260	30–300	2.76–4.14
Nylon 6	—	255	25–50	
Cellulose Acetate				

Source: Polyethylene data from Peacock (2000).

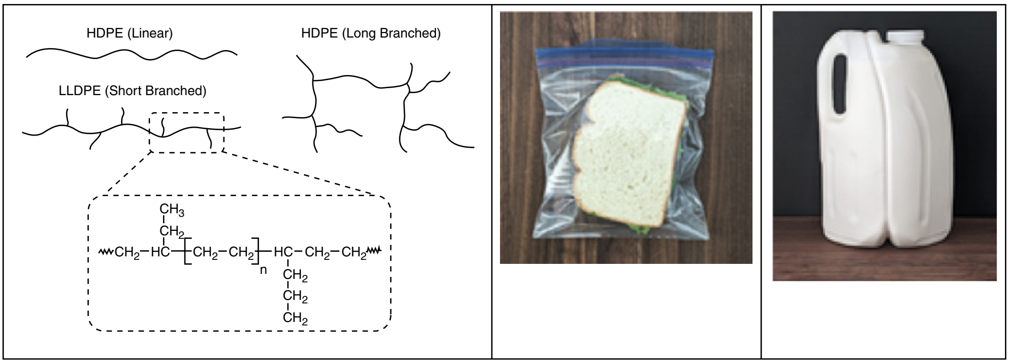


Figure 1.13 Left: Illustration of the molecular geometry of LDPE and HDPE. Middle; LDPE sandwich bag. Right: HDPE milk jug. (Images: Courtesy of Alana Andrady)

Figure 1.13 illustrates the branching in LDPE, HDPE, and LLDPE varieties of polyethylene; there are many other commercially-available PEs of different ρ (g/cm^3). (Medium-density PE-MDPE $\rho = 0.926$–0.940; very low density PE-VLDPE $\rho = 0.890$–0.895; high molecular weight PE-HMWPE $\rho = 0.947$–0.955; and ultra-high molecular weight PE-UHMWPE $\rho = 0.940$.) Also in the figure are two examples of common applications of PE.

1.7 Societal Benefits of Plastics

Behind the dramatic success of plastics as a material is the unique combination of properties that makes them particularly versatile and suitable for a broad range of applications. Plastics offer a combination of engineered functionality with a high degree of design freedom, delivered at a price that is competitive with alternative materials. To understand the consistently increasing demand for plastics worldwide, it is useful to briefly survey the main benefits of the material in several of their key application areas. Figure 1.2 that compares the mix of plastics produced worldwide annually (2015 data from Geyer et al. 2017 recalculated to exclude additives as they are not polymers) to their application areas, is a convenient starting point for the discussion. The advantages of PE and PP that account for about half the global resin in popular applications are especially impressive. Table 1.7 lists the common application areas for thermoplastics with typical uses.

Table 1.7 Applications of common types of plastics.

Application	Plastics Commonly Used	Specific Use
Packaging	PET, HDPE, PP, LDPE, PVC	Bottles, flasks
	PP, HDPE, LDPE, PVC	Closure items, bottle caps
	LDPE, PP, PVC, PET	Films
	LDPE, HDPE, PP	Bags, sacks
	PP, HDPE, LDPE, PVC	Jars, boxes, tubs
Building	PVC, PP, HDPE, LDPE, ABS	Pipes and ducts
	PU, EPS, XPS	Insulation
	PVC	Windows and other frames, flooring, and wall coverings
	PE, PVC	Lining
	PS, PMMA, PC, POM, PA	Interior fittings
Automative	PP, ABS, PC/PBT	Bumper
	PU, PP, PVC, ABS, PA	Seats
	PP, ABS, PPE, PC	Dashboard
	HDPE, POM, PA, PP, PBT	Fuel system
	PP, PPE	Body
	ABS, PP, PBT, POM, PP	Interior trim
	PC, PBT, ABS, PMMA	Lighting
Agriculture	LDPE, LLDPE, PP	Bale bags, seed bags
	LDPE, LLDPE	Greenhouse covers, silo covers, mulch film
	LDPE, HDPE	Nets and mesh
	PP	Rope, strings
	PVC, LDPE	Pipes and fittings
	HDPE, PS, PP	Pesticides containers, nursery pots
Electronics	PS, HIPS, SAN, ABS, PP	Printers/faxes
	ABS, PC/ABS, HIPS, POM	Telecommunications equipment
	PPE/PS, PC/ABS, PET	Televisions
	PC/ABS, ABS, HIPS	Monitors
	ABS, PC/ABS, HIPS	Computers
	PS, ABS, PU, PVC	Refrigeration
	PP, PS, ABS, PVC	Dishwashers

Source: Rudolph et al. (2017).

Abbreviations: ABS – Acrylonitrile-butadiene-styrene copolymer; PC – polycarbonate: PMMA (poly(methyl methacrylate); POM – poly(oxymethylene); and XPS – expanded extruded polystyrene.

1.7.1 Packaging Food and Beverage

Packaging, the leading application of plastics has a global market size exceeding US$240B. Over half the plastic packaging is used in the food and beverage sector. Industrial packaging and non-food consumer packaging, each account for less than half of that volume. About 56% of plastic packaging is PE, with PP (22%), PET (10%), while some PS is also used (Mackenzie 2019).

Packaging addresses a key problem of the Anthropocene, the unprecedented wastage of food in the supply chain as well as by consumers. Globally, an estimated 1/3 of food intended for human consumption invariably ends up as waste (Gustavsson et al. 2011); food wastage in the US is even higher, by at least a third, compared to that in other countries. Along with food, all the resources, including fossil fuel invested in their production, are also wasted and it is critical to minimize this waste. An industry study in the US recently found significantly less food wastage with packaged, compared to unpackaged, food (Ameripen 2018). Plastics packaging achieves this reduction primarily by extending the shelf life of food throughout the supply chain and by managing portion sizes. The weight fraction of packaging needed for this purpose is relatively low, compared to that of food or beverage. This is also true both in terms of the monetary, and the environmental cost of the package, compared to that of the food. Life cycle analysis (LCA) comparing different packaging materials for beverage, highlight the minimal environmental impacts of plastic packaging relative to that of the food it protects (Ghenai 2012; Sivenius et al. 2011; Vignali et al. 2016).

Spoilage of produce and meats is controlled by reducing the oxygen they are in contact with, to dramatically increase their shelf life. One way to achieve this is by vacuum packaging food with flexible plastic films having high barrier properties. Vacuum sealing extends the shelf life of refrigerated vegetables three- to four-fold and frozen meats from weeks, to months, or even years. Fresh meats in refrigerated displays, for instance, typically retain their desirable color only for three to seven days. Modified atmosphere packaging (MAP) used to pack the meat in an atmosphere of high oxygen (70–80%) with 20–30% CO_2 gas, extend its shelf life up to two weeks. The oxygen-rich environment in the package retains the red color of meat, the criterion used by consumers in judging its freshness, for a longer duration. Transparent skin packaging of cured meat products, is in fact, only possible with plastic barrier films. Vegetable and fruit packaging with MAP helps reduce the use of preservatives in produce. Other approaches such as gas flushing, scavenging/desiccant sachets, or on-package valves are all used extensively with plastic packaging to modify the atmosphere inside the package.

The use of any packaging incurs an environmental cost and often creates a post-use solid waste issue as well. In Figure 1.14, E_1 is the embodied energy of the material made from feedstock such as aluminum from ore, or PET from fossil fuel, and E_2 is the processing energy expended to form the material into the package. Energy expenses E_3 onwards are the increments of energy expended in display at store, transporting, cooling prior to use by consumer, cooking, and its post-use disposal. Quantities C_1, C_2, and C_3 (onwards) are the corresponding emissions associated with each step, that include the carbon footprint, the water footprint, and the solid waste generated. The scheme allows a simple comparison of the footprint of different packages such as glass or plastic, provided detailed, reliable, inventories for each step are available. Reported data for $(E_1 + E_2)$ and (C_1) for different beverage containers (Ghenai 2012) are shown in Table 1.8. Note however, that these values are based on LCA and therefore, may vary with location, time, and technology used (Figure 1.14).

The limited analysis has several shortcomings, but shows the plastic jug to have the second-lowest embedded energy as well as carbon emissions. Not captured in Table 1.8 is the water

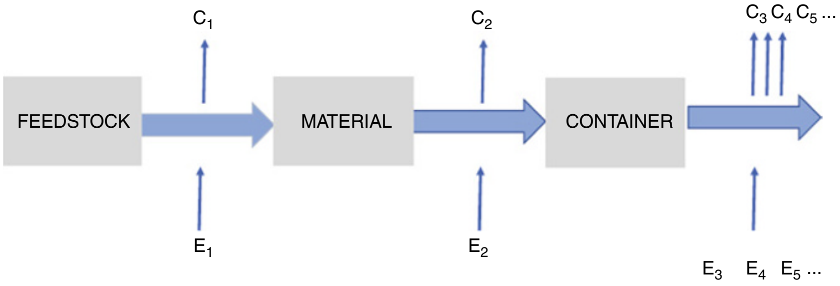


Figure 1.14 Schematic representation of manufacturing a package.

Table 1.8 Energy and carbon footprint associated with packaging milk in various containers. (The percentage of embodied energy and carbon associated with material production phase is shown in parantheses).

Container	Mass of package (kg)	Volume L	Embedded energy (10^{10} J) (E_1%)	Carbon footprint (kg) (C_1%)
HDPE jug	0.051	0.946	2.95 (82.2)	1219 (67.7)
Aluminum can	8.1	50	17.52 (95.9)	10263 (94.7)
Glass bottle	0.41	1	5.82 (68.7)	3820 (62.0)
Paperboard carton	0.057	0.942	0.65 (84.8)	278 (73.4)

Data from Ghenai, 2012

demand, especially in pulping and bleaching of paperboard, as well as the impact of toxic releases from any of the steps. Paperboard enjoys the unique advantage of being based on a renewable feedstock, partly reflected in the value of E_1 (it is also biodegradable in the environment). These estimates assume that only virgin materials are used, and if recycling is included, given the high contributions of of E_1 and C_1 to EE nd EC, these estimates can decrease considerably.

Using packaging with a high environmental cost is justified with food that also has high EE (MJ/kg) and a large carbon footprint (e.g. meats, cheese, coffee, chocolate) as it minimizes waste, and extends shelf life, assuming the consumer will responsibly dispose the packaging waste. If responsible disposal can be assured, plastics would indeed be the ideal packaging material available. A common product that does not conform to the above criteria is bottled water, a popular beverage in the US, with 13.85 Billion gallons sold worldwide in 2018. The environmental cost of the packaging, however, is several orders of magnitude higher than that of the water. The embodied energy of the PET bottle of ~8 MJ/L is enormous by comparison to that of the water of (<0.2 MJ/L) Also, the carbon footprint of the PET bottle is ~42 kg CO_2-e while it is negligible for the water! When transportation, labeling, display, and promotional costs are added, the environmental price tag of bottled water is unacceptably high, especially for water imported from other countries. It is still popular because of its convenience in serving large numbers of people and the misperception that it is more hygienic compared to tap water. An interesting, related comparison is between the environmental merits of paper grocery bags versus plastic bags is pointed out in Box 1.3.

Box 1.3 Paper or Plastic?

A cradle-to-grave LCA study in the US (Chet and Yaros 2014) compared the environmental impacts of HDPE bags, biodegradable PE/PLA bags, and Kraft paper bags (with 30% recycled fiber content). The embodied energy for the HDPE bag was 71% lower, and the gobal warming gas (GWG) emissions, 50% lower, compared to the heavier paper bag. Water demand in the manufacture of the HDPE bags was only ~5% of that used to make the paper bags. A 2018 Danish study (DEPA 2018) that included 7 bag types, as well as a 2011 British study (Edwards and Fry 2011), were in general agreement with the conclusions. A plastic bag was the better choice based on these criteria.

The two main problems with HDPE bags, not captured in such studies, are the recalcitrance of plastic bag litter in the environment (not an issue with biodegradable paper bags) and the toxicity of water/air emissions from the manufacture of either type of bag. The acid rain emissions (NOx and SOx) for HDPE bags was ~11% of that associated with paper bags (Chaffee and Yaros 2014). These values are are highly variable, depending on the location of manufacture and consumer littering behavior, and therefore difficult to quantify. The debate on whether the paper or the plastic grocery bags are better for the environment has been in the news for years. With ~5 trillion paper bags used globally each year (or over 150 000 bags a second!) clear guidance to the conscientious consumer will help the environment.

1.7.2 Plastics in Building

As with packaging, only a handful of different plastics are used in building construction; these, along with the percentage of global production used in building, are PVC (69%), HDPE (20%), PUR (29%) and PS (28%). The percentages shown are for that of the global production in 2015 (Geyer et al. 2017). Some LDPE and PP are also used in building, but to a lesser extent of only about 6% of their respective production volumes.

The most-used resin type in building construction is PVC, both as (i) rigid unplasticized compounds, uPVC, in cladding (siding), window frames, water pipes/fittings, pipes, and rainwater goods; and (ii) plasticized, flexible compounds, pPVC, in laminates as membrane roofing, flooring tiles, and cable sheaths. PVC pipes are widely used in water transport because of their low cost and convenience in installation using quick connections compared to competing water pipes. Some chlorinaed PVC (or CPVC) is also used, especially in hot-water applications, because of its relatively higher softening temperature compared to PVC. Plastic window or door profiles, also made of uPVC, are widely used because of their ease of installation and relatively low lifetime costs. Flooring made of PVC in laminate or engineered flooring, the most-used flooring in the US, is also popular in Asia, Australia and some parts of Europe (Pickard and Sharp 2020). HDPE, competes with PVC as a material for pipe applications but has a relatively shorter service life, but is the plastic of choice in constructing storage tanks for water. Table 1.9 gives a comparison of the environmental characteristics of several different pipe materials for the distribution of potable water. The savings in embodied energy (EE) on using lower-density, lower melting, non-corrosive, and easy-to-assemble PVC, in place of conventional ductile iron, concrete, or clay pipes is easy to appreciate (Uni-Bell 2017).

Another important application is the use of plastic foam insulation in building and refrigeration, that exploits their low density as well as their very low thermal conductivity. The closed cells in polyurethane foam contain inert gases that are very good thermal insulators. Until recently, the inert gas used as a blowing agent for PU foam was Freon (especially, trichlorofluoromethane), but after these were identified as ozone-depleting chemicals, pentanes were substituted in their place. The thermal conductivity of PU foam depends on the cell size and generally varies between 0.02 and

Table 1.9 Embodied energy and carbon data for 8-inch diameter water pipes.

	Iron-concrete lined (DICL)	PVC	Concrete (reinforced)	Cast Iron	HDPE
Embodied Energy (MJ/100-ft) × 10^3	33.94	19.18	9.53	25.5	23.79
Embodied Carbon (MTCO$_2$-e/100 ft)	14.4	9.69	2.08	10.76	218
Weight (Lbs/ft)	22	5.619	60	34	6.65
Expected pipe burst (50 years)	1	1	18	3	

Source: Calculated from Du et al. (2013).

0.03 W/m K, at atmospheric pressure. PU foam is used in applications such as refrigeration and cold storage as well as in insulation.

1.7.3 Plastics in Transportation

The advantage of plastics in construction, that combines strength that can exceed those of metal, but at a much lower density (mass per unit volume), is best illustrated by their applications in transportation. Airplane design, where weight and strength are particularly critical, presently uses increasing amounts plastic composites in place of aluminum. An exceptional example is the Boeing 787 Dreamliner aircraft that is 50% by weight (and 80% by volume) made of plastics or composites. Not only is the molded modular construction faster and less tedious to assemble compared to aluminum structures, but the finished lighter aircraft incurs 20% fuel savings in operation as well as significantly lower carbon emissions during its manufacture. With close to 1000 of these in the air at the time writing and another 500 on order, the energy savings achieved in the aviation industry by the use of plastics are considerable. Other models of aircraft also use increasing amounts of composites in their design.

The same is true of watercraft, a prime example being the Visby class submarine of the Swedish Navy, that uses composites for hull manufacture. The weight advantage of using plastic composites in the vessel is close to 50%, with the added strategic advantage of lower radar, magnetic, and acoustic signatures, compared to traditional metal designs (Rubino et al. 2020). Automobiles where lightweight is critical to ensure fuel savings, also use increasing amounts of plastics. Most of the plastic components in automobiles in the North American market in 2017 were made of PP, PU nylon, and PVC (32%, 17%, 10%, and 6%). In addition to the fuel efficiency that comes with a reduced weight of the automobile, plastics also contribute to corrosion resistance and design flexibility, allowing appealing and safe innovations at a reasonably low cost compared to traditional materials.

1.7.4 Plastics in Textile Fibers

A significant tonnage of plastic resin is used to spin textile fibers (73.5 MMT in 2019) but three plastics dominate the application. In 2020, of the total textile fiber market (including natural fiber) was >52% polyester, 5% Nylon, and 6% rayon fiber (Textile Exchange 2020). Unlike in the early days of the industry, the recent trend of fast-changing fashions, results in a very short service life, often less than a season, for comfort fabric. Clothing today provides physiological as well as psychological well-being to the consumer and needs to be easily laundered. Post-consumer clothing can in theory be recycled, but, only about 15% of all textile is globally recycled at present despite the benefits of the strategy in terms of savings in embodied energy and reduced externalities. Recycling textiles, however, introduces a serious complication. The process generates microfibers from mechanical fragmentation, that are difficult to contain and are released to the environment with waste water.

1.7.5 Plastics in the Energy Industry

Wind turbines generate about 11% of the energy used in the US (especially electricity) and 10–15% of that in Europe. It is the fastest-growing renewable energy source at this time, but they have significant infrastructure costs. Blades of windmill installations span 100–150 ft and have to be made of a lightweight material such as wood. Polymer composites fit the requirement ideally, and glass fiber, carbon fiber, aramid, and basalt fibers are used to reinforce either thermoplastics or thermoset polymers in the design of windmill blades (Mishnaevsky et al. 2017). Plastic blades can be conveniently molded into the complex aerodynamic geometries and are now beginning to be even recycled.

Plastics also play a significant role in the design of photovoltaic (PV) panels for production of solar energy. The active layer is encapsulated in plastic, sealing it from moisture and oxygen. Other parts of the module such as the back sheet, adhesive, and the protective film over glass, are made of plastics in modern PV modules. Another application of plastics in the energy industry is their use as a transparent exposure chambers for suspensions of microalgae in vertical algae farms employed in biodiesel production. To get high yields of oil, it is important to have a monoculture of selected oil-rich algae, by growing them in media enclosed in thin plastic tubes or bags and exposed to solar radiation. With hundreds of closely spaced transparent algae bags exposed outdoors, plastic (rather than glass) is best suited for the application.

References

Alaerts, L., Augustinus, M., Van Acker, K., 2018. Impact of bio-based plastics on current recycling of plastics. *Sustainability*, 10(5): 1487.

Ameripen 2018. Quantifying the value of packaging as a strategy to prevent food waste in America. Ameripen Report.<https://www.ameripen.org/page/foodwastereport> (accessed March 25, 2021).

Andrady, A. L., Neal, M. A. 2009. Applications and societal benefits of plastics. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526): 1977–1984.

Andrady, A., 2011. Microplastics in the marine environment. *Marine Pollution Bulletin*, 62(8): 1596–1605.

Andrady, A., 2017. The plastic in microplastics: a review. *Marine Pollution Bulletin*, 119(1): 12–22.

Arthur, C., Baker, J., Bamford, H. 2008. Proceedings of the International research workshop on the occurrence, effects, and fate of microplastic marine debris. University of WashingtonTacoma, Tacoma, WA. *In Conference Proceedings.* Sept. 9–11.

Avio, C., Gorbi, S., Milan, M., Benedetti, M., Fattorini, D., d'Errico, G., Pauletto, M., Bargelloni, L., Regoli, F., 2015. Pollutants bioavailability and toxicological risk from microplastics to marine mussels. *Environmental Pollution*, 198: 211–222.

Bakir, A., O'Connor, I., Rowland, S., Hendriks, A., and Thompson, R., 2016. The relative importance of microplastics as a pathway for the transfer of hydrophobic organic chemicals to marine life. *Environmental Pollution*, 219: 56–65.

Ball, P. 2020. The plastic legacy. *Nature Materials*, 19(9): 938.

Barboza, L. G. A., Vethaak, A. D., Lavorante, B. R. B. O., Lundebye, A. K., Guilhermino, L. 2018. Marine microplastic debris: an emerging issue for food security, food safety and human health. *Marine Pollution Bulletin*, 133: 336–348.

Barnes, D. K. A., Galgani, F., Thompson, R.C. & Barlaz, M. 2009. Accumulation and fragmentation of plastic debris in global environments. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526): 1985–1998.

Barrett, J., Chase, Z., Zhang, J., Holl, M., Willis, K., Williams, A., Hardesty, B., Wilcox, C. 2020. Microplastic Pollution in Deep-Sea Sediments from the Great Australian Bight. *Frontiers in Marine Science*, 7: 808.

Batel, A., Borchert, F., Reinwald, H., Erdinger, L., Braunbeck, T., 2018. Microplastic accumulation patterns and transfer of benzo[a]pyrene to adult zebrafish (*Danio rerio*) gills and zebrafish embryos. *Environmental Pollution*, 235: 918–930.

Beiras, R., Bellas, J., Cachot, J., Cormier, B., Cousin, X., Engwall, M., Gambardella, C., Garaventa, F., Keiter, S., Le Bihanic, F., López-Ibáñez, S., Piazza, V., Rial, D., Tato, T. and Vidal-Liñán, L., 2018. Ingestion and contact with polyethylene microplastics does not cause acute toxicity on marine zooplankton. *Journal of Hazardous Materials*, 360: 452–460.

Belboom, S., Léonard, A., 2016. Does biobased polymer achieve better environmental impacts than fossil polymer? Comparison of fossil HDPE and biobased HDPE produced from sugar beet and wheat. *Biomass and Bioenergy*, 85: 159–167.

Bergmann, M. Mützel, S., Primpke, S., Tekman, M. B., Trachsel, J., Gerdts, G. 2019. White and wonderful? Microplastics prevail in snow from the Alps to the Arctic, *Science Advances*, 5(8): eaax1157.

Billiet, S., Trenor, S. R. 2020. 100th anniversary of macromolecular science viewpoint: needs for plastics packaging circularity. *ACS Macro Letters*, 9(9): 1376–1390.

Bishop, G., Styles, D., Lens, P. N. L. 2021. Environmental performance comparison of bioplastics and petrochemical plastics: a review of life cycle assessment (LCA) methodological decisions. *Resources, Conservation and Recycling*, 168: 105451.

Borrelle, S., Ringma, J., Law, K., Monnahan, C., Lebreton, L., McGivern, A., Murphy, E., Jambeck, J., Leonard, G., Hilleary, M., Eriksen, M., Possingham, H., De Frond, H., Gerber, L., Polidoro, B., Tahir, A., Bernard, M., Mallos, N., Barnes, M., Rochman, C. 2020. Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. *Science*, 369(6510): 1515–1518.

Brizga, J., Hubacek, K., Feng, K. 2020. The unintended side effects of bioplastics: carbon, land, and water footprints. *One Earth*, 3(1): 45–53.

Browne, M., Dissanayake, A., Galloway, T., Lowe, D., Thompson, R. 2008. Ingested microscopic plastic translocates to the circulatory system of the mussel, *Mytilus edulis* (L.). *Environmental Science & Technology*, 42(13): 5026–5031.

Calabrò, P. S., Grosso, M. 2018. Bioplastics and waste management. *Waste Management.* 78: 800–801.

Campanale, C., Massarelli, C., Savino, I., Locaputo, V., Uricchio, V.F. 2020. A detailed review study on potential effects of microplastics and additives of concern on human health. *International Journal of Environmental Research and Public Health.* 17: 1212.

Carpenter, E. J., Smith, K. L. 1972. Plastics on the Sargasso Sea surface, *Science*, 175(4027): 1240–1241.

Cesa, F. S., Turra, A., Baruque-Ramos, J. 2017. Synthetic fibers as microplastics in the marine environment: a review from the textile perspective with a focus on domestic washings, *Science of the Total Environment*, 598: 1116–1129.

Cesa, F. S., Turra, A., Checon, H. H., Leonardi, B., Baruque-Ramos, J. 2020. Laundering and textile parameters influence fibers release in household washings, *Environmental Pollution*, 257, 113553.

Cheroennet, N., Pongpinyopap, S., Leejarkpai, T., Suwanmanee, U. 2017. A trade-off between carbon and water impacts in bio-based box production chains in Thailand: a case study of PS, PLAS, PLAS/starch, and PBS. *Journal of Cleaner Production*, 167, 987–1001.

Chet Chaffee, C., Yaros R. B. 2014. Life cycle assessment for three types of grocery bags – recyclable plastic; compostable, biodegradable plastic; and recycled, recyclable paper. Report by Boustead Consulting & Associates Ltd.

Chitaka, T. Y., von Blottnitz, H. 2019. Accumulation and characteristics of plastic debris along five beaches in Cape Town. *Marine Pollution Bulletin*, 138: 451–457.

Chua, E., Shimeta, J., Nugegoda, D., Morrison, P., Clarke, B. 2014. Assimilation of polybrominated diphenyl ethers from microplastics by the marine amphipod, *Allorchestes compressa. Environmental Science & Technology*, 48(14): 8127–8134.

Ciel.org. 2021. Fueling plastics untested assumptions and unanswered questions in the plastics boom. <https://www.ciel.org/wp-content/uploads/2018/04/Fueling-Plastics-Untested-Assumptions-and-Unanswered-Questions-in-the-Plastics-Boom.pdf> (accessed March 23, 2021).

Cole, M., Lindeque, P., Fileman, E., Halsband, C., Goodhead, R., Moger, J., Galloway, T. 2013. Microplastic ingestion by zooplankton. *Environmental Science & Technology*, 47(12): 6646–6655.

Cole, M., Lindeque, P., Halsband, C., Galloway, T. S. 2011. Microplastics as contaminants in the marine environment: a review, *Marine Pollution Bulletin*, 62(12): 2588–2597.

Colton, J. B., Knapp, F. D., Burns, B. R. 1974. Plastic particles in surface waters of the northwestern Atlantic. *Science*, 185(4150): 491–497.

Cox, K., Covernton, G., Davies, H., Dower, J., Juanes, F., Dudas, S. 2019. Human consumption of microplastics. *Environmental Science & Technology*, 53(12): 7068–7074.

Cozar, A., Echevarria, F., Gonzalez-Gordillo, J., Irigoien, X., Ubeda, B., Hernandez-Leon, S., Palma, A., Navarro, S., Garcia-de-Lomas, J., Ruiz, A., Fernandez-de-Puelles, M., Duarte, C. 2014. Plastic debris in the open ocean. *Proceedings of the National Academy of Sciences*, 111(28), 10239–10244.

Crutzen, P. J., Stoermer, E. F., 2000. *The anthropocene. Global Change Newsletter*, 41: 17–18.

The Danish Environmental Protection Agency 2018. Ed: Bisinella, B., Albizzati, P.F., T.F. Astrup, Damgaard, A. Lifecycle assessment of carrier bags. *Environmental Project 1985.* February 2018.

Danopoulos, E., Twiddy, M., West, R., and Rotchell, J. M. (2021). A rapid review and meta-regression analyses of the toxicological impacts of microplastic exposure in human cells. *Journal of Hazardous Materials*: 127861.

Day, R. H., Shaw, D. G., Ignell, S. E. 1998. The quantitative distribution and characteristics of Neuston Plastic in The North Pacific Ocean, 1985–1988. In Proceedings of the Second International Conference on Marine Debris, 2–7 April 1989, Honolulu, Hawaii, pp. 247–266.

De Falco, F., Di Pace, E., Cocca, M., Avella, M. 2019. The contribution of washing processes of synthetic clothes to microplastic pollution, *Scientific Reports*, 9(1): 1–11.

Deng, Y., Zhang, Y., Lemos, B., Ren, H., 2017. Tissue accumulation of microplastics in mice and biomarker responses suggest widespread health risks of exposure. *Scientific Reports*, 7(1): 1–10.

Derraik, J., 2002. The pollution of the marine environment by plastic debris: a review. *Marine Pollution Bulletin*, 44(9): 842–852.

Do Sul, J. A. I., Costa, M. F. 2014. The present and future of microplastic pollution in the marine environment, *Environmental Pollution*, 185, 352–364.

Dong, Y., Gao, M., Song, Z., Qiu, W. 2020. As (III) adsorption onto different-sized polystyrene microplastic particles and its mechanism. *Chemosphere*, 239: 124792.

Drouillard, K. G. 2008. Bio-magnification. *Ecotoxicology*, 441–448.

Du, F., Woods, G., Kang, D., Lansey, K., Arnold, R. 2013. Life cycle analysis for water and wastewater pipe materials. *Journal of Environmental Engineering*, 139(5): 703–711.

Edenhofer, O., Pichs, R., Sokona, Y., Farahani, E., Kardner, S., Seyboth, K., Adler, A., Banum, I., Brunner, S., Eickemeier, P., Kriemann, B., Savoleinan, J., Schlömer, S., Zwickel, T., Minx, J. 2014. *Climate Change 2014: Mitigation of Climate Change*. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC). Cambridge University Press, p. 1434.

Edwards, C., Fry, J. 2011. *Life Cycle Assessment of Supermarket Carrier Bags: A Review of the Bags Available in 2006*. Environment Agency, Horizon House, Bristol, BS1 5AH.

EIA. 2020. International Energy Outlook 2020. Report by US Energy Information Administration, Washington DC, October 14, 2020. Downloaded from https://www.iea.org/reports/world-energy-outlook-2020, on 1, Feb 2022.

E-marketer. 2021 In Statista. *Per capita* consumption of plastic materials worldwide in 2015 by region (in kilograms). *The Statistics Portal*. <https://www.statista.com/statistics/270312/consumption-of-plastic-materials-per-capita-since-1980/>

Enders, K., Lenz, R., Stedmon, C., Nielsen, T. 2015. Abundance, size and polymer composition of marine microplastics ≥10 µm in the Atlantic Ocean and their modelled vertical distribution. *Marine Pollution Bulletin*, 100(1): 70–81.

Eriksen, M., Mason, S., Wilson, S., Box, C., Zellers, A., Edwards, W., Farley, H., Amato, S. 2013. Microplastic pollution in the surface waters of the Laurentian Great Lakes, *Marine Pollution Bulletin*, 77(1–2), 177–182.

Eriksen, M., Lebreton, L., Carson, H., Thiel, M., Moore, C., Borerro, J., Galgani, F., Ryan, P., Reisser, J. 2014. Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. *PLoS ONE*, 9(12): e111913.

Everaert, G., Van Cauwenberghe, L., De Rijcke, M., Koelmans, A. A., Mees, J., Vandegehuchte, M., Janssen, C. R. 2018. Risk assessment of microplastics in the ocean: modelling approach and first conclusions, *Environmental Pollution*, 242: 1930–1938.

Fendall, L. S., Sewell, M. A. 2009. Contributing to marine pollution by washing your face: microplastics in facial cleansers, *Marine Pollution Bulletin*, 58(8): 1225–1228.

Fossi, M., Coppola, D., Baini, M., Giannetti, M., Guerranti, C., Marsili, L., Panti, C., de Sabata, E., Clò, S., 2014. Large filter feeding marine organisms as indicators of microplastic in the pelagic environment: the case studies of the Mediterranean basking shark (*Cetorhinus maximus*) and fin whale (*Balaenoptera physalus*). *Marine Environmental Research*, 100: 17–24.

Fry, D., Fefer, S., Sileo, L. 1987. Ingestion of plastic debris by Laysan albatrosses and wedge-tailed shearwaters in the Hawaiian Islands. *Marine Pollution Bulletin*, 18(6): 339–343.

GESAMP. 2015. Sources, fate and effects of microplastics in the marine environment: a global assessment. In: Kershaw, P. J. (Ed.), *IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection* Reports and Studies GESAMP No. 90, p. 96. https://ec.europa.eu/environment/marine/good-environmental-status/descriptor-10/pdf/GESAMP_microplastics%20full%20study.pdf

GESAMP. 2016. Sources, fate and effects of microplastics in the marine environment: part two of a global assessment. In: Kershaw, P. J. (Ed.), *IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection*. Reports and Studies GESAMP No. 93, p. 220. http://www.gesamp.org/site/assets/files/1275/sources-fate-and-effects-of-microplastics-in-the-marine-environment-part-2-of-a-global-assessment-en.pdf

Geyer, R., Jambeck, J., Law, K. 2017. Production, use, and fate of all plastics ever made. *Science Advances*, 3(7): e1700782.

Ghenai, C. 2012. Life cycle assessment of packaging materials for milk and dairy products. *International Journal of Thermal & Environmental Engineering*, *4*(2): 117–128.

Gouin, T., Avalos, J., Brunning, I., et al. 2015. Use of micro-plastic beads in cosmetic products in Europe and their estimated emissions to the North Sea environment. *SOFW Journal*, 3: 1–33.

Gouin, T., Roche, N., Lohmann, R., Hodges, G. 2011. A thermodynamic approach for assessing the environmental exposure of chemicals absorbed to microplastic. *Environmental Science & Technology*, 45(4): 1466–1472.

Groh, K. J., Backhaus, T., Carney-Almroth, B., Geueke, B., Inostroza, P. A, Lennquist, A., Leslie, H. A., Maffini, M., Slunge, D., Trasande, L., Warhurst, A. M., Muncke, J. 2019. Overview of known plastic packaging-associated chemicals and their hazards. *Science of the Total Environment.* 15(651–652): 3253–3268.

Guo, X., Wang, J. 2019. The chemical behaviors of microplastics in marine environment: a review. *Marine Pollution Bulletin*, 142: 1–14.

Guo, X., Hu, G., Fan, X., Jia, H. 2020. Sorption properties of cadmium on microplastics: the common practice experiment and a two-dimensional correlation spectroscopic study. *Ecotoxicology and Environmental Safety*, 190: 110118.

Hartline, N., Bruce, N., Karba, S., Ruff, E., Sonar, S., Holden, P. 2016. Microfiber masses recovered from conventional machine washing of new or aged garments. *Environmental Science & Technology*, 50(21): 11532–11538.

Hartmann, N., Rist, S., Bodin, J., Jensen, L., Schmidt, S., Mayer, P., Meibom, A., Baun, A. 2017. Microplastics as vectors for environmental contaminants: exploring sorption, desorption, and transfer to biota. *Integrated Environmental Assessment and Management*, 13(3): 488–493.

Henry, B., Laitala, K., Klepp, I. 2019. Microfibres from apparel and home textiles: prospects for including microplastics in environmental sustainability assessment. *Science of The Total Environment*, 652: 483–494.

Hesler, M., Aengenheister, L., Ellinger, B., Drexel, R., Straskraba, S., Jost, C., Wagner, S., Meier, F., von Briesen, H., Büchel, C. 2019. Multi-endpoint toxicological assessment of polystyrene nano- and microparticles in different biological models *in vitro*. *Toxicology in vitro.* 61, 104610.

Hong, S., Lee, J., Lim, S. 2017. Navigational threats by derelict fishing gear to navy ships in the Korean seas. *Marine Pollution Bulletin*, 119(2): 100–105.

Hüffer, T., Hofmann, T. (2016). Sorption of non-polar organic compounds by micro-sized plastic particles in aqueous solution. *Environmental Pollution*, 214: 194–201.

Hurley, R., Woodward, J., Rothwell, J. J. 2018. Microplastic contamination of river beds significantly reduced by catchment-wide flooding, *Nature Geoscience*, 11(4): 251–257.

Hussain, N. 2001. Recent advances in the understanding of uptake of microparticulates across the gastrointestinal lymphatics. *Advanced Drug Delivery Reviews*, 50(1–2): 107–142.

IEA. 2018. *The future of petrochemicals*. IEA, Paris. https://www.iea.org/reports/the-future-of-petrochemicals (accessed August 19, 2021).

IEA. 2020. *World Energy Outlook 2020*. IEA, Paris. https://www.iea.org/reports/world-energy-outlook-2020 (accessed August 19, 2021).

IPCC. 2018. *Summary for Policymakers. Special report: global warming of 1.5°C*. World Meteorological Organization, Geneva, Switzerland, 32 pp. https://www.ipcc.ch/sr15/chapter/spm/

Ivar do Sul, J., Costa, M., 2014. The present and future of microplastic pollution in the marine environment. *Environmental Pollution*, 185: 352–364.

Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A. 2015. Plastic waste inputs from land into the ocean, *Science*, 347(6223): 768–771.

Jin, Y., Lu, L., Tu, W., Luo, T. and Fu, Z., 2019. Impacts of polystyrene microplastic on the gut barrier, microbiota and metabolism of mice. *Science of The Total Environment*, 649: 308–317.

Joseph, J., Stienbarger, C., Athey, S. et al. (2020). An assessment of microplastic ingestion in the commercially important Black Sea Bass, *Centropristis striata*: a lab and field study. *Ocean Sciences Meeting.* February 16–21, San Diego, CA.

Jovanović, B., Gökdağ, K., Güven, O., Emre, Y., Whitley, E., Kideys, A. 2018. Virgin microplastics are not causing imminent harm to fish after dietary exposure. *Marine Pollution Bulletin*, 130: 123–131.

Kaiser, K., Schmid, M., Schlummer, M. 2018. Recycling of polymer-based multilayer packaging: a review. *Recycling*, 3: 1.

Kako, S., Morita, S., Taneda, T. 2020. Estimation of plastic marine debris volumes on beaches using unmanned aerial vehicles and image processing based on deep learning. *Marine Pollution Bulletin*, 155: 111127.

Kanhai, L. K, Johansson, C., Frias, J. P. G. L., Gardfeldt, K., Thompson, Richard C., O'Connor, I. 2019. Deep sea sediments of the Arctic Central Basin: a potential sink for microplastics. *Deep Sea Research Part I: Oceanographic Research Papers*, 145: 137–142.

Kaposi, K., Mos, B., Kelaher, B., Dworjanyn, S. 2014. Ingestion of microplastic has limited impact on a marine larva. *Environmental Science & Technology*, 48(3): 1638–1645.

Karlsson, T. M., Arneborg, L., Broström, G., Almroth, B. C., Gipperth, L, Hassellöv, M., 2018. The unaccountability case of plastic pellet pollution. *Marine Pollution Bulletin*, 129(1): 52–60.

Kaza, S., Yao, L., Bhada-Tata, P., Van Woerden, F. 2018. *What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050*. WorldBank publications.

Kiessling, T., Gutow, L., Thiel, M. 2015. Marine litter as habitat and dispersal vector. *Marine Anthropogenic Litter*, 141–181.

Koelmans, A., Bakir, A., Burton, G., Janssen, C. 2016. Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies. *Environmental Science & Technology*, 50(7): 3315–3326.

Kooi, M., Reisser, J., Slat, B., Ferrari, F.F., Schmid, M.S., Cunsolo, S., Brambini, R., Noble, K., Sirks, L.A., Linders, T.E., Schoeneich-Argent, R.I. 2016. The effect of particle properties on the depth profile of buoyant plastics in the ocean, *Scientific Reports*, 6: 33882.

Kong, Y., Hay, J. N. 2002. The measurement of the crystallinity of polymers by DSC. *Polymer*, 43(14): 3873–3878.

Koongolla, B., Andrady, A. L., Terney Pradeep Kumara, P. B., Gangabadage, C. S. 2018. Evidence of microplastics pollution in coastal beaches and waters in southern Sri Lanka. *Marine Pollution Bulletin*, 137: 277–284.

Kosuth, M., Mason, S., Wattenberg, E. 2018. Anthropogenic contamination of tap water, beer, and sea salt. *PLoS ONE*, 13(4): e0194970.

Kühn, S., van Franeker, J. 2020. Quantitative overview of marine debris ingested by marine megafauna. *Marine Pollution Bulletin*, 151: 110858.

Kukulka, T., Proskurowski, G., Morét-Ferguson, S., Meyer, D. W., Law, K. L. 2012 The effect of wind mixing on the vertical distribution of buoyant plastic debris. *Geophysical Research Letters*, 39(7).

La Mantia, F., Vinci, M. 1994. Recycling poly(ethyleneterephthalate). *Polymer Degradation and Stability*, 45(1): 121–125.

Lambert, S., Wagner, M. 2016. Characterisation of nanoplastics during the degradation of polystyrene, *Chemosphere*, 145: 265–268.

Law, K.L., Thompson, R.C. 2014. Microplastics in the seas. *Science*, 345: 144–145.

Law, K., Starr, N., Siegler, T., Jambeck, J., Mallos, N., Leonard, G. 2020. The United States' contribution of plastic waste to land and ocean. *Science Advances*, 6(44): eabd0288.

Lebreton, L., Andrady, A. 2019. Future scenarios of global plastic waste generation and disposal. *Palgrave Communications*, 5(1): 1–11.

Lebreton, L., Slat, B., Ferrari, F., Sainte-Rose, B., Aitken, J., Marthouse, R., Hajbane, S., Cunsolo, S., Schwarz, A., Levivier, A., Noble, K. 2018. Evidence that the great pacific garbage patch is rapidly accumulating plastic. *Scientific Reports*, 8(1): 1–15.

Lebreton, L., van der Zwet, J., Damsteeg, J., Slat, B., Andrady, A., Reisser, J., 2017. River plastic emissions to the world's oceans. *Nature Communications*, 8(1), 1–10.

Lee, H., Lee, H., Kwon, J. 2019. Estimating microplastic-bound intake of hydrophobic organic chemicals by fish using measured desorption rates to artificial gut fluid. *Science of The Total Environment*, 651: 162–170.

Leonas, K. 2017. *Textiles and clothing sustainability: recycled and upcycled textiles and fashion*. Singapore: *Springer*, pp. 55–77.

Leslie, H. A. 2014. Review of microplastics in cosmetics. *IVM Institute for Environmental Studies*, 476: 1–33.

Li, W. C., Tse, H. F., Fok, L. 2016. Plastic waste in the marine environment: a review of sources, occurrence and effects. *Science of the Total Environment*, 566: 333–349.

Lindeque, P. K., Cole, M., Coppock, R. L., Lewis, C. N., Miller, R. Z., Watts, A. J. R., Wilson-McNeal, A., Wright, S. L., Galloway, T. S. 2020. Are we underestimating microplastic abundance in the marine environment? A comparison of microplastic capture with nets of different mesh-size. *Environmental Pollution*, 265A: 114721.

Luo, T., Zhang, Y., Wang, C., Wang, X., Zhou, J., Shen, M., Zhao, Y., Fu, Z., Jin, Y. 2019. Maternal exposure to different sizes of polystyrene microplastics during gestation causes metabolic disorders in their offspring. *Environmental Pollution*, 255, 113122.

Lusher, A. 2015. *Microplastics in the marine environment: distribution, interactions and effects*. *Marine Anthropogenic Litter*, Springer, Cham, 245–307.

Mackenzie, W. 2019. *Global plastic packaging market*. Plastics News. <https://www.plasticsnews.com/article/20190128/FYI/190129903/global-plastic-packaging-market> (accessed March 25, 2021).

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., Kaminuma, T., 2001. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environmental Science & Technology*, 35(2): 318–324.

Mendoza, L. M. R., Karapanagioti, H., Álvarez, N. R. 2018. Micro (nanoplastics) in the marine environment: current knowledge and gaps. *Current Opinion in Environmental Science & Health*, 1: 47–51.

Merrell Jr, T. R. 1980. Accumulation of plastic litter on beaches of Amchitka Island, Alaska. *Marine Environmental Research*, 3(3): 171–184.

Miao, W., Zhu, H., Duan, T., Chen, H., Wu, F., Jiang, L., Wang, Z. 2018. High-density polyethylene crystals with double melting peaks induced by ultra-high-molecular-weight polyethylene fibre. *Royal Society Open Science*, 5(7): 180394.

Miller, M., Hamann, M., Kroon, F., 2020. Bioaccumulation and biomagnification of microplastics in marine organisms: a review and meta-analysis of current data. *PLoS ONE*, 15(10): e0240792.

Mills, N., Jenkins, M., Kukureka, S. 2020. Chapter 3 – Amorphous polymers and the glass transition. In: Mills, N., Jenkins, M., Kukureka, S. (Eds.), *Plastics* (4th ed.). Butterworth-Heinemann, pp. 33–48.

Mintenig, S., Int-Veen, I., Löder, M., Primpke, S., Gerdts, G. 2017. Identification of microplastic in effluents of waste water treatment plants using focal plane array-based micro-Fourier-transform infrared imaging. *Water Research*, 108: 365–372.

Mishnaevsky, L., Branner, K., Petersen, H., Beauson, J., McGugan, M., Sørensen, B. 2017. Materials for wind turbine blades: an overview. *Materials*, 10(11): 1285.

Mizukawa, K., Takada, H., Takeuchi, I., Ikemoto, T., Omori, K., Tsuchiya, K. 2009. Bioconcentration and biomagnification of polybrominated diphenyl ethers (PBDEs) through lower-trophic-level coastal marine food web. *Marine Pollution Bulletin*, 58(8): 1217–1224.

Moore, C., Moore, S., Leecaster, M., Weisberg, S. 2001. A comparison of plastic and plankton in the North Pacific Central Gyre. *Marine Pollution Bulletin*, 42(12): 1297–1300.

Moretti, C., Hamelin, L., Jakobsen, L., Junginger, M., Steingrimsdottir, M., Høibye, L., Shen, L. 2021. Cradle-to-grave life cycle assessment of single-use cups made from PLA, PP and PET. *Resources, Conservation and Recycling*, 169: 105508.

Morris, R. J. 1980. Floating plastic debris in the Mediterranean. *Marine Pollution Bulletin*, 11(5): 125.

Näkki, P., Setälä, O., Lehtiniemi, M. 2019. Seafloor sediments as microplastic sinks in the northern Baltic Sea – negligible upward transport of buried microplastics by bioturbation. *Environmental Pollution*, 249: 74–81.

Napper, I. E., Bakir, A., Rowland, S. J., Thompson, R. C. 2015. Characterisation, quantity and sorptive properties of microplastics extracted from cosmetics. *Marine Pollution Bulletin*, 99(1–2): 178–185.

Narancic T, Cerrone F, Beagan N, O'Connor KE. 2020. Recent advances in bioplastics: application and biodegradation. *Polymers (Basel)*, 12(4): 920.

Nelms, S., Barnett, J., Brownlow, A., Davison, N., Deaville, R., Galloway, T., Lindeque, P., Santillo, D., Godley, B. 2019. Microplastics in marine mammals stranded around the British coast: ubiquitous but transitory? *Scientific Reports*, 9(1), 1–8.

Ocean Conservancy. 2019. *ICC Report*. Ocean Conservancy, Washington DC.

Obbard, R. W., Sadri S, Wong Y. Q., Khitun A. A., Baker I. 2014. Global warming releases microplastic legacy frozen in Arctic Sea ice. *Earth's Future*, 2(6): 315–320.

Oehlmann, J., Schulte-Oehlmann, U., Kloas, W., Jagnytsch, O., Lutz, I., Kusk, K. O., Wollenberger, L., Santos, E. M., Paull, G. C., Van Look, K. J., Tyler, C. R. 2009. A critical analysis of the biological impacts of plasticizers on wildlife. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526): 2047–2062.

Panno, S. V., Kelly, W. R., Scott, J., Zheng, W., McNeish, R. E., Holm, N., Hoellein, T. J., Baranski, E. L. 2019. Microplastic contamination in karst groundwater systems. *Groundwater*, 57(2): 189–196.

Papong, S., Malakul, P., Trungkavashirakun, R., Wenunun, P., Chom-in, T., Nithitanakul, M. 2014. Comparative assessment of the environmental profile of PLA and PET drinking water bottles from a life cycle perspective. *Journal of Cleaner Production*, 65, 539–550.

Parida, A. K., Das, A. B. 2005. Salt tolerance and salinity effects on plants: a review, *Ecotoxicology and Environmental Safety*, 60(3): 324–349.

Pascall, M., Zabik, M., Zabik, M., Hernandez, R. 2005. Uptake of polychlorinated biphenyls (PCBs) from an aqueous medium by polyethylene, polyvinyl chloride, and polystyrene films. *Journal of Agricultural and Food Chemistry*, 53(1): 164–169.

Peacock, A.J. 2000. *Handbook of Polyethylene – Structures, Properties and Applications*. Marcel Dekker, New York.

Peeken, I., Primpke, S., Beyer, B., Gütermann, J., Katlein, C., Krumpen, T., Bergmann, M., Hehemann, L., Gerdts, G. 2018. Arctic sea ice is an important temporal sink and means of transport for microplastic. *Nature Communications*, 9(1): 1–12.

Peng, L., Fu, D., Qi, H., Lan, C.Q., Yu, H., Ge, C. 2020. Micro-and nano-plastics in marine environment: source, distribution and threats – a review. *Science of the Total Environment*, 698: 134254.

Petroff, A. 2017. These countries want to ban gas and diesel cars. *CNN Money*, p. 11.

Pham, C., Rodríguez, Y., Dauphin, A., Carriço, R., Frias, J., Vandeperre, F., Otero, V., Santos, M., Martins, H., Bolten, A., Bjorndal, K., 2017. Plastic ingestion in oceanic-stage loggerhead sea turtles (*Caretta caretta*) off the North Atlantic subtropical gyre. *Marine Pollution Bulletin*, 121(1–2): 222–229.

Pickard, S., Sharp, S. 2020. *Phasing out plastics*. Climate Works Foundation and 11th Hour Project. ODI, London.

Pitt, J. A., Kozal, J. S., Jayasundara, N., Massarsky, A., Trevisan, R., Geitner, N., Wiesner, M., Levin, E. D., Di Giulio, R. T. 2018. Uptake, tissue distribution, and toxicity of polystyrene nanoparticles in developing zebrafish (*Danio rerio*). *Aquatic Toxicology (Amsterdam, Netherlands)*, *194*, 185–194.

Qu, H., Ma, R., Barrett, H., Wang, B., Han, J., Wang, F., Chen, P., Wang, W., Peng, G. and Yu, G., 2020. How microplastics affect chiral illicit drug methamphetamine in aquatic food chain? From green alga (*Chlorella pyrenoidosa*) to freshwater snail (*Cipangopaludian cathayensis*). *Environment International*, 136: 105480.

Ragusa, A., Svelato, A., Santacroce, C., Catalano, P., Notarstefano, P., Carnevali, P., Papa, F., Rongioletti, M. C. A., Baiocco, F., Draghi, S., D'Amore, E., Rinaldo, D., Matta, M., Giorgini, E. 2021. Plasticenta: first evidence of microplastics in human placenta. *Environment International*, 146: 106274.

Ramirez-Llodra, E., Tyler, P. A., Baker, M. C., Bergstad, O. A., Clark, M. R., Escobar, E., Levin, L. A., Menot, L., Rowden, A. A., Smith, C. R., Van Dover, C. L. 2011. Man and the last great wilderness: human impact on the deep sea. *PLoS ONE.* 6(8): e22588.

Rech, S., Borrell Pichs, Y., García-Vazquez, E. 2018. Anthropogenic marine litter composition in coastal areas may be a predictor of potentially invasive rafting fauna. *PLoS ONE*, 13(1): e0191859.

Reinert, T., Spellman, A., Bassett, B. 2017. Entanglement in and ingestion of fishing gear and other marine debris by Florida manatees, 1993 to 2012. *Endangered Species Research*, 32: 415–427.

Reisser, J. W., Slat, B., Noble, K. D., Plessis, K. D., Epp, M., Proietti, M. C., Sonneville, J. D., Becker, T., Pattiaratchi, C. 2015. The vertical distribution of buoyant plastics at sea: an observationalstudy in the North Atlantic Gyre. *Biogeosciences*, 12: 1249–1256.

Revel, M., Châtel, A., Mouneyrac, C., 2018. Micro(nano)plastics: a threat to human health? *Current Opinion in Environmental Science & Health*, 1: 17–23.

Reynolds, C., Ryan, P. 2018. Micro-plastic ingestion by waterbirds from contaminated wetlands in South Africa. *Marine Pollution Bulletin*, 126: 330–333.

Richardson, K., Asmutis-Silvia, R., Drinkwin, J., Gilardi, K., Giskes, I., Jones, G., O'Brien, K., Pragnell-Raasch, H., Ludwig, L., Antonelis, K., Barco, S., Henry, A., Knowlton, A., Landry, S., Mattila, D., MacDonald, K., Moore, M., Morgan, J., Robbins, J., van der Hoop, J., Hogan, E. 2019. Building evidence around ghost gear: global trends and analysis for sustainable solutions at scale. *Marine Pollution Bulletin*, 138: 222–229.

Rochman, C. M. 2013. Plastics and priority pollutants: a multiple stressor in aquatic habitats. *Environmental Science & Technology*, 47(6): 2439–2440.

Rochman, C., Browne, M., Halpern, B., Hentschel, B., Hoh, E., Karapanagioti, H., Rios-Mendoza, L., Takada, H., Teh, S., Thompson, R. 2013. Classify plastic waste as hazardous. *Nature*, 494(7436): 169–171.

Rochman, C., Manzano, C., Hentschel, B., Simonich, S., Hoh, E. 2013. Polystyrene plastic: a source and sink for polycyclic aromatic hydrocarbons in the marine environment. *Environmental Science & Technology*, 47(24): 13976–13984.

Romera-Castillo, C., Pinto, M., Langer, T., Álvarez-Salgado, X., Herndl, G. 2018. Dissolved organic carbon leaching from plastics stimulates microbial activity in the ocean. *Nature Communications*, 9(1), 1–7.

Rubino, F., Nisticò, A., Tucci, F., Carlone, P. 2020. Marine application of fiber reinforced composites: a review. *Journal of Marine Science and Engineering*, 8: 26.

Rudolph, N., Kiesel, R., Aumnate, C. 2017. *Understanding Plastic Recycling. Economic, Ecological and Technical Aspects of Plastics Waste Handling*. Hanser Publishers, Liberty Township, OH.

Ryan, P. 2015. A brief history of marine litter research. In: Bergmann M., Gutow L., Klages M. (eds) Marine Anthropogenic Litter. Springer, Cham. https://doi.org/10.1007/978-3-319-16510-3_1In, 1–25.

Ryan, P., 2018. Entanglement of birds in plastics and other synthetic materials. *Marine Pollution Bulletin*, 135: 159–164.

Sait, S., Sørensen, L., Kubowicz, S., Vike-Jonas, K., Gonzalez, S., Asimakopoulos, A., Booth, A. 2021. Microplastic fibres from synthetic textiles: environmental degradation and additive chemical content. *Environmental Pollution*, 268: 115745.

Santos, R., Andrades, R., Boldrini, M., Martins, A. 2015. Debris ingestion by juvenile marine turtles: an underestimated problem. *Marine Pollution Bulletin*, 93(1–2), 37–43.

Schrank, I., Trotter, B., Dummert, J., Scholz-Böttcher, B., Löder, M., Laforsch, C. 2019. Effects of microplastic particles and leaching additive on the life history and morphology of *Daphnia magna*. *Environmental Pollution*, 255: 113233.

Schwarz, A., Ligthart, T., Boukris, E., van Harmelen, T. 2019. Sources, transport, and accumulation of different types of plastic litter in aquatic environments: a review study. *Marine Pollution Bulletin*, 143: 92–100.

Schymanski, D., Goldbeck, C., Humpf, H., Fürst, P. 2018. Analysis of microplastics in water by micro-Raman spectroscopy: release of plastic particles from different packaging into mineral water. *Water Research*, 129: 154–162.

Schyns, Z., Shaver, M. 2020. Mechanical recycling of packaging plastics: a review. *Macromolecular Rapid Communications*, 42(3): 2000415.

Scopetani, C., Cincinelli, A., Martellini, T., Lombardini, E., Ciofini, A., Fortunati, A., Pasquali, V., Ciattini, S., Ugolini, A. 2018. Ingested microplastic as a two-way transporter for PBDEs in *Talitrus saltator*. *Environmental Research*, 167: 411–417.

Seidlitz, A., Thurn-Albrecht, T. 2016. Chapter 9: Small-angle x-ray scattering for morphological analysis of semicrystalline polymers. In: Guo, Q. (Ed.), *Polymer Morphology: Principles, Characterization, and Processing*. Wiley International.

Shiber, J. G. 1982. Plastic pellets on Spain's Costa del Sol'beaches. *Marine Pollution Bulletin*, 13(12): 409–412.

Shruti, V., Pérez-Guevara, F., Elizalde-Martínez, I., Kutralam-Muniasamy, G. 2020. First study of its kind on the microplastic contamination of soft drinks, cold tea and energy drinks – future research and environmental considerations. *Science of The Total Environment*, 726: 138580.

Silvenius, F., Katajajuuri, J. M., Grönman, K., Soukka, R., Koivupuro, H. K., Virtanen, Y. 2011. Role of packaging in LCA of food products. In: Finkbeiner, M. (Ed.), *Towards Life Cycle Sustainability Management*. Springer, Dordrecht.

Simon B., Amor M. B., Földényi, R. 2016. Life cycle impact assessment of beverage packaging system: focus onthe collection of post-consumer bottles. *Journal of Cleaner Production*, 112: 238–248.

Singh, B., Sharma, N. 2008. Mechanistic implications of plastic degradation. *Polymer Degradation and Stability*, 93(3): 561–584.

Smith, M., Love, D., Rochman, C., Neff, R. 2018. Microplastics in seafood and the implications for human health. *Current Environmental Health Reports*, 5(3): 375–386.

Song, Y. K., Hong, S. H., Jang, M., Han, G. M., Jung, S. W., Shim, W. J. 2017. Combined effects of UV exposure duration and mechanical abrasion on microplastic fragmentation by polymer type. *Environmental Science & Technology*, 51(8): 4368–4376.

Spierling, S., Knüpffer, E., Behnsen, H., Mudersbach, M., Krieg, H., Springer, S., Albrecht, S., Herrmann, C., Endres, H. 2018. Bio-based plastics – a review of environmental, social and economic impact assessments. *Journal of Cleaner Production*, 185: 476–491.

Steffen, W., Broadgate, W., Deutsch, L., Gaffney, O., Ludwig, C. 2015. The trajectory of the anthropocene: the great acceleration. *The Anthropocene Review*, 2(1): 81–98.

Straková, J., DiGangi, J., Jensen, G. K., Petrlik, J., Bell, L. 2018. *Toxic Loophole*, *Recycling Hazardous Waste into New Products*. Arnika, IPEN, HEAL, Sweden.

Sun, Q., Ren, S., Ni, H. 2020. Incidence of microplastics in personal care products: an appreciable part of plastic pollution. *Science of The Total Environment*, 742: 140218.

Sun, X., Li, Q., Zhu, M., Liang, J., Zheng, S., Zhao, Y. 2017. Ingestion of microplastics by natural zooplankton groups in the northern South China Sea. *Marine Pollution Bulletin*, 115(1–2): 217–224.

Suzuki, Y., Akamatsu, F., Nakashita, R., Korenaga, T. 2010. A novel method to discriminate between plant- and petroleum-derived plastics by stable carbon isotope analysis. *Chemistry Letters*, 39(9): 998–999.

Tang, S., Lin, L., Wang, X., Feng, A., Yu, A. 2020. Pb (II) uptake onto nylon microplastics: interaction mechanism and adsorption performance. *Journal of Hazardous Materials*, 386: 121960.

Tavares, D. C., Moura, J. F., Ceesay, A., Merico, A. 2020. Density and composition of surface and buried plastic debris in beaches of Senegal. *Science of the Total Environment*, 737: 139633.

Ter Halle, A., Jeanneau, L., Martignac, M., Jardé, E., Pedrono, B., Brach, L., Gigault, J. 2017. Nanoplastic in the north Atlantic Subtropical Gyre. *Environmental Science & Technology*, 51(23): 13689–13697.

Textile Exchange. 2020. Preferred Fiber and Materials Market Report. https://www.textileexchange.org (accessed August 19, 2021).

Thompson, R. 2004. Lost at sea: where is all the plastic? *Science*, 304(5672): 838–838.

Trucost, P. L. C. 2013. *Natural Capital at Risk: The Top 100 Externalities of Business*. TEEB, Geneva.

Uni-Bell PVC Pipe Association. 2017. *Life Cycle Assessment of PVC Water and Sewer Pipe and Comparative Sustainability Analysis of Pipe Materials*. Uni-Bell, Dallas, TX.

Van Cauwenberghe, L., Devriese, L., Galgani, F., Robbens, J., Janssen, C. 2015. Microplastics in sediments: a review of techniques, occurrence and effects. *Marine Environmental Research*, 111: 5–17.

Van Cauwenberghe, L., Vanreusel, A., Mees, J., Janssen, C. R. 2013. Microplastic pollution in deep-sea sediments. *Environmental Pollution*, 182: 495–499.

Van Sebille, E., Wilcox, C., Lebreton, L., Maximenko, N., Hardesty, B. D., Van Franeker, J. A., Eriksen, M., Siegel, D., Galgani, F., Law, K. L. 2015. A global inventory of small floating plastic debris. *Environmental Research Letters*, 10(12): 124006.

Vignali G. 2016. Life-cycle assessment of food-packaging systems. In: Muthu, S. (Ed.), *Environmental Footprints of Packaging. Environmental Footprints and Eco-design of Products and Processes*. Springer, Singapore.

Viršek, M. K., Lovšin, M. N., Koren, Š., Kržan, A., Peterlin, M. 2017. Microplastics as a vector for the transport of the bacterial fish pathogen species *Aeromonas salmonicida*. *Marine Pollution Bulletin*, 125(1–2): 301–309.

Waller, C. L., Griffiths, H. J., Waluda, C. M., Thorpe, S. E., Loaiza, I., Moreno, B., Pacherres, C. O., Hughes, K. A. 2017. Microplastics in the Antarctic marine system: an emerging area of research. *Science of the Total Environment*, 598: 220–227.

Wan, T., Lu, S., Cheng, W., Ren, J., Wang, M., Hu, B., Jia, Z., Li, Y., Sun, Y. 2019. A spectroscopic and theoretical investigation of interaction mechanisms of tetracycline and polystyrene nanospheres under different conditions. *Environmental Pollution*, 249: 398–405.

Wang, W., Jing Ge, J., Yu, X. 2020. Bioavailability and toxicity of microplastics to fish species: a review. *Ecotoxicology and Environmental Safety*, 189: 109913.

Ward, J., Sutton, P., Werner, A., Costanza, R., Mohr, S., Simmons, C. 2016. Is decoupling GDP growth from environmental impact possible? *PLoS ONE*, 11(10): e0164733.

Woodall, L.C., Sanchez-Vidal, A., Canals, M., Paterson, G.L.J., Coppock, R., Sleight, V., Calafat, A., Rogers, A.D., Narayanaswamy, B.E., Thompson, R. 2014. The deep sea is a major sink for microplastics debris. *R. Soc. Open Sci.* 1(4): 140317.

World Economic Forum. 2016. *The New Plastics Economy: Rethinking the Future of Plastics*. Ellen MacArthur Foundation and McKinsey & Company.

Wright, S., Thompson, R., Galloway, T. 2013. The physical impacts of microplastics on marine organisms: a review. *Environmental Pollution*, 178: 483–492.

Yang, Y., Liu, G., Song, W., Ye, C., Lin, H., Li, Z., Liu, W. 2019. Plastics in the marine environment are reservoirs for antibiotic and metal resistance genes. *Environment International*, 123: 79–86.

Yong, C. Q. Y., Valiyaveetill, S., Tang, B. L. 2016. Toxicity of microplastics and nanoplastics in mammalian systems. *International Journal of Environmental Research and Public Health*, 17(5): 1509.

Zalasiewicz, J., Waters, C. N., do Sul, J. A. I., Corcoran, P. L., Barnosky, A. D., Cearreta, A., Edgeworth, M., Gałuszka, A., Jeandel, C., Leinfelder, R., McNeill, J. R. 2016. The geological cycle of plastics and their use as a stratigraphic indicator of the Anthropocene. *Anthropocene*, 13: 4–17.

Zambrano, M. C., Pawlak, J. J., Daystar, J., Ankeny, M., Cheng, J. J., Venditti, R. A. 2019. Microfibers generated from the laundering of cotton, rayon and polyester based fabrics and their aquatic biodegradation. *Marine Pollution Bulletin*, 142: 394–407.

Zhang, J., Suh, S. 2019. Strategies to reduce the global carbon footprint of plastics. *Nature Climate Change*, 9(5): 374–378.

Zheng, Y., Li, J., Sun, C., Cao, W., Wang, M., Jiang, F., Ju, P., 2021. Comparative study of three sampling methods for microplastics analysis in seawater. *Science of the Total Environment*, 765: 144495.

Zhu, Y., Romain, C., Williams, C. K. 2016. Sustainable polymers from renewable resources. *Nature*, 540(7633): 354–362.

Zhu, L., Zhao, S., Bittar, T., Stubbins, A., Li, D. 2020. Photochemical dissolution of buoyant microplastics to dissolved organic carbon: rates and microbial impacts. *Journal of Hazardous Materials*, 383: 121065.

Ziccardi, L., Edgington, A., Hentz, K., Kulacki, K., Kane Driscoll, S. 2016. Microplastics as vectors for bioaccumulation of hydrophobic organic chemicals in the marine environment: a state-of-the-science review. *Environmental Toxicology and Chemistry*, 35(7): 1667–1676.

2

Plastic Additives in the Ocean

Jennifer M. Lynch[1,2], Katrina Knauer[3], and Katherine R. Shaw[1,2]

[1] *Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD, USA*
[2] *Center for Marine Debris Research, Hawaii Pacific University, Honolulu, HI, USA*
[3] *Novoloop, Inc., Menlo Park, CA, USA*

2.1 Function of Plastic Additive Classes

The ecological and toxicological effects of plastic in the marine environment are generally discussed or modeled as if they were "pure" polymers (Cole et al. 2015; Kaiser et al. 2019; Yin et al. 2018); yet, no plastic that exists in the waste stream today is manufactured without additives or as a "barefoot" formulation. Every piece of plastic is made up of a unique combination of the host polymer, with some residual monomers or catalysts, as well as chemical additives added during processing of the plastic (Hahladakis et al. 2018; Hermabessiere et al. 2017). A staggering amount of different kinds of additives are used in plastic formulations and each of them plays a distinct role in delivering/enhancing the functional properties, performance, or appearance of a plastic product (Marturano et al. 2016). Depending on the formulation, plastics may contain anywhere from <1 to 50% or more by weight of plasticizers (Chaudhary et al. 2016; Marturano et al. 2016). Typically, plasticizers, fillers, and flame retardants (FRs) are used at high weight fractions in plastic formulations and, therefore, account for about three-quarters of all additives produced. Other additives, such as antioxidants and light stabilizers, are used at much lower loadings. Despite the popular conception that plastics last forever, they are organic materials that undergo significant degradation when exposed to processing or environmental conditions, including high temperatures, ultraviolet (UV) radiation, oxygen in the atmosphere, and water (see Chapter 8). The durability and performance that is expected from thermoplastics would not be possible without these intentionally added chemical compounds. The production and use of plastics (and, therefore, plastic additives) has continued to increase exponentially since the mid-20th century (Binetti et al. 2008). If current production rates continue, a total of 2000 million metric tons of additives will have been produced by the end of 2050 (Geyer et al. 2017). This is based on an estimate of plastics containing on average 7% additives by mass (Geyer et al. 2017). It has been estimated that at least 190 metric tons of additive chemicals entered the ocean in 2015 alone, a rate that is expected to double by 2025 (De Frond et al. 2019). The decades' worth of plastics already in the ocean was formulated without consideration for marine disposal.

This chapter aims to introduce plastic additives with a focus on their chemistry and function, transport and fate, detection in marine environments, and toxicities. The extensive list of additives can be simplified by dividing the types of additives into three groups: functional additives, colorants, and

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

Table 2.1 Classes of plastic additives, typical loadings, and percent share in plastics production.

Type	Additive Class	Typical loadings (wt%)	Share (%)	Market size (USD million)[a]	Examples	Purpose
Plasticizers	Functional	10–70	34	1550	Phthalates, tris(2-chloroethyl) phosphate	Soften polymer and make more flexible
Flame retardants	Functional	3–25	13	7000	Poly(bromo diphenyl ethers), organophosphorus	Prevent ignition or flame propagation
Antioxidants	Functional	0.05–3	6	5770	Hindered phenols, alkylphenols[b], phosphites[c], lactones, hydroxylamines	To prevent discoloration and degradation during processing, use, and weathering
Heat stabilizers	Functional	0.1–8	5	3630	Dialkyl maleates or laureates and dialkyl mercaptides of tin in PVC formulations to retard HCl evolution during processing	To prevent thermal degradation during processing
Fillers	Fillers	1–50	28	10 000	Clays, silica, glass, chalk, talc, asbestos, alumina, rutile, carbon black, carbon nanotubes	To provide mechanical reinforcement or formulation cost reductions
Impact modifiers	Functional	0.5–30	5	3280	Acrylonitrile butadiene styrene (ABS), acrylonitrile styrene acrylate (ASA)	To increase flexibility and impact strength to meet physical property requirements of rigid parts
Colorants	Colorants	0.25–5	2	37 000	Cadmium, chromium, lead, and cobalt compounds, titanium dioxide, carbon black; organic dyes	To impart a desired color on the finished product
Lubricants	Functional	0.1–3	2	4558	Waxes, oils, long-chain esters of polymeric alcohols	Allows easier processing of the plastic (i.e., lower temperatures, faster processing times)
Light stabilizers	Functional	0.05–3	1	373	Hindered amine light stabilizers, benzo-phenone light-absorbing compounds	To prevent degradation of the plastic upon exposure to light sources
Other (anti-static, anti-microbial, etc.)	—	—	4	—	Silver, thiabendazole, aliphatic amines	—
Monomers, catalysts	Unintended Additives	—	—	—	Bisphenol-A, styrene, antimony	Unreacted monomers or residual catalyst left over from the polymer synthesis

Source: "Typical loadings" are the max and min ranges reported by Geyer et al. 2017, Zweifel et al. (2001), Hahladakis et al. (2018), Andrady and Rajapaske (2019), and Ambrogi et al. (2017).

[a] These are market sizes for all applications, not just in plastics.

[b] The majority of alkylphenols (APs) found in the environment are degradation products of surfactants, not plastic additives.

[c] If phosphites are used, the loadings can be higher than the range indicated.

fillers/reinforcements. The most common types of additives used are outlined in Table 2.1 along with typical loadings in the polymer, percent share in global plastics production, market sizes, key examples, and desired effects.

2.2 Functional Additives

2.2.1 Plasticizers

Plasticizers are added to plastics to improve their flexibility, durability, and elasticity over a broad range of temperatures while also reducing the glass transition temperature (T_g) and the melt flow. The dissolved plasticizer molecules, not being covalently linked to the polymer backbone (Greco et al. 2010), can migrate freely within the resin matrix. The exact mechanism of plasticization is not fully understood; however, studies demonstrate that strong association of the polymer chains with the plasticizer molecules creates additional free volume in the bulk plastic matrix, yielding a softer and more flexible material (Greco et al. 2010; Ramos-Devalle and Gilbert 1990).

Relatively high concentrations of plasticizers are required to achieve these desired changes in plastics, accounting for 34% of the total additives used in global plastics production from 2000 to 2014 (Geyer et al. 2017). Phthalic acid esters, or phthalates, are the most widely used plasticizers. Of the reported 8.4 million metric tons of plasticizers manufactured worldwide in 2017, about 65% were phthalate plasticizer used by the poly(vinyl chloride) (PVC) industry (IHS Markit 2018), with di(2-ethylhexyl) phthalate (DEHP) being the most widely applied phthalates in PVC (Table 2.2). Because DEHP is highly regulated, it has gradually been replaced by diisononyl phthalate (DiNP), diisodecyl phthalate (DiDP), and di(2-propylheptyl) phthalate (DPHP). In 2015, DPHP represented 57% of plasticizer consumption in Europe (ECPI 2016). However, the high loadings and migration of plasticizers from plastic materials have led to significant concern about the effects of phthalates in the marine environment as early as 1978 (Giam et al. 1978).

2.2.2 Flame Retardants

Plastics, especially those with a high carbon content, are inherently flammable. For many resins, the most cost-effective method for increasing fire safety is to blend a FR additive into polymer formulations (Troitzsch and Antonatus 2021; Zweifel et al. 2001). FRs can be classified into halogen-based, phosphorus-based, and metal hydrate compounds. Halogen-based FRs can vary widely in chemical structure, but the most common types are brominated organic compounds (BFRs), including polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA), and polybrominated biphenyls (PBBs; Figure 2.1). HBCDs are the most widely used BFRs, with 31 000 metric tons produced in 2011 (UNEP 2015).

These FRs work in the vapor or gas state and interfere with the radical mechanism of the combustion process. Plastics, such as polyethylene (PE), high-impact polystyrene, ethylene-vinyl acetate copolymer, and acrylonitrile-butadiene-styrene (ABS) copolymer, use PBDEs as FRs (Andrady and Rajapakse 2019; Delva et al. 2018; Rahman et al. 2001). Recently, many PBDEs, such as penta-BDE, octa-BDE, and deca-BDE, have been phased out due to their significant persistence and toxicity. New BFRs, such as 1,2-bis(2,4,6-tribromophenoxy) ethane, have been developed as substitutes (Sun et al. 2019). Phosphate-based FRs, such as tri(2-chloroethyl) phosphate (TCEP) or tris(2-ethylhexyl)phosphate are char formers that produce phosphoric acids that react with the substrate to generate a char that protects the polymer itself from combustion (Ambrogi et al. 2017; Samani

Table 2.2 Eight of the most commonly used phthalate plasticizers in PVC.

Name	Abbreviation	Common metabolites	Banned in toys and childcare articles in EU	Banned in U.S. toys or childcare articles
Butyl benzyl phthalate	BBP	Mono benzyl phthalate (MBzP)	X	X
Di-n-butyl phthalate	DnBP	Mono-n-butyl phthalate (MnBP); mono-isobutyl phthalate (MiBP)	X	X
Di-(2-ethylhexyl) phthalate	DEHP	Mono-(2-ethylhexyl) phthalate (MEHP); mono-(2-ethyl-5-hydroxyhexyl) phthalate (MEHHP); mono-(2-ethyl-5-oxohexyl) phthalate (MEOHP); mono-(2-ethyl-5-carboxypentyl) phthalate (MECPP)	X	X
Diethyl phthalate	DEP	Monoethyl phthalate (MEP)		
Di-isodecyl phthalate	DiDP	Mono-(carboxynonyl) phthalate (MCNP)	X	
Di-isononyl phthalate	DiNP	Mono-isononyl phthalate (MiNP)	X	X
Di-n-hexyl phthalate	DnHP			X
Di-n-octyl phthalate	DnOP	Mono-(3-carboxypropyl) phthalate (MCPP); mono-n-octyl phthalate (MOP)	X	

Source of data: Zero Breast Cancer. (2014). “Phthalates: The Everywhere Chemical.” Retrieved October 8 2020, from https://www.niehs.nih.gov/research/supported/assets/docs/j_q/phthalates_the_everywhere_chemical_handout_508.pdf.

Note: Several phthalates have been banned by the European Union (EU) or the United States for use in toys or childcare articles at concentrations >0.1% (ZBC 2018).

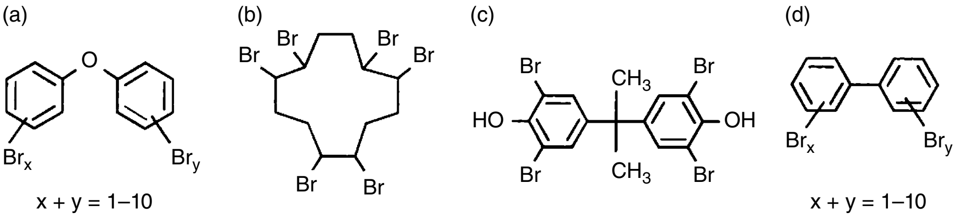


Figure 2.1 Chemical structures of (a) PBDE, (b) HBCD, (c) TBBPA, and (d) PBB.

and van der Meer 2020). Metal hydrate FRs are typically aluminum trihydroxide and magnesium hydroxide that hydrates decompose under high heat to release water, preventing propagation (Innes and Innes 2002).

FRs have a high propensity to migrate out of the plastic into surrounding environments. Some FRs are used as mixtures of congeners, such as commercial PBDEs, with certain congeners more toxic than others. Although some commercial PBDEs (penta-BDE, octa-BDE, and deca-BDE) have been phased out (Sharkey et al. 2020), they will remain in the environment for many years because of their persistence.

2.2.3 Antioxidants

Plastic materials are organic substances that are susceptible to oxidative degradation. For example, polyolefins (i.e. PE, polypropylene) degrade by autoxidation, a cycle that can be slowed by the action of antioxidants. Throughout a plastic's life cycle (i.e. production, processing, use, and disposal), the polymer is subjected to a variety of damaging stresses. This includes high temperatures and shear rates from the multiple melt compounding steps as the product is transformed from reactor powder or pellets into a finished article and ultimately processed again through recycling. In addition to temperature and shear, catalyst residues, entrained oxygen, and other types of impurities might also play a role in promoting further degradation of the polymer (Zweifel et al. 2001).

During these repeated heat histories, polymers undergo a series of free-radical-mediated oxidation reactions. These result in the formation of polymer hydroperoxides that thermally dissociate into additional free radicals (see Chapter 8 for detailed reactions). In addition to introducing oxygen-containing functionalities into the plastic, the oxidative reactions also facilitate chain scission altering its average molecular weight (MW), MW distribution, and structure of the polymer backbone. When not stabilized adequately, the plastic will ultimately begin to lose its mechanical integrity; this will also limit the recyclability of the polymer and can lead to the formation of microplastics (Zweifel et al. 2001).

Antioxidants are used to prevent the formation of free radicals. Phenolic antioxidants scavenge oxygen-centered free radicals, such as alkoxy-, hydroxy-, and peroxy-type species, and prevent reaction with the polymer backbone (see Chapter 8). These substances include hindered phenols their and APs. Phosphites and thioesters are used to decompose the hydroperoxides into relatively inert products. These additives are used to impart longevity and stability in the plastic article. Since they are designed to remain active in the matrix for a long time, they continue to protect the article after disposal, which leads to long life spans of polymers in the environment. The most common antioxidants are listed in Table 2.3 along with their corresponding class and structures.

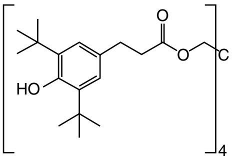
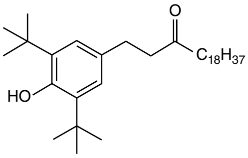
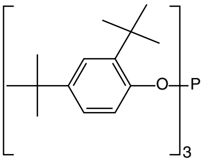
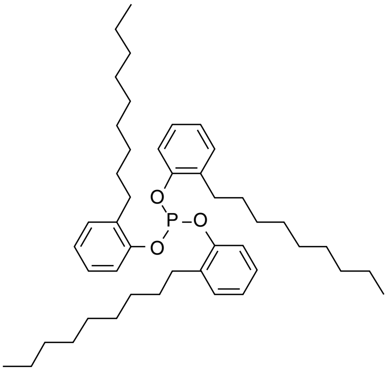
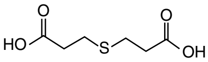
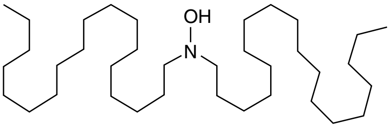
2.2.4 Heat Stabilizers

Heat stabilizers are added to plastics to protect the material from heat during processing and using the product. The most common application of heat stabilizers is in medical grade PVC where it is used at a concentration of 10–15% to protect the polymer during autoclaving (Sastri 2013). Due to the labile chlorine group, PVC is particularly susceptible to heat. Heat stabilizers work by trapping the hydrogen chloride (HCl) that is generated when PVC thermally degrades. They are also used in recycled materials, where they play the double role of inhibiting degradation and re-stabilizing post-use plastic waste (Ambrogi et al. 2017). Heat stabilizers are typically either metallic salts, organometallic compounds or nonmetallic organic stabilizers. Metallic salt heat stabilizers used in PVC, polystyrene (PS), and PE are commonly based on barium, cadmium, lead, or zinc and often used together to obtain a synergistic effect. Organometallic heat stabilizers are typically tin based.

2.2.5 Impact Modifiers

Impact modifiers (IMs) are a class of toughening functional additives that increase the impact strength of the plastic articles. Many commodity thermoplastics, such as PVC and PS, are brittle at ambient conditions (i.e., poor impact strength) and easily undergo cracking and crazing. In order to meet the physical requirements for certain applications, an IM additive is used. IMs are

Table 2.3 Examples of common antioxidant additives used in plastics.

Chemical name	Antioxidant class	Structure
Pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4-hydroxyphenyl] propionate	Hindered phenol	
Octadecyl-3-[3,5-di-tert-butyl-4-hydroxyphenyl] propionate	Hindered phenol	
Tris(2,4-di-tert. -butylphenyl)phosphite	Phosphite	
Trisnonylphenyl phosphite	Phosphite	
Dialkyl ester of thiodipropionic acid	Thioester	
N,N-Octadecyl hydroxylamine	Hydroxylamine	

elastomeric and rubbery and have a lower modulus than the host polymer system. When effectively dispersed into the polymer matrix, the rubbery phase of the IM acts to absorb or dissipate the energy from impact in order to stop craze or crack propagation. IMs can be grafted to the polymer during polymerization or physically blended during compounding. Styrenic oligomers/copolymers, such as ABS and methyl methacrylate-butadiene-styrene, make up the largest category of IMs, accounting for about 45% of the market (Markarian 2004). These along with acrylics that command 30% of the market and are used mostly in PVC. Elastomers, including ethylene-propylene-diene terpolymer (EPDM) and thermoplastic elastomers, make up about 10% used with polyolefins. The remainder is made up of chlorinated polyethylenes (CPE) and other types. IMs, such as ABS, EPDM, and CPE, are also “stand-alone” plastic products. These materials are used as IMs in their oligomeric forms (i.e. MWs of 5000–20 000 g/mol; Ambrogi et al. 2017). Similar to plasticizers and FRs, IMs are often used at relatively high concentrations in the plastic formulation. However, since most IMs are large molecules, leaching from the plastic into the environment has not been a major concern.

2.2.6 Lubricants

Lubricants are added to polymer formulations to ensure homogenous flow, uniform compositions, and quick release during processing and molding. There are three main types of lubricants: antislip agents that reduce the coefficient of friction of the plastic laminates; external lubricants that coat the metal/polymer interface during processing to minimize the plastic from sticking to the machinery; and a third group of low mass compounds that promote the flow of the polymer in the melt (Brydson 1999). Some of the most commonly used lubricants in thermoplastics are fatty acid amides (primary erucamide and oleamide), fatty acid esters, metallic stearates (e.g. zinc stearate), silicones, and waxes (Bhunia, et al. 2013). There is not much information available on the toxicity of lubricants (Andrady and Rajapakse 2019). However, some lubricants are nonylphenol based, which are known as endocrine disruptors (Boehme et al. 2010).

2.2.7 Light Stabilizers

Plastics are also susceptible to degradation via photo-oxidation, which is the result of the combined action of light and oxygen, that follows a similar oxidation cycle as in thermal oxidation that was previously discussed (see also Chapter 8). Light stabilizers interfere with the physical and chemical processes of light-induced polymer degradation. The most important light stabilizer classes are benzophenones, benzotriazoles, organic nickel compounds, and sterically hindered amines (HALS; Jia et al. 2007). UV absorbers, such as benzophenones and benzotriazoles, are extensively used to stabilize thick sections of polyolefins, poly(ethylene terephthalate) (PET), polyurethane (PU), poly(vinyl acetate) (PVA), natural rubber, and epoxy formulations. Organic nickel compounds quench or deactivate the excited states of chromophores arresting oxidation. HALS is a particular potent free-radical quencher that is effective at very low concentrations (≈0.1%).

The protection of plastics from the effects of light can also be achieved through the addition of carbon black (CB) and other pigments such as titanium dioxide (Accorsi et al. 2001) that essentially shield the plastic from UV radiation. Light stabilizers significantly control the weathering of plastics exposed to sunlight as well as fragmentation via loss of MW from photo-oxidation of the polymer. Typical loadings in plastics are relatively low, with <1%, and migration and toxicity have not received special attention.

2.2.8 Colorants

Colorants are chemical compounds that not only impart color to plastic materials but can also affect other properties, such as weather resistance, light stability, and transparency of the plastic. Colorants fall into two distinct classes: dyes and pigments; main distinction being dyes are soluble in the plastic matrix while pigments are insoluble. Most commonly used are the azo dyes that make up >50% of all dyes listed in the Color Index (Ambrogi et al. 2017) and used in textiles, paper, leather, rubber, or even foodstuffs (Ambrogi et al. 2017). Since organic dyes dissolve in the polymer, they do not scatter but only absorb light. Therefore, even at high concentrations of the dye, the plastic tends to be transparent or translucent. Some dyes such as aromatic amines, are known carcinogens and phthalocyanines have detectable estrogenic activity (Yang et al. 2011).

Pigments remain discrete particles that are well dispersed in the polymer matrix (Bolgar et al. 2016). Scattering and absorption of light by the pigment particles makes the plastic partly opaque (Andrady and Rajapakse 2019). Pigments are classified as either organic or inorganic. Organic pigments include benzimidazoles, quinacridones, and mono-azos and provide the most brilliant opaque colors available (Ambrogi et al. 2017). Inorganic pigments are based on metals and can be divided into three classes: white pigments (TiO_2), carbon black (CB), and special effect pigment (Huckle and Lalor 1955). TiO_2 is the most widely used pigment in the plastic industry due to its high refractive index and ability to provide a high degree of opacity and whiteness. In addition, TiO_2 is known for its excellent durability and general nontoxicity. Black pigmentation in plastics is typically based on CB, the second most used pigments in volume by the plastic industry. CB also has dual functionality in that it can also act as a reinforcing filler, conductive filler, and light stabilizer improving the weatherability and stability of the plastic (Huang 2002). Special pigments impart vibrant colors to plastic materials and include fluorescent pigments, pearlescent pigments (mica coated with TiO_2), and metallic pigments (aluminum bronzes, copper, copper-zinc alloys, and zinc).

2.2.9 Fillers and Reinforcements

Fillers are relatively cheap, solid substances that are added to plastic formulations in high percentages to adjust volume, weight, and mechanical performance (Zweifel et al. 2001). Inert fillers often do not compromise the functional properties of the plastic; they are cheaper than resin and can significantly reduce the cost of the formulation. Fillers can also serve as reinforcing agents that improve the mechanical performance and durability of the plastic. They are used as powders, fibers, or nanotubes.

Filler consumption globally in 1999 was 66% calcium carbonate, 6% talc, 6% clays, 3% wollastonite ($CaSiO_3$), and the remaining 19% included silica, glass, asbestos, alumina, rutile, CB, and carbon nanotubes (CNTs; Civancik-Uslu et al. 2018; Zweifel et al. 2001). Reinforcements are generally strong fibers including glass, carbon, or aramide fibers (Alam et al. 2019; Hansen et al. 2013). Fillers and reinforcements are used virtually in all polymers, but the largest fraction (i.e. over 90%) is used primarily in rubbers, PVC, and polyolefins. The improved mechanical properties in a filled plastic are derived from the interface layer between the polymer and the filler. The stronger the interfacial interactions, the better the mechanical performance of the composite (i.e. polymer/filler mix). The efficacy of the filler is also dependent on adequate dispersion in the polymer matrix. Good dispersion is achieved through extrusion, dispersing agents, or by surface treatment of the filler to improve compatibility with the polymer matrix.

Fillers can be microscopic (1 μm) or macroscopic (<100 μm) in size and have a very low propensity to leach out of the plastic. However, degradation and wear of a filled plastic can release fibers into surrounding environments either during use or after disposal (Froggett et al. 2014). In addition, the use of nano-particulate fillers, such as CNTs or silica nanoparticles (silica-NPs), has gained popularity over the past 20 years due to the superior material properties of nanocomposites when compared to conventional composites. Currently, commercial availability is low as these materials are relatively new. Nonetheless, production volumes are increasing with market sizes projected to grow significantly (Hendren et al. 2011).

2.3 Sources, Transport, and Fate of Additives in the Ocean

Despite the growing concerns of plastic waste accumulation in the ocean, the environmental transport and fate of plastic additives are not well understood (Tian et al. 2020). Additives in plastics can be released from products into the air, water, and soil in all phases of the product life cycle and can be transported to the marine environment by numerous, interconnected, pathways (Figure 2.2).

Additives are well known to leach from plastics in the marine environment (De Frond et al. 2019; Koelmans et al. 2014; Paluselli et al. 2019; Pereao et al. 2020; Sun et al. 2019; Teuten et al. 2009). However, in addition to leaching, there are other sources of the same chemicals present in the ocean, some of which may even be more important, including direct industrial releases, wastewater effluents, atmospheric deposition, runoff, and river transport resulting from all human activities, including tire wear and application of sewage sludge in agriculture, resuspension from sediments, among other routes (Figure 2.2). For example, 14,742 metric tons of styrene were released into the environment from U.S. industries in 2019, independent from its leaching from plastic products, as reported to the U.S. Environmental Protection Agency's Toxic Release Inventories (Table 2.4). Studies have shown that effluent from wastewater treatment plants and runoff, especially near plastic product manufacturing, as well as atmospheric deposition, are major sources of already leached plastic additives to aquatic environments (Kim et al. 2021; Liu et al. 2020; Peng et al. 2007; Staples et al. 1997; Zhang et al. 2013, 2018c).

Many discussions on movement of plastic additives within the ocean focus on the plastic itself as the main carrier but it is not the only significant transport mechanism (Zarfl and Matthies 2010). Koelmans et al. (2016) states that the fraction of hydrophobic organic compounds (HOCs), including organic additives, held by plastic is negligible compared to that held by other media (i.e. seawater, atmosphere, sediment, and biota), implying the plastic-mediated transport to be generally unimportant in terms of HOC abundance.

The fate of plastic additives in the marine environment often differs from that of the plastic itself and is complicated (Figure 2.2). For example, additives that leach out of plastic can bioaccumulate

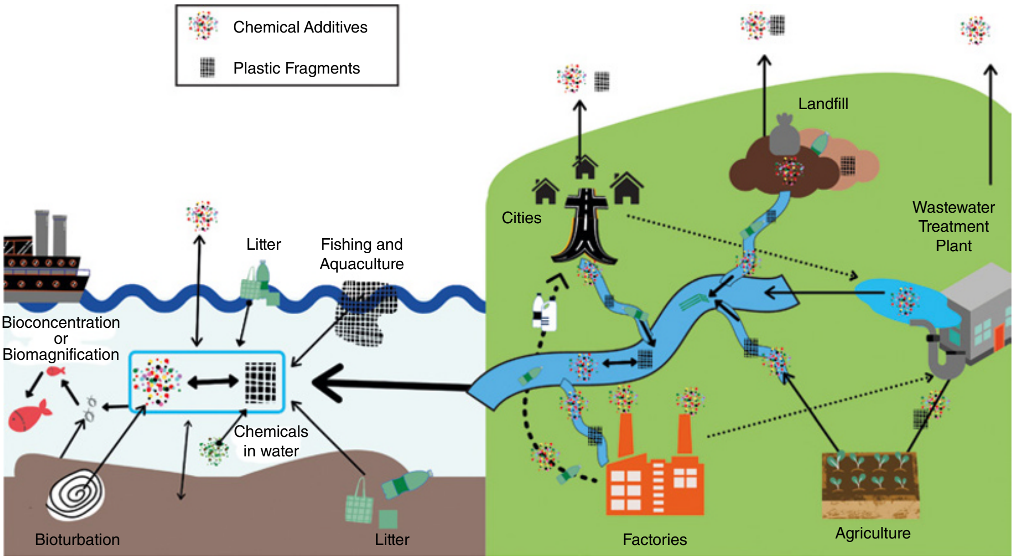


Figure 2.2 Complex sources and transport of plastic additives to, from, and within the ocean.

Table 2.4 Industrial releases of toxic plastic additives as reported to the U.S. EPA's Toxic Release Inventory in 2019.

Chemical name	Abbreviation	Additive class	Total onsite and offsite disposal (metric tons)
Styrene	—	Monomer	14,742
Nonylphenol	NP	Antioxidant/surfactant	142
Dimethyl phthalate	DMP	Plasticizer	69
Dibutyl phthalate	DBP	Plasticizer	135
PBBs	PBB	Flame retardant	0.6
Hexabromocyclododecane	HBCD	Flame retardant	60
Tetrabromobisphenol A	TBPPA	Flame retardant	98

Source: United States Environmental Protection Agency (2021). Toxic Release Inventory National Analysis 2019.

in organisms or degrade, while the plastic itself might drift away. Alternatively, additives dissolved in water may be adsorbed by a different plastic particle that originally did not contain that chemical. Sorption and desorption of additives among multiple environmental compartments (plastic debris, water, sediment, air, and organic matter) are constantly and simultaneously happening through chemical equilibrium kinetics.

2.3.1 The Simple Release of Additives From Plastics to Water

Since additives are not covalently bound to the polymer, they can migrate from plastic into surrounding environments (Bieber et al. 1984; Garde et al. 1998; Yagoubi et al. 1993). The leaching of plastic additives can be described in four major steps: (i) diffusion of the chemical through the polymer matrix, (ii) desorption of the chemical from the polymer surface, (iii) sorption of the compound at the polymer–water/biota/sediment interface, and (iv) absorption of the compound into the surrounding environment (Bhunia et al. 2013). Step 1, the mass diffusion process, is the rate-limiting step and governed by Fick's second law.

The diffusion rate is influenced by MW, concentration, and solubility of the additive in the plastic matrix, as well as the thickness and the fractional crystallinity of the plastic material (Hansen et al. 2013). Small molecules with low boiling point, such as residual monomers, migrate quickly through plastic materials, whereas larger additive molecules migrate more slowly. This has led to the innovative design of larger molecules for use as antioxidants, FRs, and plasticizers to slow down their migration and leaching. Good solubility of the additive in the plastic leads to stronger physical interactions with the polymer chains and therefore a lower propensity to leach out. Therefore, formulators aim to use hydrophobic additives with low water solubility. Plastic additives migrate almost exclusively through the amorphous phase of a polymer matrix and will leach much faster from amorphous polymers (e.g. PS) than crystalline polymers (e.g. high-density polyethylene [HDPE]). In fact, this has been demonstrated in HDPE systems with varying degrees of crystallinity (Teuten et al. 2009). Another example is organotin heat stabilizers that are more readily released from flexible polymers than from rigid ones (Teuten et al. 2009).

Steps 2 through 4, or the migration of additives at the plastic–seawater boundary, are mainly determined by the partition coefficient between plastic and water (K_{pw}; Endo et al. 2013). Additives with higher K_{pw} (more hydrophobic) will leach slower because they diffuse away from the polymer–water interface toward the plastic core. Despite its importance, K_{pw} values for most additives in common plastics have not been measured or reported. Fortunately, the water solubility and octanol–water partition coefficient (K_{ow}) can be used as chemical properties to estimate the leaching kinetics of plastic additives in seawater (also see Chapter 9). Table 2.5 provides these properties for a list of additives commonly identified in the marine environment.

Leaching of additives into seawater is strongly influenced by environmental conditions, such as temperature, sunlight, and salinity (Reimann et al. 2012; Westerhoff et al. 2008; Zaki and Shoeib 2018). Several studies show the leaching kinetics of common additives (Fikarova et al. 2019; Kedzierski et al. 2018; Koelmans et al. 2014) and even residual monomers (Koelmans et al. 2014; Tian et al. 2020) from plastics into seawater to be highly dependent on additive type, environmental conditions, and the host polymer. High temperatures can accelerate the diffusion of chemicals in polymers leading to greater leaching from plastics in warmer climates (Joo et al. 2004).

Photo-oxidation leads to dramatic changes in the plastic surface structure, such as increased crystallinity, changes in chemical properties, and cracking which perpetuates fragmentation (Gewert et al. 2015; ter Halle et al. 2017). Fragmentation increases the surface area-to-volume ratio, accelerating plastic additive leaching. Likewise, styrene is released at higher rates upon degradation of PS in aquatic conditions (Date et al. 2002; Kwon et al. 2014), as are bisphenol A (BPA) and isocyanates from polycarbonate (PC) and PU, respectively (Biles et al. 1997; Kubwabo et al. 2009). Furthermore, BFR release rates greatly increase from PE as it degrades, and the process is even more accelerated by the actions of digestive fluid once the plastic is ingested by organisms (Sun et al. 2019). Field evidence of enhanced additive leaching with increased fragmentation was demonstrated, in which levels of UV stabilizers were lower in “small” versus “large” plastic fragments collected from the same beach (Tanaka et al. 2020).

Additive concentrations measured in collected marine debris are typically lower than the target loadings in original plastic formulations (Table 2.1), indicating that some degree of leaching into seawater has occurred (Hermabessiere et al. 2017). Tanaka et al. (2020) found that concentrations of UV stabilizers in large plastic fragments were within the range of typical loadings. These results indicate that some additives are sufficiently stable in the polymer even after being fragmented or exposed to harsh conditions. Diffusion of additives from within plastics is rate limiting, and is why phase equilibrium between plastic and water may not be attained in marine conditions (Kwon et al. 2017). Recently, evidence of this was provided in highly weathered and fragmented PE marine debris (Tanaka et al. 2020). Lower concentrations of UV stabilizers were measured in the surface layers of these fragments compared to the inner core.

2.3.2 The Complexity of Intentionally Added Versus Adsorbed Additives

The reverse of the above process of leaching results in plastics absorbing free additives and other chemicals or acting as a *sink* for these compounds in the ocean (see Chapter 9; Amelia et al. 2021; Liu et al. 2016; Menéndez-Pedriza et al. 2020). In fact, the sorption of nonadditives, such as metals and HOCs, to the surface of the polymer can even affect the leaching kinetics of intended additives from a plastic (Kedzierski et al. 2018).

Field studies investigating environmental transport of additives are, therefore, confounded by additives that contain contributions from intentionally added compounds as well as those adsorbed by the plastic from water. Chen et al. (2019) found higher additive concentrations in smaller versus larger marine plastic fragments, a finding opposite to that from Tanaka et al. (2020). The two studies examined the same polymer type, highly weathered PE fragments, from the same general region, central North Pacific, but differed in the additive classes targeted. Chen et al.

Table 2.5 Reported log K_{ow} values, water solubility, molecular weight, and LD_{50} values of common plastic additives.

Chemical name	Abbreviation	Additive class	Log K_{ow}	Water solubility (μg/L)	Molecular weight (g/mol)	*D. magna* 48 h LD_{50} (mg/L)
Butyl benzyl phthalate	BBP	Plasticizer	4.70	2.7	312.65	3.24
Di(2-ethylexyl) phthalate	DEHP	Plasticizer	4.88–7.73	23–340	390.57	0.35
Diethyl phthalate	DEP	Plasticizer	2.54	1 080 000	222.24	86
Diisodecyl phthalate	DiDP	Plasticizer	9.46–10.36	0.0022	446.68	>0.02
Diisononyl phthalate	DiNP	Plasticizer	8.60–9.37	0.023	418.62	>0.06
Di-n-butyl phthalate	DnBP	Plasticizer	4.27	11 200 000	278.34	2.99
Di-n-octyl phthalate	DnOP	Plasticizer	7.73	22	390.6	>0.16
Tris-(2-chloropropyl) phosphate	TCPP	Plasticizer	2.59	1 600 000	327.6	81
Di-2-ethylhexyl adipate	DEHA	Plasticizer	8.12	0.53	370.58	>54
Acetyl tributyl citrate	ATBC	Plasticizer	4.92	1700	402.48	5.1
Hexabromocyclododecane	HBCD	Flame retardant	5.07–5.47	2.1–48.8	641.7	146
2,2′,4,4′-Tetrabromodiphenyl ether	PBDE 47	Flame retardant	6.81	15	485.79	0.00789
2,2′,4,4′,5-Pentabromodiphenyl ether	PBDE 99	Flame retardant	7.39	9.0	564.7	0.00261
Decabromodiphenyl ether	PBDE 209	Flame retardant	9.97	<0.1	959.2	>2.5
Tetrabromobisphenol A	TBBPA	Flame retardant	4.50	171.00	543.9	0.69
2,2-bis(bromomethyl)-1,3-propanediol	BBMP	Flame retardant	0.85	38 000	261.94	653
Tris-(2-chloropropyl) phosphate	TCEP	Flame retardant	2.59	1600	285.48	381
2,6-ditert-butyl-4-methylphenol	BHT	Antioxidant	5.03	5.7	220.36	0.42[a]
Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)	Irganox 1010	Antioxidant	19.6	0.0052	1177.67	86[b]
Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	Irganox 1076	Antioxidant	13.8	0.00004	530.9	>100
Tris(2,4-di-tert-butylphenyl)phosphite	Irgafos 168	Antioxidant	15.5	0.0010	646.937	>180[b]

Triphenyl phosphate	TPP	Antioxidant	4.59	1900	326.3	1.7
2-Tert-butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol	UV326	Light stabilizer	5.55	0.68	315.8	100^b
2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol	UV327	Light stabilizer	6.91	0.026	358	N/A
2-(benzotriazol-2-yl)-4,6-bis(2-methylbutan-2-yl)phenol	UV328	Light stabilizer	7.25	0.015	351.5	>0.083
Nonylphenol	NP	Multiple	4.48–4.80	4.9	220.35	0.31
Styrene	Styrene	Monomer	5.23–5.64	300	104.15	23
Bisphenol A	BPA	Monomer	3.40	120–300	228.29	11.9
Titanium dioxide	TiO2	Colorant	2.23	1.634	79.87	5.5
Carbon black	CB	Colorant	3.97–5.74	Insoluble	12.011	$>5{,}600^b$
Basic Red 51	BR51	Colorant	N/A	97.91	279.77	0.10
Cadmium	Cd	Colorant, etc.	N/A	N/A	112.41	0.054
Copper	Cu	Colorant, etc.	N/A	N/A	63.55	0.10
Zinc	Zn	Heat stabilizer, etc.	N/A	N/A	65.4	0.928
Calcium carbonate	$CaCO_3$	Filler	−2.12	1000	100.09	>>>800

Source:

Note: [a] Not experimentally derived, rather estimated from ECOSAR program.

[b] 24-hour exposure.

> means the LD50 is above the water solubility; >>> means the LD_{50} is well above this measured concentration of water hardness in toxicity test water.

Red shades indicate >5 log K_{ow} (concern for bioaccumulation/biomagnification) or $LD_{50} < 1$ (concern for acute aquatic toxicity).

(2019) measured BPA and APs, which are not common additives in PE, but instead are globally distributed chemicals free from plastics, whereas Tanaka et al. (2020) measured UV stabilizers that are almost always added to PE. The findings contradict because the dominant transport mechanisms were different for the two cases. UV stabilizers were leaching out of, while the BPA and APs were sorbing to the smaller fragments. Both leaching and adsorbing, however, were enhanced by the smaller fragments' increased surface area-to-volume ratio.

These two mechanisms influence the modeling of additive transport, leading to another comparison of seemingly conflicting results. Koelmans et al. (2016) concluded that most plastic additives in the ocean had already reached equilibrium between seawater and plastic debris. This interpretation was based on the estimate that 80–90% of plastic in the ocean has been there for two to four years, much longer than it takes *free* additives to reach equilibrium between the plastic and water. In contrast, Kwon et al. (2017) concluded that plastic additives *intentionally* added may not ever attain equilibrium between plastic and water in the marine environment. Both perspectives can be correct – certain additives especially those that have already escaped plastics (e.g. BFRs, APs, BPA) may already be at *sorption equilibrium* with plastics in the ocean. Incorporating both perspectives into models will make for the most accurate real-world estimates of plastic additive mass balance and fluxes.

2.3.3 The Complexity of Multiple Compartments

The ocean consists of multiple compartments, not just plastic and water, that can carry additive chemicals (Figure 2.2). Some of the dynamic processes that determine the transport and fate of plastic additives in the marine environment, and the role of the host plastic, are presented in Figure 2.3. For the complete understanding of chemical additive transport and fate in the ocean, all environmental compartments must be considered, including air, soil, sediments, freshwater,

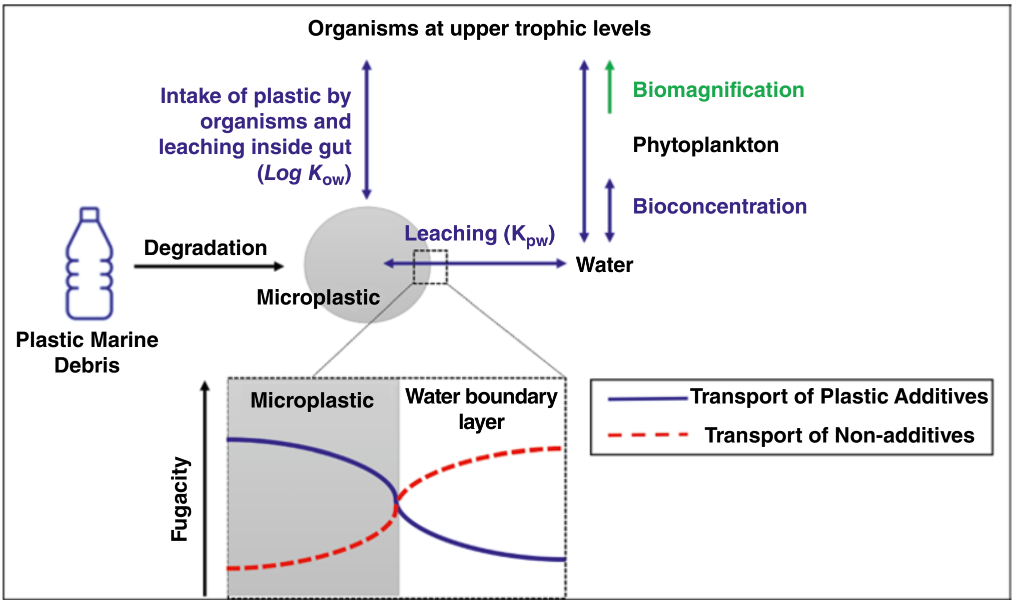


Figure 2.3 Transport and fate of hydrophobic organic chemicals to/from marine plastic particles, seawater, and biota. *Source:* Adapted from Kwon et al. (2017).

seawater, and biological matter. For this reason, several physicochemical properties beyond K_{pw}, water solubility, and K_{ow} are important. Vapor pressure, Henry's constant, octanol–air partition coefficient (K_{oa}), and the organic carbon partition coefficient (K_{oc}) also dictate the transport and fate of plastic additives, especially exchanges between various compartments (Net et al. 2015).

2.3.3.1 Transport of Plastic Additives to/From Marine Sediment

Marine sediments are thought of as the final sink compartment for plastic additives and often have the highest concentrations among all compartments. Sources of plastic additives to sediment include leaching from sunken plastic debris into the sediment, partitioning from overlying water or pore water, and settlement of sinking organic material (Figure 2.2). Resuspension of sediment constituents into the water column from bioturbation or currents can transport additives back to the water column (Gallo et al. 2018). Additives with low polarity and high K_{oc} values likely accumulate in sediment. K_{oc} values are commonly correlated with hydrophobicity or lipophilic properties, measured by K_{ow}.

2.3.3.2 Transport of Plastic Additives to/From Marine Biota

Marine organisms may be exposed to plastic additives via inhalation, dermal sorption, or ingestion of plastics or the free additives. Significant debate exists in the scientific literature whether the dominant route of exposure is from additives leaching from ingested plastics in the gut or from direct exposure to additives in water or prey. Early studies argued that plastic ingestion is a dominant exposure route since a wide range of marine animals eat plastics, and experimental studies have proven this mechanism in laboratory animals (Browne et al. 2013; GESAMP 2015; Rochman et al. 2013; Tanaka et al. 2013; Teuten et al. 2009). Other studies argue that the contribution of plastics to the bioaccumulation of additives in marine organisms is likely small; rather bioaccumulation is predominantly from ingesting prey tissues that already contain these compounds (Bakir et al. 2014; Clukey et al. 2018; Koelmans et al. 2014, 2016; Rochman et al. 2013; Zarfl and Matthies 2010). In fact, ingesting "clean" plastics reduces HOC concentrations in the body by sorption of the compounds to plastic as it moves through the gut and elimination *via* feces (Koelmans et al. 2014). Koelmans et al. (2016) provides a critical review of the literature concerning the role of plastic as a carrier/vector of additives and concluded that for the majority of marine habitats, bioaccumulation of HOCs from microplastic is likely overwhelmed by uptake via natural diet. However, in some cases, exposure to additives by the ingestion of plastic may be substantial if the amount of additives in ingested plastic is sufficiently larger than the amount in other diet items (Koelmans et al. 2016).

2.4 Degradation of Plastic Additives in the Marine Environment

Like their plastic counterparts, plastic additives are also susceptible to oxidative degradation and biodegradation. The final products from degradation of plastic additives and the kinetics of these processes in the ocean are not well understood. Basic understanding of the effects of UV, oxygen, water, pH, and temperature certainly allow scientists to predict potential degradation/transformation structures to some extent. The biological degradation pathways that can occur in marine environments remain, for the most part, a mystery.

With phthalates, biodegradation is likely the most important removal process from water (Net et al. 2015). Many phthalates biodegrade into less toxic metabolites, for instance DEP to MEP and phthalic acid (PA) in soils (Cartwright et al. 2000). Both aerobic or anaerobic microorganisms, including marine-derived fungi, biodegrade phthalates, and higher order animals, also can rapidly biotransform phthalates (Net et al. 2015, Carstens et al. 2020). Paluselli et al. (2019) found that DnBP, DiDP, BzBP, and DEHP were >85% degraded within 49 days of incubation in aerobic seawater. In marine sediments, half-lives of monoalkyl phthalate esters were between (18 ± 4 and 35 ± 10) hours (Otton et al. 2008). Phthalates can also degrade in the marine environment *via* photodegradation and hydrolysis of the ester moiety to PA and the corresponding alcohols via the monoesters. These processes, however, are recognized to be less important than biodegradation (Yan et al. 1995).

2.5 Detection in the Marine Environment

To write this chapter, we compiled a database of 193 studies that reported concentrations of plastic additives in marine plastic pollution, seawater, marine sediment, and marine organisms from 1978 to 2021.

2.5.1 Plastic Samples

The diversity of detected chemical additives in plastic samples from the marine environment is staggering (Gauquie et al. 2015), but often, the measured concentrations of pollutants are lower than typical loadings expected in plastic consumer goods (Table 2.1). In fact, all additives were lower than 1% by weight of the debris (Figure 2.4). Possible reasons for the lower than expected levels are numerous.

The first reason is that not all polymers are expected to have high loadings of particular additives. Polymer composition of the marine debris samples is fundamental to interpreting the measured additive concentrations, as only some of the diverse polymers require high additive loadings. For example, flexible PVC products often contain high loadings of phthalates, but PVC is a rare

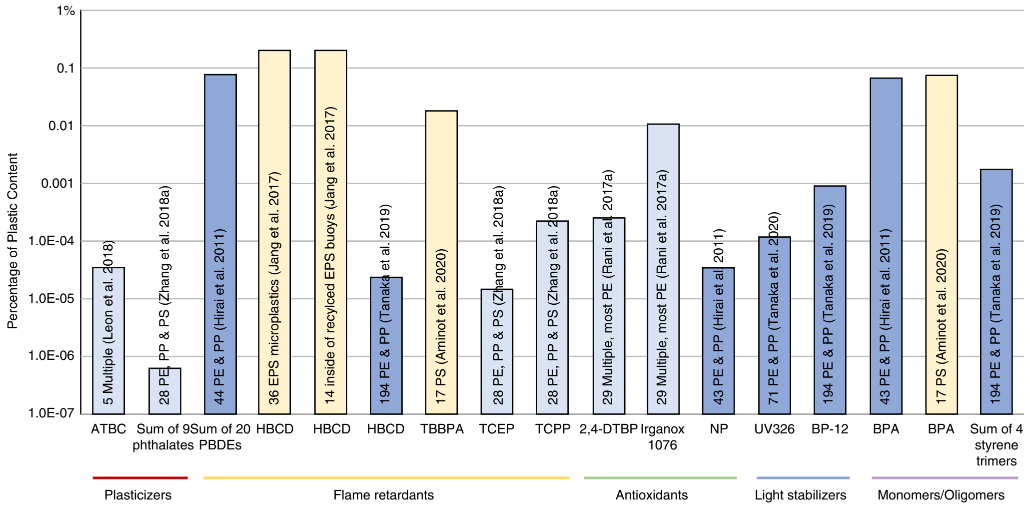


Figure 2.4 Mean concentrations of additives measured in plastics found in the marine environment, shown in logarithmic units of percent content of the plastic sample. *Note:* Sample size, polymer type, and reference are shown inside the bars. Data bars are color coded by polymer of samples (light blue = mostly PE and PP; dark blue = only PE and/or PP; yellow = PS only).

polymer in marine debris unless the study focuses on the seafloor (Brignac et al. 2019). PE and polypropylene (PP) that do not contain phthalates are abundant in ocean surface and beach debris (Brignac et al. 2019; Hermabessiere et al. 2017; Figure 2.4). In another example, HBCDs were found at the highest concentrations within plastic debris in expanded polystyrene (EPS) fishing buoy debris (Figure 2.4). But, the HBCD levels were four orders of magnitude lower in PE and PP fragments, indicating that HBCD was intentionally added to the EPS, but not to the PE or PP products.

Plastic goods tend to contain higher concentrations of additives than in preproduction resin pellets, although pellets also contain some additives (Prunier et al. 2019; Teuten, et al. 2009). Plastic debris originating from fisheries, which is a pervasive and large problem (UNEP 2009), had higher concentrations of Irganox 1076, BHT, 2,4-DTBP, UV320, and UV327, whereas Irganox 1010 was found at relatively higher levels in food-contact plastic debris (Rani et al. 2017a). These differences stem from the optimal levels selected by manufacturers driven by the desire to make fishing gear as durable as possible in harsh exposure environments and to meet regulations for food packaging. Some concentrations can be lower than the detection limits; and nondetects should never be ignored and were included as zeros while calculating the average additive concentrations, as shown in Figure 2.4.

A second reason why additives are in lower concentrations than expected is prior leaching from plastic into the environment or degradation of the additive (Rani et al. 2017b; Tanaka et al. 2020). The third reason is some of the additives detected in marine plastic debris could be adsorbed from the surrounding environment rather than being intentionally added. Plastic polymers are routinely used as passive samplers to monitor environmental pollutants in water, because they are excellent at adsorbing compounds from the surrounding environment (Koelmans et al. 2016). Because of this difficulty in determining the source of additives, the use of plastic debris samples to assess global spatial and temporal trends is complicated. Even so, Prunier et al. (2019) noted that mesoplastics from English coastal areas (Massos and Turner 2017; Turner and Solman 2016) or Chinese littoral areas (Wang et al. 2017) had element concentrations in the same order of magnitude as those from the open ocean (Prunier et al. 2019). This differs for organic pollutants, whose concentrations are greater in plastic debris from coastal areas than from the open ocean (Hirai et al. 2011). These findings are likely driven by the global distribution of naturally occurring elements in seawater and point sources influx from human activities in coastal regions (Net et al. 2015).

2.5.2 Abiotic Samples

Water and sediment are more frequently sampled than biota in plastic additive studies. For organic additives the sediment concentrations are routinely two to three orders of magnitude greater compared to that in water (Figure 2.5), as expected based on their log K_{ow} or sediment water partition coefficients.

Monitoring surface water for additives is particularly well suited for assessing global spatial and temporal comparisons, because many plastic additives are soluble enough in water to be detectable by standard monitoring techniques. Also, seawater is a globally accessible sampling matrix that is regionally influenced by local point sources. By performing a meta-analysis of phthalate concentrations in surface waters, Berge et al. (2013) reported that the European and Chinese coastal waters had higher median DEHP concentrations of approximately 1 μg/L, compared to North American waters (approximately 0.3 μg/L). However, an updated analysis of DEHP in marine waters only shows that the range of means in Asia are relatively higher than America, followed by Europe (Figure 2.6). The variability within each continental region, and the differences in sampling times, are too large to make definitive spatial comparisons. Berge et al. (2013) observed

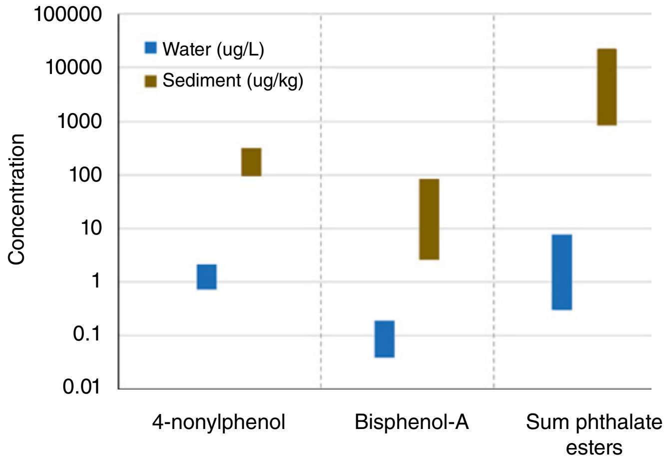


Figure 2.5 Range of concentrations of three plastic additive classes measured in paired seawater and sediment samples. *Note:* Data were taken from de los Rios et al. (2012) for 4-nonylphenol and bisphenol A in natural samples from the Bay of Biscay; and from Zhang et al. (2018b) for phthalates in Bohai and Yellow Seas.

temporal trends in the phthalate concentrations in European fresh and seawaters, which were increasing until around 2000, then decreasing due to regulatory influence (Berge et al. 2013). The marine surface waters do not reflect this trend, but no studies before 2000 were included (Figure 2.6). Zhang et al. (2018b) found a vertical distribution of phthalates in seawater with greater concentrations at the surface of the ocean that decreased slightly with depth until increasing near the bottom.

Sediment cores can offer an in situ sample archive for environmental monitoring programs to signal when regulations were needed and also to track changes in pollutant levels resulting from regulations or societal shifts. Radionuclide dating is especially valuable in determining when different sediment layers with additives were deposited. Five studies have used sediment coring methods to understand temporal trends in plastic-related chemical concentrations in Asian coastal waters only (Hashimoto et al. 2005; Moon et al. 2009; Peng et al. 2007; Wang et al. 2018; Zhang et al. 2013). Three of these studies focused on APs and/or BPA, revealing temporal trends that could be explained by local/regional land-use or policy changes. Wang et al. (2018) observed increasing concentrations of plastic additive phenolic antioxidants, such as BHT, from the bottom to the top of cores collected close to the coast, indicating increasing temporal trends of these compounds in Chinese marine habitats. Zhang et al. (2013) explained complex periodic spikes in HBCDs measured in layers of a sediment core by China's national economic development initiatives and the opening of a nearby corporation in 2005.

2.5.3 Biotic Samples

Within biota studies, plastic additives were detectable in tissues from at least 134 species. The first sampling began before 1978 (Giam et al. 1978), and most studies have focused on fish, bivalves, and other invertebrates with a few studies addressing plants, turtles, birds, and mammals (Figure 2.7).

Attempting spatial and temporal comparisons in similar species for a particular compound class, other than PBDEs and HBCDs, is difficult because the published data is sparse. Past reviews have shown elevated levels of HBCDs in samples near chemical production or application facilities,

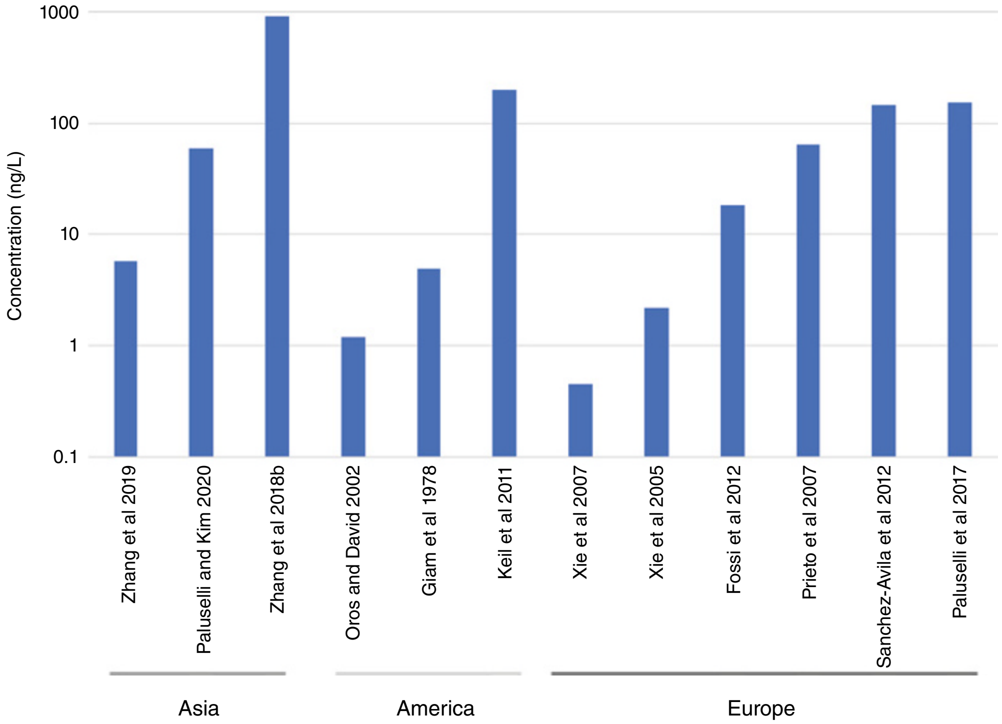
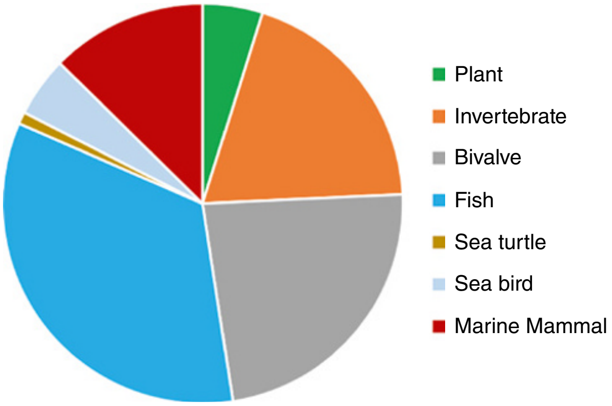


Figure 2.6 An updated spatial comparison of mean concentrations of DEHP measured in marine surface waters from Asia, America, and Europe.

Figure 2.7 Distribution of plastic additive studies assessing different taxonomic groups.



indicating that some plastic additives are released directly into the environment instead of being leached from plastic products (Covaci et al. 2006). Several temporal trends show increasing BFR concentrations until approximately 2000, reflecting usage of the compounds in developed countries (Law et al. 2014). The continual increasing trends observed in the Arctic indicate their transportation to polar regions. For the other additive classes, fish offers the best sample type, but data are very limited after filtering the data for similar trophic level, habitat type, tissue analyzed, particular chemical reported in the same or convertible units, and summary statistic (e.g., mean or median). Filtering criteria are critical because additive concentrations can vary widely among fish

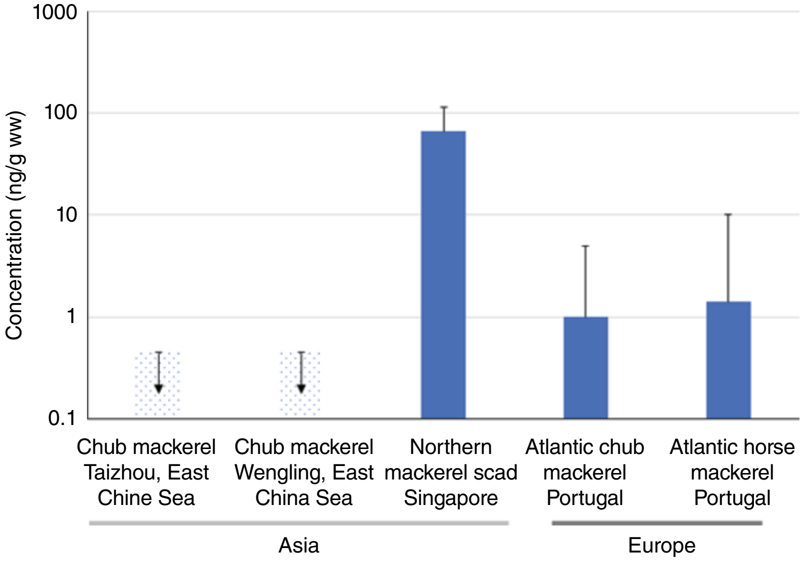


Figure 2.8 Spatial comparison of bisphenol A mean concentrations in muscle tissue from mackerel and scad fish species. *Source:* Data were taken from Gu et al. (2016), Basheer et al. (2004), and Barboza et al. (2020). *Note:* Sample sizes are 1, 4, 5, 50, and 50 from left to right, respectively. Dotted bars indicate all fish were below the shown limit of quantification. Error bars indicate standard deviation or standard error provided in respective paper.

species even from the same location (Gu et al. 2016), and additives do not distribute evenly throughout the body (Barboza et al. 2020). Filtered data available for comparison often include <20 individual fish from two or three locations on the global map and at different snapshots in time (Figure 2.8). It is not advisable to make global spatial generalizations with data like these.

For human dietary intake studies, the tissue that is most frequently consumed (e.g. fillets) was analyzed. In trophic transfer studies, the whole fish was analyzed including the gastrointestinal tract which may contain ingested plastics. On fewer occasions, fish liver was analyzed and compared to muscle tissue for APs (Lye et al. 1999), bisphenols (Barboza et al. 2020), and also to gill and kidney for phthalates (Adeogun et al. 2015). Seabird eggs offer lipid-rich samples suitable for long-term monitoring programs (Law et al. 2014), and have been analyzed for additives beyond BFRs (Lundebye et al. 2010) and compared to liver concentrations (Hallanger et al. 2015). Likewise, marine mammal blubber is commonly analyzed for BFRs, because of their accumulation in fatty tissues. Blubber and plasma have been analyzed for benzotriazole UV stabilizers and for substituted diphenylamine antioxidants (Lu et al. 2016; Nakata et al. 2010). Phosphate-based additive concentrations have been compared among the blubber, brain, kidney, liver, muscle, and plasma of marine mammals (Hallanger et al. 2015; Sala et al. 2019). Phthalate concentrations have been compared among sea turtle fat, gonads, liver, and muscle (Savoca et al. 2018), detected in seabird preen oil (Provencher et al. 2020) and in marine mammal liver (Rian et al. 2020). Since phthalates are quickly metabolized and eliminated from the body (Staples et al. 1997), some studies have targeted phthalate metabolites, instead of or in addition to the parent compound, in fish muscle (Fossi et al. 2014). Also, marine mammal blubber (Fossi et al. 2012), skin (Fossi et al. 2016), and urine (Hart et al. 2018, 2020) have also been studied in this regard. Urine concentrations of phthalates are the most widely used approach in human biomonitoring studies (Wang et al. 2019).

Certain additives can biomagnify in food webs, while others, like plastics themselves, do not (Coverton et al. 2021; Koelmans et al. 2016; Tomy et al. 2008). From our database, 12 studies investigated biomagnification of additives in marine food webs (see Box 1.2 in Chapter 1 for a discussion of biomagnification). Phthalates did not biomagnify significantly (Mackintosh et al. 2004; Morin 2003). Certain congeners of PBDEs biomagnified in several marine food webs (Brandsma et al. 2015; Mizukawa et al. 2009; Tomy et al. 2008), but conflicting results have been obtained for HBCDs (Brandsma et al. 2015; Tomy et al. 2008; Zhang et al. 2018c). One study provided evidence of TBBPA biomagnification (Li et al. 2021). Phosphate-based FRs also did not biomagnify in three marine food webs but tentatively did in a benthic food web (Brandsma et al. 2015; Garcia-Garin et al. 2020; Hallanger et al. 2015). There is some tentative evidence of biomagnification of benzotriazole UV stabilizers (Nakata et al. 2010; Peng et al. 2017). BPA most likely does not biomagnify (Corrales et al. 2015; Gu et al. 2016), and there is only weak correlative evidence for the biomagnification of 4-t-OP and 4-n-NP (Gu et al. 2016). We are unaware of trophic transfer studies for additive classes such as other antioxidants, heat stabilizers, fillers, IMs, colorants, or lubricants.

2.6 Toxicity of Additives

The toxicity of plastic additives is quite variable given the diversity of their chemical classes. Determining the dose that kills 50% of a test animal (LD_{50}), such as *Daphnia magna* in 48-hour exposures, is a basic standard aquatic toxicity test that allows for simple comparisons of toxicity across compounds. The range of LD_{50} values for plastic additives exemplifies this diversity (Table 2.5). Acutely toxic additives (e.g., LD_{50} values <1 mg/L) include lower brominated PBDEs, APs, some phthalates, such as DEHP, Basic Red 51 azo dye, cadmium, copper, and zinc. In contrast, other additives, considered not harmful because their LD_{50} values are >10 mg/L, include 2,2 -bis(bromomethyl)-1,3-propanediol (BBMP), TCEP, and DEP. The antioxidant, Irganox 1010 has a high LD_{50} for *D. magna* (86 mg/L, Table 2.5) and other animals; therefore, it is allowed in food-contact plastic packaging (USFDA 2019). Lower toxicity provides some justification for replacing conventional additives with newer replacements. Even so, many replacements still exhibit some level of toxicity, some even at similar concentrations than the original additive, and should be more thoroughly studied (Behl et al. 2016; Luo et al. 2021).

The toxicity of many plastic additives has been reviewed previously (Table 2.6). Endocrine disruption is a prominent toxicological mechanism noted in the literature for many plastic additives. Endocrine-disrupting chemicals (EDCs) are so-called because they disturb any step in the complex feedback systems of hormones that regulate reproduction, growth, metabolism, and many other biological functions. Mechanisms of toxic action include interfering in the synthesis, activity, or elimination of hormones or their receptors. Phthalates, FRs, antioxidants, monomers, and metal-based additives are known as EDCs, disrupting a range of different hormonal systems (Table 2.7). The main concern over EDCs is that they act at concentrations much lower than lethal concentrations and results in sublethal effects, such as reduced reproduction or slower growth, both of which could significantly harm populations or communities of marine organisms. For example, thyroid disruption and neurobehavioral effects were observed in crucian carp (*Carassius auratus*) at concentrations of HBCDs 10–100 times higher than environmental concentrations, leaving only a small margin of safety for wild fish populations (Dong et al. 2018).

Additives can also exert neurological, carcinogenic, developmental, immunotoxic, and organ toxicities. DEHP, for instance, is an animal and human carcinogen (Campanale et al. 2020). Toxicity tests of organophosphorous flame retardants (OPFRs) with mammals, birds, and fish resulted in neurotoxicity, oxidative stress, altered metabolic processes, developmental toxicity, and effects on the liver, kidney, and other organs (Du et al. 2019). Hindered phenolic antioxidants, including 2,6-di-tert-butyl-4-methylphenol (BHT) and butylated hydroxyanisole (BHA) and their metabolites, exhibit diverse toxicities, including endocrine disruption, kidney and liver effects,

Table 2.6 Examples of review articles discussing the toxicities of plastic additives.

Reference	Chemical class	Toxicological effect	Organismal focus for toxicology
Hermabessiere et al. (2017)	Multiple	Multiple	Marine
Liu et al. (2020)	Multiple	Ecotox proteomics	Aquatic
Pérez-Albaladejo et al. (2020)	Multiple	Oxidative stress	Human and Aquatic
Oehlmann et al. (2009)	Phthalates, bisphenol A	Multiple	Aquatic and terrestrial
Staples et al. (1997)	Phthalates	Acute and Chronic	Aquatic
Bradlee and Thomas (2003)	Phthalates	Multiple	Aquatic
Yost et al. (2019)	Diisobutyl phthalate	Multiple	Human and mammals
Weaver et al. (2020)	Diethyl phthalate	Multiple	Human and mammals
Caldwell (2012)	De(ethylhexyl) phthalate	Genotoxicity	Human and Rodent
Brehm and Flaws (2019)	Phthalates, BPA	Transgenerational	Human
Luo et al. (2021)	Phthalate replacements	Multiple	Multiple
de Wit (2002)	BFRs (PBDEs, HBCD, TBBPA)	Multiple	Environment
Yu et al. (2015)	PBDEs	Thyroid, reproduction	Fish
Akortia et al. (2016)	PBDEs	Multiple	Environment
Covaci et al. (2006)	HBCD	Multiple	Mammal
Koch et al. (2015)	HBCD	Multiple	Mammal, bird, fish
Du et al. (2019)	OPFR	Multiple	Mammal, Bird, Fish
Liu and Mabury (2020)	Phenolic antioxidants	Multiple	Mammal and aquatic
Servos (1999)	Alkylphenols	Multiple (endocrine)	Aquatic
Tchounwou et al. (2012)	Metals	Multiple	Environment
Canesi and Fabbri (2015)	Bisphenol A	Multiple	Aquatic
Bhandari et al. (2015a)	Bisphenol A	Multiple (endocrine)	Aquatic Vertebrates and humans
Liu et al. (2021)	Bisphenol A	Multiple	Aquatic
Sharma (2009)	Titanium oxide nanoparticles	Multiple	Aquatic
Turan et al. (2019)	Engineered nanoparticles	Multiple	Aquatic

genotoxicity, tumor promotion or enhancement, reproductive effects, and lipid disruption (Liu and Maybury 2020). The diverse toxic effects of priority metals, such as As, Cd, Cr, Pb, and Hg, to multiple organs are well known (Liu et al. 2008).

Data on toxicity of the newer nanoscale inorganic fillers are well under way. Titanium oxide nanoparticles, smaller than 100 nm in diameter, may be toxic to aquatic organisms because of their bioavailability (Sharma 2009). Suspensions of CB nanoparticles causes oxidative stress and activates lysosomal biomarkers in the digestive gland of mussels (Canesi et al. 2010), but the extent to which nanoparticles leach out of polymer nanocomposites is unknown. Estrogenicity of BPA and NP is well documented, but more recently, immunotoxicity their has also been observed in fish

Table 2.7 Plastic additives that are endocrine-disrupting compounds.

Additive class	Chemical	Endocrine-disrupting action
Plasticizers	Phthalates	Anti-androgenic
Flame retardants	PBDEs	Thyroid disruption
Flame retardants	HBCDs	Thyroid disruption
Antioxidants	Nonylphenol	Estrogenic
Monomers	Bisphenol A	Estrogenic
Monomers	Styrene	Inconclusive
Multiple	Cd, Pb, Zn	Multiple
UV stabilizer	Benzotriazoles	Thyroid disruption

(Canesi and Fabbri 2015; Rastgar et al. 2019; Servos 1999). Benzotriazole UV stabilizers changed many immune response genes in zebrafish brain, liver, and embryos, as revealed by transcriptomics (Li et al. 2020). As toxicological tests become more sophisticated, such as rapidly advancing omics research (Liu et al. 2020), and our understanding of chronic, chemical mixtures, and multigenerational effects grows, and toxicological effects may be observed at even lower concentrations.

For ideal risk assessments, the doses, route of exposure, and species used in toxicity tests must be relevant to environmental exposures. Many studies use doses far higher than those found in the environment (Brehm and Flaws 2019). These tests may miss sublethal, chronic effects or U-shaped dose responses. Toxicology studies on marine species are rare in the literature. Studies that use rats and mice are common and important for assessing mammalian toxicology, but are not relevant to most marine species. The use of freshwater model species, such as *D. magna* and zebrafish, is more relevant but may not always be the best surrogate for marine organisms (Duran and Beiras 2017). For example, toxicity thresholds of BPA and NP spanned two to three orders of magnitude across saltwater species alone. Current regulatory standards for admissible concentrations in water are often based on freshwater organisms and may not adequately protect marine organisms (Duran and Beiras 2017). More testing is needed on model and nonmodel marine species, like the studies of Duran and Beiras (2017) and Delorenzo et al. (2008).

A common method for testing the toxicity of mixtures of plastic additives is to expose cells or organisms to leachate from plastic products. Sometimes, but not always, the chemicals are identified in the leachate to understand which could be causing the toxicity. For example, the leachate from three polymers (PVC, PET, and polybutylene adipate co-terephtalate) in seawater was tested for in vitro estrogenic activity (Kedzierski et al. 2018). Microplastics collected from the North Pacific gyre leached chemicals that were estrogenic in *in vitro* bioassays, but upon analysis of the leachate they detected estradiol, a natural hormone found in pharmaceuticals but not a plastic additive, indicating that plastics are perhaps absorbing environmental contaminants that may interfere with studies that intend to focus only on plastic additives (Chen et al. 2019).

2.7 NIST Disclaimer

Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

References

Accorsi, J. 2001. The impact of carbon black morphology and dispersion on the weatherability of polyethylene. *Kautschuk Gummi Kunststoffe*, 54(6): 321–326.

Adeogun, A. O., Ibor, O. R., Omogbemi, E. D., Chukwuka, A. V., Adegbola, R. A., Adewuyi, G. A., Arukwe, A. 2015. Environmental occurrence and biota concentration of phthalate esters in Epe and Lagos Lagoons, Nigeria. *Marine Environmental Research*, 108: 24–32.

Akortia, E., Okonkwo, J. O., Lupankwa, M., Osae, S. D., Daso, A. P., Olukunle, O. I., Chaudhary, A. 2016. A review of sources, levels, and toxicity of polybrominated diphenyl ethers (PBDEs) and their transformation and transport in various environmental compartments. *Environmental Reviews*, 24(3): 253–273.

Alam, P., Mamalis, D., Robert, C., Floreani, C., Brádaigh, C. M. O., 2019. The fatigue of carbon fibre reinforced plastics – a review. *Composites Part B: Engineering.*166: 555–579.

Ambrogi, V., Carfagna, C., Cerruti, P., Marturano, V. 2017. Additives in polymers. *Modification of Polymer Properties*. Cambridge, MA, William Andrew Publishing, pp. 87–108.

Amelia, T. S. M., Khalik, W. M. A. W. M., Ong, M. C., et al. 2021. Marine microplastics as vectors of major ocean pollutants and its hazards to the marine ecosystem and humans. *Progress in Earth and Planetary Sciences*, 8: 12.

Aminot, Y., Lanctot, C., Bednarz, V., Robson, W. J., Taylor, A., Ferrier-Pages, C., Metian, M., Tolosa, I. 2020. Leaching of flame-retardants from polystyrene debris: Bioaccumulation and potential effects on coral. *Marine Pollution Bulletin*, 151: 110862.

Andrady, A. L., Rajapakse, N. 2019. *Additives and chemicals in plastics. Hazardous Chemicals Associated with Plastics in the Marine Environment*. Cham, Springer: 1–17.

Bakir, A. B., Rowland, S. J., Thompson, R. C. 2014. Transport of persistent organic pollutants by microplastics in estuarine conditions. *Estuarine, Coastal and Shelf Science* 140: 14–21.

Barboza, L. G. A., Cunha, S. C., Monteiro, C., Fernandes, J. O., Guilhermino, L. 2020. Bisphenol A and its analogs in muscle and liver of fish from the North East Atlantic Ocean in relation to microplastic contamination. Exposure and risk to human consumers. *Journal of Hazardous Materials*, 393: 122419.

Basheer, C., Lee, H. K., Tan, K. S. 2004. Endocrine disrupting alkylphenols and bisphenol-A in coastal waters and supermarket seafood from Singapore. *Marine Pollution Bulletin* 48(11–12): 1161–1167.

Behl, M., Rice, J. R., Smith, M. V., Co, C. A., Bridge, M. F., Hsieh, J.-H., Freedman, J. H., Boyd, W. A. 2016. Comparative toxicity of organophosphate flame retardants and polybrominated diphenyl ethers to *Caenorhabditis elegans*. *Toxicological Sciences*, 154(2): 241–252.

Berge, A., Cladiere, M., Gasperi, J., Coursimault, A., Tassin, B., Moilleron, R. 2013. Meta-analysis of environmental contamination by phthalates. *Environmental Science and Pollution Research International*, 20(11): 8057–8076.

Bhandari, R. K., Deem, S. L., Holliday, D. K., Jandegian, C. M., Kassotis, C. D., Nagel, S. C., Tillitt, D. E., Vom Saal, F. S., Rosenfeld, C. S. 2015. Effects of the environmental estrogenic contaminants bisphenol A and 17alpha-ethinyl estradiol on sexual development and adult behaviors in aquatic wildlife species. *General and Comparative Endocrinology* 214: 195–219.

Bhunia, K., Sablani, S. S., Tang, J., Rasco, B. 2013. Migration of chemical compounds from packaging polymers during microwave, conventional heat treatment, and storage. *Comprehensive Reviews in Food Science and Food Safety*, 12(5): 523–545.

Bieber, W. D., Freytag, W., Figge, K., Vom Bruck, C. G. 1984. Transfer of additives from plastics materials into foodstuffs and into food simulants – a comparison. *Food Chem Toxic* 22(9): 737–742.

Biles, J. E., McNeal, T. P., Begley, T. H., Hollifield, H. C. 1997. Determination of bisphenol-A in reusable polycarbonate food-contact plastics and migration to food-simulating liquids. *Journal of Agricultural and Food Chemistry*, 45(9): 3541–3544.

Binetti, R., Costamagna, F. M., Ceccarelli, F., D'angiolini, A., Fabri, A., Riva, G., Satalia, S., Marcello, I. 2008. The ISS National Inventory of Chemical Substances (INSC). *Annali dell'Istituto Superiore di Sanità*, 44(1): 16–26.

Boehme, R. M., Andries, T., Dötz, K. H., Thiele, B., Guenther, K. 2010. Synthesis of defined endocrine-disrupting nonylphenol isomers for biological and environmental studies. *Chemosphere* 80 (7): 813–821.

Bolgar, M., Hubball, J., Groeger, J., Meronek, S., Eds. 2016. *Handbook for the Chemical Analysis of Plastic and Polymer Additives*. Boca Raton, FL, CRC Press.

Bradlee, C. A., Thomas, P. 2003. Aquatic toxicity of phthalate esters. Series anthropogenic compounds. In: Staples, C.A. (Ed.), *The Handbook of Environmental Chemistry*. Berlin, Heidelberg, Springer, pp. 263–298.

Brandsma, S. H., Leonards, P. E., Leslie, H. A., de Boer, J. 2015. Tracing organophosphorus and brominated flame retardants and plasticizers in an estuarine food web. *Science of the Total Environment*, 505: 22–31.

Brehm, E., Flaws, J. A. 2019. Transgenerational effects of endocrine-disrupting chemicals on male and female reproduction. *Endocrinology*, 160(6): 1421–1435.

Brignac, K. C., Jung, M. R., King, C., Royer, S. J., Blickley, L., Lamson, M. R., Potemra, J. T., Lynch, J. M. 2019. Marine debris polymers on main Hawaiian island beaches, sea surface, and seafloor. *Environmental Science & Technology*, 53(21): 12218–12226.

Browne, M. A., Niven, S. J., Galloway, T. S., Rowland, S. J., Thompson, R. C. 2013. Microplastic moves pollutants and additives to worms, reducing functions linked to health and biodiversity. *Current Biology*, 23(23): 2388–2392.

Brydson, J. 1999. *Plastic Materials*. Woburn, MA, Butterworth-Heinemann.

Caldwell, J. C. 2012. DEHP: genotoxicity and potential carcinogenic mechanisms – a review. *Mutation Research*, 751(2): 82–157.

Campanale, C., Massarelli, C., Savino, I., Locaputo, V., Uricchio, V. F. 2020. A detailed review study on potential effects of microplastics and additives of concern on human health. *International Journal of Environmental Research and Public Health*, 17(4): 1212.

Canesi, L., Fabbri, E. 2015. Environmental effects of BPA: focus on aquatic species. *Dose Response*, 13(3): 1559325815598304.

Canesi, L., Fabbri, R., Gallo, G., Vallotto, D., Marcomini, A., Pojana, G. J. A. T. 2010. Biomarkers in *Mytilus galloprovincialis* exposed to suspensions of selected nanoparticles (Nano carbon black, C60 fullerene, Nano-TiO2, Nano-SiO2). *Aquatic Toxicology* 100 (2): 168–177.

Carstens, L., Cowan, A. R., Seiwert, B., Schlosser, D. 2020. Biotransformation of phthalate plasticizers and bisphenol A by marine-derived, freshwater, and terrestrial fungi. *Frontiers in Microbiology*, 11: 317.

Cartwright, C. D., Owen, S. A., Thompson, I. P., Burns, R. G. 2000. Biodegradation of diethyl phthalate in soil by a novel pathway. *FEMS Microbiology Letters* 186: 27–34.

Chen, Q., Allgeier, A., Yin, D., Hollert, H. 2019. Leaching of endocrine disrupting chemicals from marine microplastics and mesoplastics under common life stress conditions. *Environment International*, 130: 104938.

Chaudhary, B. I., Liotta, C. L., Cogen, J. M., Gilbert, M. 2016. *Plasticized PVC, Reference Module in Materials Science and Materials Engineering*. Amsterdam, Elsevier.

Civancik-Uslu, D., Ferrer, L., Puig, R., Fullana-i-Palmer, P. 2018. Are functional fillers improving environmental behavior of plastics? A review on LCA studies. *Science of The Total Environment*, 626: 927–940.

Clukey, K. E., Lepczyk, C. A., Balazs, G. H., Work, T. M., Li, Q. X., Bachman, M. J., Lynch, J. M. 2018. Persistent organic pollutants in fat of three species of Pacific pelagic longline caught sea turtles: accumulation in relation to ingested plastic marine debris. *Science of The Total Environment* 610–611: 402–411.

Cole, M., Lindeque, P., Fileman, E., Halsband, C., Galloway, T. S. 2015. The impact of polystyrene microplastics on feeding, function and fecundity in the marine copepod *Calanus helgolandicus*. *Environmental Science & Technology*, 49(2): 1130–1137.

Corrales, J., Kristofco, L. A., Steele, W. B., Yates, B. S., Breed, C. S., Williams, E. S., Brooks, B. W. 2015. Global assessment of bisphenol A in the environment: review and analysis of its occurrence and bioaccumulation. *Dose Response*, 13(3): 1559325815598308.

Covaci, A., Gerecke, A. C., Law, R. J., Voorspoels, S., Kohler, M., Heeb, N. V., Leslie, H., Allchin, C. R. de Boer, J. 2006. Hexabromocyclododecanes (HBCDs) in the environment and humans: a review. *Environmental Science & Technology*, 40(12): 3679–3688.

Covernton, G. A., Davies, H. L., Cox, K. D., El-Sabaawi, R., Juanes, F., Dudas, S. E., Dower, J. F. 2021. A Bayesian analysis of the factors determining microplastics ingestion in fishes. *Journal of Hazardous Materials*, 413: 125405.

Date, K., Ohno, K., Azuma, Y., Hirano, S., Kobayashi, K., Sakurai, T., Nobuhara, Y., Yamada, T. 2002. Endocrine-disrupting effects of styrene oligomers that migrated from polystyrene containers into food. *Food and Chemical Toxicology*, 40(1): 65–75.

De Frond, H. L., van Sebille, E., Parnis, J. M., Diamond, M. L., Mallos, N., Kingsbury, T., Rochman, C. M. 2019. Estimating the mass of chemicals associated with ocean plastic pollution to inform mitigation efforts. *Integr Environ Assess Manag*, *15*(4): 596–606.

Delva, L., Hubo, S., Cardon, L., Ragaert, K., 2018. On the role of flame retardants in mechanical recycling of solid plastic waste. *Waste Management*, 82: 198–206.

de los Rios, A., Juanes, J. A., Ortiz-Zarragoitia, M., Lopez de Alda, M., Barcelo, D., Cajaraville, M. P. 2012. Assessment of the effects of a marine urban outfall discharge on caged mussels using chemical and biomarker analysis. *Marine Pollution Bulletin*, 64(3): 563–573.

de Wit, C. A. 2002. An overview of brominated flame retardants in the environment. *Chemosphere*, 46: 583–624.

Delorenzo, M. E., Keller, J. M., Arthur, C. D., Finnegan, M. C., Harper, H. E., Winder, V. L., Zdankiewicz, D. L. 2008. Toxicity of the antimicrobial compound triclosan and formation of the metabolite methyl-triclosan in estuarine systems. *Environmental Toxicology*, 23(2): 224–232.

Dong, H., Lu, G., Yan, Z., Liu, J., Yang, H., Nkoom, M. 2018. Bioconcentration and effects of hexabromocyclododecane exposure in crucian carp (*Carassius auratus*). *Ecotoxicology*, 27(3): 313–324.

Du, J., Li, H., Xu, S., Zhou, Q., Jin, M., Tang, J. 2019. A review of organophosphorus flame retardants (OPFRs): occurrence, bioaccumulation, toxicity, and organism exposure. *Environmental Science and Pollution Research International*, 26(22): 22126–22136.

Duran, I., Beiras, R. 2017. Acute water quality criteria for polycyclic aromatic hydrocarbons, pesticides, plastic additives, and 4-nonylphenol in seawater. *Environmental Pollution*, 224: 384–391.

ECPI. 2016. *Plasticisers*. <https://www.plasticisers.org/plasticisers/> (accessed February 28, 2021).

Endo, S., Yuyama, M., Takada, H. 2013. Desorption kinetics of hydrophobic organic contaminants from marine plastic pellets. *Marine Pollution Bulletin*, 74(1): 125–131.

Fikarova, K., Cocovi-Solberg, D. J., Rosende, M., Horstkotte, B., Sklenarova, H., Miro, M. 2019. A flow-based platform hyphenated to on-line liquid chromatography for automatic leaching tests of chemical additives from microplastics into seawater. *Journal of Chromatography A*, 1602: 160–167.

Fossi, M. C., Panti, C, Guerranti, C., Coppola, D., Giannetti, M., Marsili, L., Minutoli, R. 2012. Are baleen whales exposed to the threat of microplastics? A case study of the Mediterranean fin whale (*Balaenoptera physalus*). *Marine Pollution Bulletin*, 64(11): 2374–2379.

Fossi, M. C., Coppola, D., Baini, M., Giannetti, M., Guerranti, C., Marsili, L., Panti, C., de Sabata, E., Clo, S. 2014. Large filter feeding marine organisms as indicators of microplastic in the pelagic environment: the case studies of the Mediterranean basking shark (*Cetorhinus maximus*) and fin whale (*Balaenoptera physalus*). *Marine Environmental Research*, 100: 17–24.

Fossi, M. C., Marsili, L., Baini, M., Giannetti, M., Coppola, D., Guerranti, C., Caliani, I., Minutoli, R., Lauriano, G., Finoia, M. G., Rubegni, F, Panigada, S., Berube, M., Urban Ramirez, J., Panti, C. 2016. Fin whales and microplastics: the Mediterranean Sea and the Sea of Cortez scenarios. *Environmental Pollution*, 209: 68–78.

Froggett, S. J., Clancy, S. F., Boverhof, D. R., Canady, R. A. 2014. A review and perspective of existing research on the release of nanomaterials from solid nanocomposites. *Particle and Fibre Toxicology*, 11(1): 1–28.

Gallo, F., Fossi, C., Weber, R. et al. 2018. Marine litter plastics and microplastics and their toxic chemicals components: the need for urgent preventive measures. *Environmental Science Europe* 30: 13.

Garcia-Garin, O., Sala, B., Aguilar, A., Vighi, M., Vikingsson, G. A., Chosson, V., Eljarrat, E., Borrell, A. 2020. Organophosphate contaminants in North Atlantic fin whales. *Science of the Total Environment* 721: 137768.

Garde, J. A., Catala, R., Gavara, R. 1998. Global and specific migration of antioxidants from polypropylene films into food simulants. *Journal of Food Protection*, 61(8): 1000–1006.

Gauquie, J., Devriese, L., Robbens, J., De Witte, B. 2015. A qualitative screening and quantitative measurement of organic contaminants on different types of marine plastic debris. *Chemosphere*, 138: 348–356.

GESAMP (2015). Sources, Fate and Effects of Microplastics in the Marine Environment: A Global Assessment (ed. P.J. Kershaw). (IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). *Rep. Stud. GESAMP No. 90*, 96 p.

Gewert, B., Plassmann, M. M., MacLeod, M. 2015. Pathways for degradation of plastic polymers floating in the marine environment. *Environmental Science: Processes & Impacts*, 17(9): 1513–1521.

Geyer, R., Jambeck, J. R., Law, K. L. 2017. Production, use, and fate of all plastics ever made. *Science Advances*, 3(7): e1700782.

Giam, C. S., Chan, H. S., Neef, G. S., Atlas, E. L. 1978. Phthalate ester plasticizers: a new class of marine pollutant. *Science*, 199(4327): 419–421.

Greco, C. A., Zhang, J. G., Kalab, M., Yi, Q. L., Ramirez-Arcos, S. M., Gyongyossy-Issa, M. I. 2010. Effect of platelet additive solution on bacterial dynamics and their influence on platelet quality in stored platelet concentrates. *Transfusion*, 50(11): 2344–2352.

Gu, Y., Yu, J., Hu, X., Yin, D. 2016. Characteristics of the alkylphenol and bisphenol A distributions in marine organisms and implications for human health: a case study of the East China Sea. *Science of the Total Environment*, 539: 460–469.

Hahladakis, J. N., Velis, C. A., Weber, R., Iacovidou, E., Purnell, P. 2018. An overview of chemical additives present in plastics: migration, release, fate and environmental impact during their use, disposal and recycling. *Journal of Hazardous Materials*, 344: 179–199.

Hallanger, I. G., Sagerup, K., Evenset, A., Kovacs, K. M., Leonards, P., Fuglei, E., Routti, H., Aars, J., Strom, H., Lydersen, C., Gabrielsen, G. W. 2015. Organophosphorous flame retardants in biota from Svalbard, Norway. *Marine Pollution Bulletin*, 101(1): 442–447.

Hansen, E., Nillson, N. H., Lithner, D., Lassen, C. 2013. *Hazardous Substances in Plastic Materials*. COWI, Danish Technological Institute.

Hart, L. B., Beckingham, B., Wells, R. S., Alten Flagg, M., Wischusen, K., Moors, A., Kucklick, J., Pisarski, E., Wirth, E. 2018. Urinary phthalate metabolites in common bottlenose dolphins (*Tursiops truncatus*) from Sarasota Bay, FL, USA. *GeoHealth* 2(10): 313–326.

Hart, L. B., Dziobak, M. K., Pisarski, E. C., Wirth, E. F., Wells, R. S. 2020. Sentinels of synthetics – a comparison of phthalate exposure between common bottlenose dolphins (*Tursiops truncatus*) and human reference populations. *PLoS One*, 15(10): e0240506.

Hashimoto, S., Horiuchi, A., Yoshimoto, T., Nakao, M., Omura, H., Kato, Y., Tanaka, H., Kannan, K., Giesy, J. P. 2005. Horizontal and vertical distribution of estrogenic activities in sediments and waters from Tokyo Bay, Japan. *Archives of Environmental Contamination and Toxicology* 48(2): 209–216.

Hendren, C. O., Mesnard, X., Droge, J., Wiesner, M. R. 2011. Estimating production data for five engineered nanomaterials as a basis for exposure assessment. *Environmental Science & Technology*, 45(7): 2562–2569.

Hermabessiere, L., Dehaut, A., Paul-Pont, I., Lacroix, C., Jezequel, R., Soudant, P., Duflos, G. 2017. Occurrence and effects of plastic additives on marine environments and organisms: a review. *Chemosphere* 182: 781–793.

Hirai, H., Takada, H., Ogata, Y., Yamashita, R., Mizukawa, K., Saha, M., Kwan, C., Moore, C., Gray, H., Laursen, D., Zettler, E.R., Farrington, J. W., Reddy, C. M., Peacock, E. E., Ward, M. W. 2011. Organic micropollutants in marine plastics debris from the open ocean and remote and urban beaches. *Marine Pollution Bulletin* 62(8): 1683–1692.

Huang, J.-C. 2002. Carbon black filled conducting polymers and polymer blends. *Advances in Polymer Technology*, 21(4): 299–313.

Huckle, W. G., Lalor, E. 1955. Inorganic pigments. *Industrial & Engineering Chemistry* 47(8): 1501–1506.

IHS Markit. 2018. *Plasticizers Chemical Economic Handbook*. London, IHS Markit. https://ihsmarkit.com/products/plasticizers-chemical-economics-handbook.html.

Innes, J., Innes, A. 2002. Compounding metal hydrate flame retardants. *Plastics, Additives, and Compounding*, 4(4): 22–26.

Jang, M., Shim, W. J., Han, G. M., Rani, M., Song, Y. K., Hong, S. H. 2017. Widespread detection of a brominated flame retardant, hexabromocyclododecane, in expanded polystyrene marine debris and microplastics from South Korea and the Asia-Pacific coastal region. *Environmental Pollution*, 231: 785–794.

Jia, H., Wang, H., Chen, W., 2007. The combination effect of hindered amine light stabilizers with UV absorbers on the radiation resistance of polypropylene. *Radiation Physics and Chemistry*, 76(7): 1179–1188.

Joo, J. C., Kim, J. Y., Nam, K. 2004. Mass transfer of organic compounds in dilute aqueous solutions into high density polyethylene geomembranes. *Journal of Environmental Engineering*, 130(2): 175–183.

Kaiser, D., Estelmann, A., Kowalski, N., Glockzin, M., Waniek, J. J. 2019. Sinking velocity of sub-millimeter microplastic. *Marine Pollution Bulletin*, 139: 214–220.

Kedzierski, M., D'Almeida, M., Magueresse, A., Le Grand, A., Duval, H., Cesar, G., Sire, O., Bruzaud, S., Le Tilly, V. 2018. Threat of plastic ageing in marine environment. Adsorption/desorption of micropollutants. *Marine Pollution Bulletin*, 127: 684–694.

Keil, R., Salemme, K., Forrest, B., Neibauer, J., Logsdon, M. 2011. Differential presence of anthropogenic compounds dissolved in the marine waters of Puget Sound, WA and Barkley Sound, BC. *Marine Pollution Bulletin*, 62(11): 2404–2411.

Kim, S., Kim, Y., Moon, H.B. 2021. Contamination and historical trends of legacy and emerging plasticizers in sediment from highly industrialized bays of Korea. *Science of The Total Environment* 765: 142751.

Koch, C., Schmidt-Kotters, T., Rupp, R., Sures, B. 2015. Review of hexabromocyclododecane (HBCD) with a focus on legislation and recent publications concerning toxicokinetics and -dynamics. *Environmental Pollution*, 199: 26–34.

Koelmans, A. A., Besseling, E., Foekema, E. M. 2014. Leaching of plastic additives to marine organisms. *Environmental Pollution*, 187: 49–54.

Koelmans, A. A., Bakir, A., Burton, G. A., Janssen, C. R. 2016. Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies. *Environmental Science & Technology*, 50(7): 3315–3326.

Kubwabo, C., Kosarac, I., Stewart, B., Gauthier, B. R., Lalonde, K., Lalonde, P. J. 2009. Migration of bisphenol A from plastic baby bottles, baby bottle liners and reusable polycarbonate drinking bottles. *Food Additives & Contaminants: Part A: Chemistry, Analysis, Control, Exposure & Risk Assessment* 26(6): 928–937.

Kwon, B. G., Saido, K., Koizumi, K., Sato, H., Ogawa, N., Chung, S. Y., Kusui, T., Kodera, Y., Kogure, K. 2014. Regional distribution of styrene analogues generated from polystyrene degradation along the coastlines of the North-East Pacific Ocean and Hawaii. *Environmental Pollution*, 188: 45–49.

Kwon, J. H., Chang, S., Hong, S. H., Shim, W. J. 2017. Microplastics as a vector of hydrophobic contaminants: Importance of hydrophobic additives. *Integrated Environmental Assessment and Management* 13(3): 494–499.

Law, R. J., Covaci, A., Harrad, S., Herzke, D., Abdallah, M. A., Fernie, K., Toms, L. M., Takigami, H. 2014. Levels and trends of PBDEs and HBCDs in the global environment: status at the end of 2012. *Environment International*, 65: 147–158.

Leon, V. M., Garcia, I., Gonzalez, E., Samper, R., Fernandez-Gonzalez, V., Muniategui-Lorenzo, S. 2018. Potential transfer of organic pollutants from littoral plastics debris to the marine environment. *Environment Pollution*, 236: 442–453.

Li, K., Liszka, M., Zhou, C., Brehm, E., Flaws, J. A. Nowak, R. A. 2020. Prenatal exposure to a phthalate mixture leads to multigenerational and transgenerational effects on uterine morphology and function in mice. *Reproductive Toxicology*, 93: 178–190.

Li, H., Zhang, Z., Sun, Y., Wang, W., Xie, J., Xie, C., Hu, Y., Gao, Y., Xu, X., Luo, X., Mai, B. 2021. Tetrabromobisphenol A and hexabromocyclododecanes in sediments and biota from two typical mangrove wetlands of South China: distribution, bioaccumulation and biomagnification. *Science of the Total Environment*, 750: 141695.

Liu, R., Mabury, S. A. 2020. Synthetic phenolic antioxidants: a review of environmental occurrence, fate, human exposure, and toxicity. *Environmental Science & Technology*, 54(19): 11706–11719.

Liu, J., Goyer, R. A., Waalkers, M. P. 2008. Toxic effects of metals. In: Klassen, C. D. (Ed.), *Casarett & Doull's Toxicology: The Basic Science of Poisons*. New York, NY: McGraw Hill.

Liu, L., Fokkink, R., Koelmans, A. A., 2016. Sorption of polycyclic aromatic hydrocarbons to polystyrene nanoplastic. *Environmental Toxicology and Chemistry*, 35: 1650–1655.

Liu, J., Zhang. L., Lu, G., Jiang, R., Yan, Z., Li, Y. 2021. Occurrence, toxicity and ecological risk of bisphenol A analogues in aquatic environment – a review. *Ecotoxicology and Environmental Safety*, 208: 111481.

Liu, W., Zhao, Y., Shi, Z., Li, Z., Liang, X. 2020. Ecotoxicoproteomic assessment of microplastics and plastic additives in aquatic organisms: a review. *Comparative Biochemistry and Physiology – Part D: Genomics and Proteomics*, 36: 100713.

Lu, Z., Peart, T. E., Cook, C. J., De Silva, A. O. 2016. Simultaneous determination of substituted diphenylamine antioxidants and benzotriazole ultra violet stabilizers in blood plasma and fish homogenates by ultra high performance liquid chromatography-electrospray tandem mass spectrometry. *Journal of Chromatography A*, 1461: 51–58.

Lundebye, A. K., Hove, H., Mage, A., Bohne, V. J., Hamre, K. 2010. Levels of synthetic antioxidants (ethoxyquin, butylated hydroxytoluene and butylated hydroxyanisole) in fish feed and commercially farmed fish. *Food Additives & Contaminants: Part A: Chemistry, Analysis, Control, Exposure & Risk Assessment*, 27(12): 1652–1657.

Luo, Y., Gao. P., Yan, L., Zhang, X., Yu, H., Shi, W., Yu, N. 2021. Research progress on endocrine disruption effect of di-n-butyl phthalate, diisobutyl phthalate and substitutes. *Environmental Chemistry*, 1: 11–27.

Lye, C. M., Frid, C. L. J., Gill, M. E., Cooper, D. W., Jones, D. M. 1999. Estrogenic alkylphenols in fish tissues, sediments, and waters from the U.K. Tyne and Tees Estuaries. *Environmental Science & Technology*, 33(7): 1009–1014.

Mackintosh, C. E., Maldonado, J., Hongwu, J., Hoover, N., Chong, A., Ikonomou, M. G., Gobas, F. A. 2004. Distribution of phthalate esters in a marine aquatic food web: comparison to polychlorinated biphenyls. *Environmental Science & Technology*, 38(7): 2011–2020.

Markarian, J. 2004. Advances in PVC heat and light stabilization. *Plastics, Additives and Compounding*, 6(5): 46–49.

Marturano, V., Cerruti, P., Ambrogi, V. 2016. Polymer additives. *Physical Sciences Reviews*, 2(6): 1–20.

Massos, A., Turner, A. 2017. Cadmium, lead and bromine in beached microplastics. *Environmental Pollution*, 227: 139–145.

Menéndez-Pedriza, A., Jaumot, J. 2020. Interaction of environmental pollutants with microplastics: a critical review of sorption factors, bioaccumulation and ecotoxicological effects. *Toxics* 8(2): 40.

Mizukawa, K., Takada, H., Takeuchi, I., Ikemoto, T., Omori, K., Tsuchiya, K. 2009. Bioconcentration and biomagnification of polybrominated diphenyl ethers (PBDEs) through lower-trophic-level coastal marine food web. *Marine Pollution Bulletin*, 58(8): 1217–1224.

Moon, H. B., Choi, M., Choi, H. G., Ok, G., Kannan, K. 2009. Historical trends of PCDDs, PCDFs, dioxin-like PCBs and nonylphenols in dated sediment cores from a semi-enclosed bay in Korea: tracking the sources. *Chemosphere*, 75(5): 565–571.

Morin, A. 2003. *Distribution of phthalate esters in a marine mammal food chain from Canada's eastern artic* (Master of Resource Management). Simon Fraser University.

Nakata, H., Shinohara, R., Murata, S., Watanabe, M. 2010. Detection of benzotriazole UV stabilizers in the blubber of marine mammals by gas chromatography-high resolution mass spectrometry (GC-HRMS). *Journal of Environmental Monitoring*, 12(11): 2088–2092.

Net, S., Sempere, R., Delmont, A., Paluselli, A., Ouddane, B. 2015. Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. *Environmental Science & Technology*, 49(7): 4019–4035.

Oehlmann, J., Schulte-Oehlmann, U., Kloas, W., Jagnytsch, O., Lutz, I., Kusk, K. O., Wollenberger, L., Santos, E. M., Paull, G. C., Van Look, K. J., Tyler, C. R. 2009. A critical analysis of the biological impacts of plasticizers on wildlife. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526): 2047–2062.

Oros, D. R., David, N. 2002. *Identification and evaluation of unidentified organic contaminants in the San Franciso estuary*. RMP Technical Report: SFEI Contribution 45. Oakland, CA, San Francisco Estuary Institute.

Otton, S. V., Sura, S., Blair, J., Ikonomou, M. G., Gobas, F. A. 2008. Biodegradation of mono-alkyl phthalate esters in natural sediments. *Chemosphere*, 71(11): 2011–2016.

Paluselli, A., Aminot, Y., Galgani, F., Net, S., Sempere, R. 2017. Occurrence of phthalate acid esters (PAEs) in the northwestern Mediterranean Sea and the Rhone River. *Progress in Oceanography*, 163: 221–231.

Paluselli, A., Fauvelle, V., Galgani, F., Sempere, R. 2019. Phthalate release from plastic fragments and degradation in seawater. *Environmental Science & Technology*, 53(1): 166–175.

Paluselli, A., Kim, S. K. 2020. Horizontal and vertical distribution of phthalates acid ester (PAEs) in seawater and sediment of East China Sea and Korean South Sea: traces of plastic debris? *Marine Pollution Bulletin*, 151: 110831.

Peng, X., Wang, Z., Mai, B., Chen, F., Chen, S., Tan, J., Yu, Y., Tang, C., Li, K., Zhang, G., Yang, C. 2007. Temporal trends of nonylphenol and bisphenol A contamination in the Pearl River Estuary and the adjacent South China Sea recorded by dated sedimentary cores. *Science and the Total Environment*, 384(1–3): 393–400.

Peng, X., Fan, Y., Jin, J., Xiong, S., Liu, J., Tang, C. 2017. Bioaccumulation and biomagnification of ultraviolet absorbents in marine wildlife of the Pearl River Estuarine, South China Sea. *Environmental Pollution*, 225: 55–65.

Pereao, O., Opeolu, B., Fatoki, O. 2020. Microplastics in aquatic environment: characterization, ecotoxicological effect, implications for ecosystems and developments in South Africa. *Environmental Science and Pollution Research International*, 27(18): 22271–22291.

Pérez-Albaladejo, E., Solé, M., Porte, C. 2020. Plastics and plastic additives as inducers of oxidative stress. *Current Opinion in Toxicology* 20–21: 69–76.

Prieto, A., Zuloaga, O., Usobiaga, A., Etxebarria, N., Fernandez, L. A. 2007. Development of a stir bar sorptive extraction and thermal desorption-gas chromatography-mass spectrometry method for the simultaneous determination of several persistent organic pollutants in water samples. *Journal of Chromatography A*, 1174(1–2): 40–49.

Provencher, J. F., Avery-Gomm, S., Braune, B. M., Letcher, R. J., Dey, C. J., Mallory, M. L. 2020. Are phthalate ester contaminants in northern fulmar preen oil higher in birds that have ingested more plastic? *Marine Pollution Bulletin*, 150: 110679.

Prunier, J., Maurice, L., Perez, E., Gigault, J., Pierson Wickmann, A. C., Davranche, M., Halle, A. T., 2019. Trace metals in polyethylene debris from the North Atlantic subtropical gyre. *Environmental Pollution*, 245: 371–379.

Rahman, F., Katherine, H. L., Scrimshaw, M. D., Lester, J. N. 2001. Polybrominated diphenyl ether (PBDE) flame retardants. *Science of the Total Environment*, 275(1–3): 1–17.

Ramos-Devalle, L., Gilbert, M. 1990. PVC/plasticizer compatibility: evaluation and its relation to processing. *Journal of Vinyl and Additive Technology*, 12: 222–225.

Rani, M., Shim, W. J., Han, G. M., Jang, M., Song, Y. K., Hong, S. H. 2017a. Benzotriazole-type ultraviolet stabilizers and antioxidants in plastic marine debris and their new products. *Science of the Total Environment*, 579: 745–754.

Rani, M., Shim, W. J., Jang, M., Han, G. M., Hong, S. H. 2017b. Releasing of hexabromocyclododecanes from expanded polystyrenes in seawater-field and laboratory experiments. *Chemosphere*, 185: 798–805.

Rastgar, S., Movahedinia, A., Salamat, N., Salati, A. P. Zabihi, E. 2019. Interruption of immune responses in primary macrophages exposed to nonylphenol provides insights into the role of ER and NF-KB in immunotoxicity of Persian sturgeon. *Fish and Shellfish Immunology*, 86: 125–134.

Reimann, C., Birke, M., Filzmoser, P. 2012. Temperature-dependent leaching of chemical elements from mineral water bottle materials. *Applied Geochemistry*, 27(8): 1492–1498.

Rian, M. B., Vike-Jonas, K., Gonzalez, S. V., Ciesielski, T. M., Venkatraman, V., Lindstrom, U., Jenssen, B. M., Asimakopoulos, A. G. 2020. Phthalate metabolites in harbor porpoises (*Phocoena phocoena*) from Norwegian coastal waters. *Environment International*, 137: 105525.

Rochman, C. M., Hoh, E., Kurobe, T., the, S. J. 2013. Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress. *Scientific Reports*, 3: 3263.

Sala, B., Gimenez, J., de Stephanis, R., Barcelo, D., Eljarrat, E. 2019. First determination of high levels of organophosphorus flame retardants and plasticizers in dolphins from Southern European waters. *Environmental Research*, 172: 289–295.

Samani, P., van der Meer, Y. 2020. Life cycle assessment (LCA) studies on flame retardants: a systematic review. *Journal of Cleaner Production*, 274: 123259.

Sanchez-Avila, J., Tauler, R., Lacorte, S. 2012. Organic micropollutants in coastal waters from NW Mediterranean Sea: sources distribution and potential risk. *Environment International*, 46: 50–62.

Sastri, V. R. 2013. *Plastics in Medical Devices: Properties, Requirements, and Applications*. Chadds Ford, PA, William Andrew Publishing.

Savoca, D., Arculeo, M., Barreca, S., Buscemi, S., Caracappa, S., Gentile, A., Persichetti, M. F., Pace, A. 2018. Chasing phthalates in tissues of marine turtles from the Mediterranean Sea. *Marine Pollution Bulletin*, 127: 165–169.

Servos, M. R. 1999. Review of the aquatic toxicity, estrogenic responses and bioaccumulation of alkylphenols and alkylphenol polyethoxylates. *Water Quality Research Journal of Canada*, 34(1): 123–177.

Sharkey, M., Harrad, S., Abdallah, M. A., Drage, D. S., Berresheim, H. 2020. Phasing-out of legacy brominated flame retardants: The UNEP Stockholm Convention and other legislative action worldwide. *Environment International*, 144: 106041.

Sharma, V. K. 2009. Aggregation and toxicity of titanium dioxide nanoparticles in aquatic environment – a review. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 44(14): 1485–1495.

Staples, C. A., Adams, W. J., Parkerton, T. F., Gorsuch, J. W., Biddinger, G. R., Reinert, K. H. 1997. Aquatic toxicity of eighteen phthalate esters. *Environmental Toxicology and Chemistry*, 16(5): 875–891.

Sun, B., Hu, Y., Cheng, H.,Tao, S. 2019. Releases of brominated flame retardants (BFRs) from microplastics in aqueous medium: kinetics and molecular-size dependence of diffusion. *Water Research*, 151: 215–225.

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M. A. Watanuki, Y. 2013. Accumulation of plastic-derived chemicals in tissues of seabirds ingesting marine plastics. *Marine Pollution Bulletin*, 69(1–2): 219–222.

Tanaka, K., van Franeker, J. A., Deguchi, T., Takada, H. 2019. Piece-by-piece analysis of additives and manufacturing byproducts in plastics ingested by seabirds: Implication for risk of exposure to seabirds. *Marine Pollution Bulletin*, 145: 36–41.

Tanaka, K., Takada, H., Ikenaka, Y., Nakayama, S. M. M., Ishizuka, M. 2020. Occurrence and concentrations of chemical additives in plastic fragments on a beach on the island of Kauai, *Hawaii. Marine Pollution Bulletin*, 150: 110732.

Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., Sutton, D. J. (Eds.) 2012. Heavy metal toxicity and the environment. In: Luch, A. (Ed.), *Molecular, Clinical and Environmental Toxicology*. *Experientia Supplementum*. Basel, Switzerland, Springer Basel, pp.133–164.

ter Halle, A., Ladirat, L., Martignac, M., Mingotaud, A. F., Boyron, O., Perez, E. 2017. To what extent are microplastics from the open ocean weathered? *Environmental Pollution*, 227: 167–174.

Teuten, E. L., Saquing, J. M., Knappe, D. R., Barlaz, M. A., Jonsson, S., Bjorn, A., Rowland, S. J., Thompson, R. C., Galloway, T. S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P. H., Tana, T. S., Prudente, M., Boonyatumanond, R., Zakaria, M. P., Akkhavong, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H. 2009. Transport and release of chemicals from plastics to the environment and to wildlife. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526): 2027–2045.

Tian, Z., Kim, S. K., Hyun, J. H. 2020. Environmental distribution of styrene oligomers (SOs) Coupled with their source characteristics: tracing the origin of SOs in the environment. *Journal of Hazardous Material*, 398: 122968.

Tomy, G. T., Pleskach, K., Oswald, T., Halldorson, T., Helm, P. A., Macinnis, G., Marvin, C. H. 2008. Enantioselective bioaccumulation of hexabromocyclododecane and congener-specific accumulation of brominated diphenyl ethers in an Eastern Canadian Artic marine food web. *Environmental Science & Technology*, 42(10): 3634–3639.

Troitzsch, J., Antonatus, E. 2021. 3 – Flame retardants and flame-retarded plastics. In: Troitzsch, J., Antonatus, E. (Eds.), *Plastics Flammability Handbook (Fourth Edition)*. Liberty Twp, OH: Hanser Publications, 53–128.

Turan, N. B., Erkan, H. S., Engin, G. O., Bilgili, M. S. 2019. Nanoparticles in the aquatic environment: usage, properties, transformation and toxicity – a review. *Process Safety and Environmental Protection* 130: 238–249.

Turner, A., Solman, K. R. 2016. Analysis of the elemental composition of marine litter by field-portable-XRF. *Talanta*, 159: 262–271.

UNEP. 2009. *Abandoned, lost or otherwise discarded fishing gear*. Rome, UNEP.

UNEP. 2015. *Drafted guidance for the inventory, identification and substitution of hexabromocyclododecane (HBCD)*. Châtelaine, Switzerland: Stockholm Convention. http://chm.pops.int/Implementation/NIPs/Guidance/GuidanceforHBCD/tabid/5332/Default.aspx (accessed 29 November 2021).

USFDA. 2019. *Indirect additives used in food contact substances: pentaerythrityl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)*. https://www.cfsanappsexternal.fda.gov/scripts/fdcc/?set=IndirectAdditives (accessed February 27, 2021).

Wang, J., Peng, J., Tan, Z., Gao, Y., Zhan, Z., Chen, Q., Cai, L. 2017. Microplastics in the surface sediments from the Beijiang River littoral zone: composition, abundance, surface textures and interaction with heavy metals. *Chemosphere*, 171: 248–258.

Wang, X., Hou, X., Zhou, Q., Liao, C., Jiang, G. 2018. Synthetic phenolic antioxidants and their metabolites in sediments from the coastal area of Northern China: spatial and vertical distributions. *Environmental Science & Technology*, 52(23): 13690–13697.

Wang, Y., Zhu, H., Kannan, K. 2019. A review of biomonitoring of phthalate exposures. *Toxics* 7(2): 21.

Weaver, J. A., Beverly, B. E. J., Keshava, N., Mudipalli, A., Arzuaga, X., Cai, C., Hotchkiss, A. K., Makris, S. L., Yost, E. E. 2020. Hazards of diethyl phthalate (DEP) exposure: a systematic review of animal toxicology studies. *Environment International*, 14: 105848.

Westerhoff, P., Prapaipong, P., Shock, E., Hillaireau, A. 2008. Antimony leaching from polyethylene terephthalate (PET) plastic used for bottled drinking water. *Water Research*, 42(3): 551–556.

Xie, Z., Ebinghaus, R., Temme, C., Caba, A., Ruck, W. 2005. Atmospheric concentrations and air–sea exchanges of phthalates in the North Sea (German Bight). *Atmospheric Environment*, 39(18): 3209–3219.

Xie, Z., Ebinghaus, R., Temme, C., Lohmann, R., Caba, A., Ruck W. 2007. Occurrence and air-sea exchange of phthalates in the Artic. *Environmental Science & Technology*, 41: 4555–4560.

Yagoubi, N., Baillet, A., Mur, C., Baylocq-Ferrier, D. 1993. Determination of phenolic antioxidants in pharmaceutical formulations by liquid chromatography and migration study on HDPE packages. *Chromatographia*, 35(7/8): 455–458.

Yan, H., Ye, C., Yin, C. 1995. Kinetics of phthalate ester biodegradation by *Chlorella pyrenodosa*. *Environmental Toxicology and Chemistry*, 14(6): 931–938.

Yang, C. Z., Yaniger, S. I., Jordan, V. C., Klein, D. J., Bittner, G. D., 2011. Most plastic products release estrogenic chemicals: a potential health problem that can be solved. *Environmental Health Perspectives*, 119(7): 989–996.

Yin, L., Chen, B, Xia, B., Shi, X., Qu, K. 2018. Polystyrene microplastics alter the behavior, energy reserve and nutritional composition of marine jacopever (*Sebastes schlegelii*). *Journal of Hazardous Material*, 360: 97–105.

Yost, E. E., Euling, S. Y., Weaver, J. A., Beverly, B. E. J., Keshava, N., Mudipalli, A., Arzuaga, X., Blessinger, T., Dishaw, L., Hotchkiss, A., Makris, S. L. 2019. Hazards of diisobutyl phthalate (DIBP) exposure: a systematic review of animal toxicology studies. *Environment International*, 125: 579–594.

Yu, L., Han, Z., Liu, C. 2015. A review on the effects of PBDEs on thyroid and reproduction systems in fish. *General and Comparative Endocrinology*, 219: 64–73.

Zaki, G., Shoeib, T. 2018. Concentrations of several phthalates contaminants in Egyptian bottled water: effects of storage conditions and estimate of human exposure. *Science of the Total Environment*, 618: 142–150.

Zarfl, C., Matthies, M. 2010. Are marine plastic particles transport vectors for organic pollutants to the Arctic? *Marine Pollution Bulletin*, 60(10): 1810–1814.

Zero Breast Cancer. 2014. Phthalates: The Everywhere Chemical. Retrieved October 8 2020, from https://www.niehs.nih.gov/research/supported/assets/docs/j_q/phthalates_the_everywhere_chemical_handout_508.pdf.

ZBC. 2018. *Phthalates: The Everywhere Chemical*. San Rafael, CA, Z. B. Cancer.

Zhang, Y., Ruan, Y., Sun, H., Zhao, L., Gan, Z. 2013. Hexabromocyclododecanes in surface sediments and a sediment core from rivers and harbor in the northern Chinese city of Tianjin. *Chemosphere*, 90(5): 1610–1616.

Zhang, H., Zhou, Q., Xie, Z., Zhou, Y., Tu, C., Fu, C., Mi, W., Ebinghaus, R., Christie, P., Luo, Y. 2018a. Occurrences of organophosphorus esters and phthalates in the microplastics from the coastal beaches in north China. *Science of the Total Environment*, 616–617: 1505–1512.

Zhang, Z. M., Zhang, H. H., Zou, Y. W. Yang, G. P. 2018b. Distribution and ecotoxicological state of phthalate esters in the sea-surface microlayer, seawater and sediment of the Bohai Sea and the Yellow Sea. *Environmental Pollution*, 240: 235–247.

Zhang, Y., Lu, Y., Wang, P., Shi, Y. 2018c. Biomagnification of hexabromocyclododecane (HBCD) in a coastal ecosystem near a large producer in China: human exposure implication through food web transfer. *Science of the Total Environment*, 624: 1213–1220.

Zhang, Q., Song, J., Li, X., Peng, Q., Yuan, H., Li, N., Duan, L., Ma, J. 2019. Concentrations and distribution of phthalate esters in the seamount area of the Tropical Western Pacific Ocean. *Marine Pollution Bulletin*, 140: 107–115.

Zweifel, H., Maier, R. D., Schiller, M., Amos, S. E. 2001. *Plastics Additives Handbook*. Cincinnati, OH, Hanser Gardner.

3

Deconstructing the Plastic Soup

Methods to Identify and Quantify Marine Plastic Pollution Sources

Anna Schwarz[1] *and Tim van Emmerik*[2]

[1] *Netherlands Organisation for Applied Scientific Research (TNO), Utrecht, The Netherlands*
[2] *Hydrology and Quantitative Water Management Group, Wageningen University, Wageningen, The Netherlands*

3.1 Introduction

Pollution of plastics to the environment is uninhibitedly increasing, from densely populated city centers to remote oceans (Lebreton et al. 2018; van Emmerik et al. 2019b). Causes for this increase are a combination of a growing world population, rising plastic consumptions, and poor waste management (Lebreton and Andrady 2019; Borrelle et al. 2020; Lau et al. 2020). It becomes increasingly apparent that plastic pollution in the environment has damaging consequences to species, ecosystems, and human health (Gall and Thompson 2015; van Emmerik and Schwarz 2020). Since the ubiquity of environmental plastic pollution and its negative effects have become more evident, the common goal of NGOs, government, science, and industries is to solve the environmental plastic pollution problem. Examples of initiatives include the European Union implementing the single-use plastics ban (SUPD; Elliot et al. 2020), Indonesia pledging to reduce marine plastic debris with 70% by 2025 (Nurhati and Cordova 2020), and the industry-led alliance to end plastic waste (Peake 2020).

For science, environmental plastic pollution is a relatively new field of research. Early scientific work was mainly focused on observational data of both micro (<5 cm) and macroplastics (>5 cm) in aquatic environments, to increase awareness of this new and upcoming environmental threat (Carpenter et al. 1972; Ryan and Watkins 1988; Yates and Simmons 1999; Moore et al. 2001). Since then, studies related to plastic pollution have increased in both number and diversity, displaying the complexity of the topic (Blettler et al. 2018; Aetoulaki et al. 2020). New scientific goals are included on determining the magnitude and significance of plastic pollution sources, but also on plastic ‘behavior’ in the environment, including interactions with ecosystems, degradation, transport, and removal. With the growing role of science in tackling the plastic pollution problem, new methodologies and approaches are applied to find new insights, hypotheses, and conclusions on the sources of plastic pollution. These include methods from other scientific fields (Kawecki and Nowack 2019; Meijer et al. 2021). However, a sprawl in terms of methodology can result in scientific hurdles. With these alternative methods and approaches, also the results, data, and conclusions are becoming more diverse, scattered, and often incompatible with other studies in the plastic pollution field. Such incompatibility results in different perspectives on where and how to tackle plastic pollution sources, creating confusion and ambiguity with stakeholders who have to develop

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

best practice solutions for plastic pollution reduction (Borrelle et al. 2020; Lau et al. 2020). Additionally, when results and conclusions are extracted from studies without their methodological context, this can result in misinterpretations of scientific work. These include conclusions that are outdated or have been revised by other studies but can still be found in popular works. One of these is the contribution of marine-based sources to plastic pollution in oceans. This is estimated at 6.4 million tonnes per year by the US academy of sciences in 1997, but this value has not been revised since. Furthermore, another discrepancy is created by the contribution from rivers, where more recent studies have shown that 80% of plastic pollution originates from more than 1000 rivers (Meijer et al. 2021). This is opposed to earlier studies that mention an 80% emission from 10 major rivers (Schmidt et al. 2017). Another example is the so-called Teflon theory, which assumes that all plastics leaked into the riverine environment flow directly into the ocean, and contribute to the garbage patches. Literature and observations show that this is not the case (Schwarz et al. 2019; Olivelli et al. 2020). In short, both the increase of methodologies to collect plastic pollution data, values and conclusions, and extraction from their original context and methodology can obstruct a clear perspective on solving the plastic pollution problem.

A clear and uniform scientific perspective on tackling this problem is essential for the role of science to deliver efficient and useful approaches for plastic pollution reduction measures. By supplying knowledge on methodological approaches for plastic pollution source studies in a structured manner, results and conclusions can be better understood and context can be given back to the scientific background. Additionally, when presented in a structured manner, a valuable perspective can be given to a future vision for the methodological future of determining sources of plastic pollution.

In the following chapter, different methodologies and approaches for scientific studies on ocean plastic pollution are identified and discussed. We present three general methodologies with a focus on the scientific background and the contributions to plastic pollution research. Furthermore, the main methodological struggles and open questions are identified, including several solution pathways, remaining knowledge gaps, and the potential synergies stated with other plastic pollution source methods. The chapters finish with an outlook and recommendations for future research. Subsequently, we present three strategies to stimulate synergies between the three determined methodologies.

3.2 Methods for Determining Plastic Pollution Sources

Besides effective clean-up operations, the main mechanism to reduce plastic pollution in the environment is to prevent plastic emissions at its source. However, determining these sources is complex. A main factor is the high diversity in potential sources, as plastics are used in all aspects and sectors of human society (Thompson 2006). However, not all sectors contribute in the same extent to environmental plastic pollution and ecosystems are not equally affected (Schwarz et al. 2019). Additionally, plastic items have the tendency to be transported in the environment, potentially over long distances. This is the result of their lightweight characteristics (Lavers et al. 2019; Dunlop et al. 2020). Transport through the environment occurs through natural processes, including water flow (river or oceanic currents), wind, and slopes (Yadav et al. 2020). It is often hypothesized that plastics transport may be driven by similar processes as natural material transport, where microplastics behave as suspended particles and low-density plastics as woody debris (Liro et al. 2020). This results in plastic pollution observed in environments far from their presumed emission sources, such as observed in the subtropical accumulation zones (Maximenko et al. 2012; Cózar et al. 2014; Eriksen et al. 2014). It is widely assumed that observed plastic pollution in these remote oceans originated from areas with high human activities, such as coastal areas and rivers (Jambeck et al. 2015; Schmidt et al. 2017). Hence, the emission source and fate location of plastic pollution can differ considerably from each other because of environmental transport. Interestingly, available estimates on plastic pollution emissions to the environment are orders of magnitude higher than that observed afloat in oceans (Eriksen et al. 2014; Table 3.1). Hence, floating ocean plastics are only a fraction of the environmental plastic mass budget, with plastics are accumulating in other environmental sinks, such as oceanic beaches and sediments,

Table 3.1 (A) Emission rates and quantities of plastic to the environment and (B) estimates of quantities floating plastic pollution. The studies are selected based on size of the study (global level). Material flows to the environment are still only assessed on local scale and included as well. The studies are sorted from lowest estimates to highest estimates

Emission type	Average quantity plastic pollution	High and low estimate	Study
(A) Material flows (losses) to environment	628.1 g/capita/year (Switzerland)	±160 g/cap/year	Kawecki and Nowack (2019)
(A) Material flows (losses) to environment	0.75 million metric tons/year from China to ocean	0.65–0.87 million metric tons/year from China to ocean	Bai et al. (2020)
(A) Plastic from littering and mismanaged waste, transported from river to ocean	1.78 million metric tons enters the ocean from rivers/year	1.15–2.41 million tonnes/year	Lebreton et al. (2017)
(A) Plastic from littering and mismanaged waste, transported from river to ocean	1.8 million metric tons enters the ocean from rivers/year	0.8–2.7 million metric tons per year	Meijer et al. (2021)
(A) Plastic from littering and mismanaged waste, transported from river to ocean	2.2 million metric tons enters the ocean from rivers/year	0.41–4 million metric tons/year	Schmidt et al. (2017)
(A) Plastic transport from land to ocean during floods	1.8 million metric tons per year (accounting for existing flood defenses)	0.8–9.6 million metric tons per year between the non-flooded and 500-year return-period flood	Roebroek et al. (2021)
(A) Plastics from littering and mismanaged waste, transported from land to ocean	8.8 million metric tons entering the ocean per year	4.8–12.7 million MT/year	Jambeck et al. (2015)
(A) Plastic from littering and mismanaged waste, emitted to aquatic environments	21 million metric tons (average) in 2016 (~11% of generated waste)	19–23 million metric tons	Borelle et al. (2020)
(B) Floating plastic debris in the Mediterranean ocean	295 metric tons (average) remains afloat in the Mediterranean ocean in 2015 (~11% of input from land).	170–420 metric tons	Kaandorp et al. (2020)
(B) Floating plastic debris in the ocean	14 400 metric tons afloat in oceans ranging from 0.2 mm to 100 mm (2010–2011)	6600–35 200 metric tons	Cózar et al. (2014)
(B) Floating plastic debris in the ocean	165 000 metric tons (average) in 2014 for small plastics (<200 mm)	93 000–236 000 metric tons	Van Sebille et al. (2015)
(B) Floating plastic debris in the ocean	269 000 metric tons which are 0.33–200 mm in size		Eriksen et al. (2014)

but also within river systems, estuaries, or terrestrial environments (Woodall et al. 2014; Egger et al. 2020; Kaandorp et al. 2020; Olivelli et al. 2020; van Emmerik et al. 2020a, 2020b). Hence, the different plastics pollution sinks in the environment and their extent are still unknown due to the imbalance of the environmental plastic mass budget. Therefore the identification of all plastic pollution sources is still far away as well.

In order to effectively reduce plastic pollution, including remote ecosystems like oceans, any method to identify where the item could be used, potential transportation mechanisms, and/or identification of the material are important tools to identify plastic pollution sources. In the last decades, multiple studies try to identify and quantify sources of plastic pollution. We summarized and categorized the available methods in the published studies over the last decade. From this desk study, three general methodological approaches were identified to obtain knowledge on sources of environmental plastic pollution. The first two are model-based approaches and the third an observation-based approach:

- Assessing **plastic emissions** from source to the environment, based on production and use data of plastics, in combination with local waste management data, littering rates, population, and in some cases hydrometeorological data. This method focuses on the source of the problem, and from source, the potential emissions of plastic pollution to the environment can be modeled. Well-known studies that use this method include Jambeck et al. (2015), Schmidt et al. (2017), Lebreton et al. (2017), Kawecki and Nowack (2019), and Lebreton and Andrady (2020).
- Tracking plastics in the environment through **transport models**. This method identifies plastic pollution ‘behavior’ in the environment and the transport pathways through the environment. These pathways are used to determine both accumulation zones of floating debris in rivers and oceans, but can also work inversely to determine potential emission locations. Studies that work with these models are studies observing riverine transport or accumulation in oceanic regions, including gyres: van Emmerik et al. (2018), Lebreton et al. (2018), van Sebille et al. (2012), van der Mheen et al. (2020), and Kaandorp et al. (2020).
- Assessing plastic pollution through **pollution identification.** Through determining and identifying specific characteristics of plastic items in the environment, it can be estimated how, where and when the plastic was released to the environment. A plastic item can give various clues on this which can be studied and observed. This is often done with consumer articles or packaging items, which are well recognized by a large audience. Studies that actively use item identification to track down emission sources are Lebreton et al. (2018), OSPAR Commission (2010), van Emmerik et al. (2020a), and Strietman et al. (2020).

Furthermore, studies using either one of these three methods can also be divided based on the spatial scale they are applied on. Roughly, they can be divided into global assessments and local assessments. Global assessments try to give a global overview on the plastic pollution problem, where at least multiple countries or river systems are addressed simultaneously in order to shed light on the severity of the total problem. Often, assumptions are made to overcome unknown parameters, or generalizations are made for effects that vary strongly. Local plastic studies focus on one region up to one country, and tackle unknowns in these areas which result in a high level of detail on plastic pollution in a specific area.

The three methodologies and spatial scales are displayed in Figure 3.1, where exemplary studies are categorized depending on their methodological approach. There are only several studies available that combined methodologies to obtain more insight in plastic pollution sources. In the following chapters, the three methodologies are explained more in depth, with additional attention to open questions and future research suggestions. Furthermore, potential connections to the other two methodologies are explored.

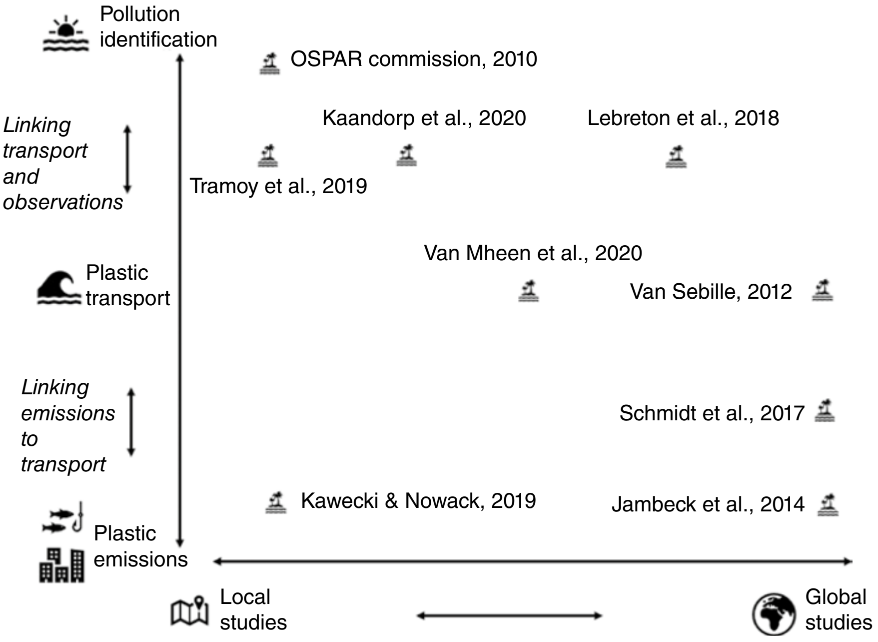


Figure 3.1 Schematic overview of three methodological approaches to identify plastic pollution sources, ranked from global to local scale. Studies that are exemplary for the overall method are visualized along the axes. Studies that combine methodologies are placed in between the categories.

3.2.1 Approach 1: Plastic Emission Rates

3.2.1.1 Methodology Description

The first method determined in this study is the assessment of plastic pollution to the environment directly from the emission source. When the plastic pollution sources are identified, a quantification in terms of volume or mass can be determined, which can be considered the 'plastic emission rate' from source to environment. Two main approaches can be identified to determine a quantification: Material flow analysis, and using littering and mismanaged waste values.

Material flow analysis (MFA) is an analytical method to track material and substances throughout the economic system. This methodology is used widely in the study of industrial ecology. A plastic MFA can be described as the flow from plastics through different 'nodes' within the system; from raw material to polymer production, to manufacturing, to use sector, and to waste or recycling afterward (Figure 3.2). Several studies have executed an MFA for plastics (Kawecki et al. 2018; Bai et al. 2020; Deshphande et al. 2020). When sufficient data are available, an MFA can be used to estimate losses of plastics to the environment (Kawecki and Nowack 2019; Bai et al. 2020; Deshpande et al. 2020). This can be extracted when flows from one node to another do match in terms of quantity. In various studies, this is done on a country level. For example, Kawecki and Nowack (2019) determined plastic pollution to the environment on a polymer level in Switzerland through detailed data on littering of plastic flows. Bai et al. (2020) assessed plastic pollution from China on a temporal scale. These studies demonstrate that a high level of detail and data is required to use MFA for plastic pollution data, as plastic flows in the system are large, and plastic pollution quantities are dispersed and relatively small compared to the total amount of plastic in the system. The high level of detail can pose barriers for a global MFA.

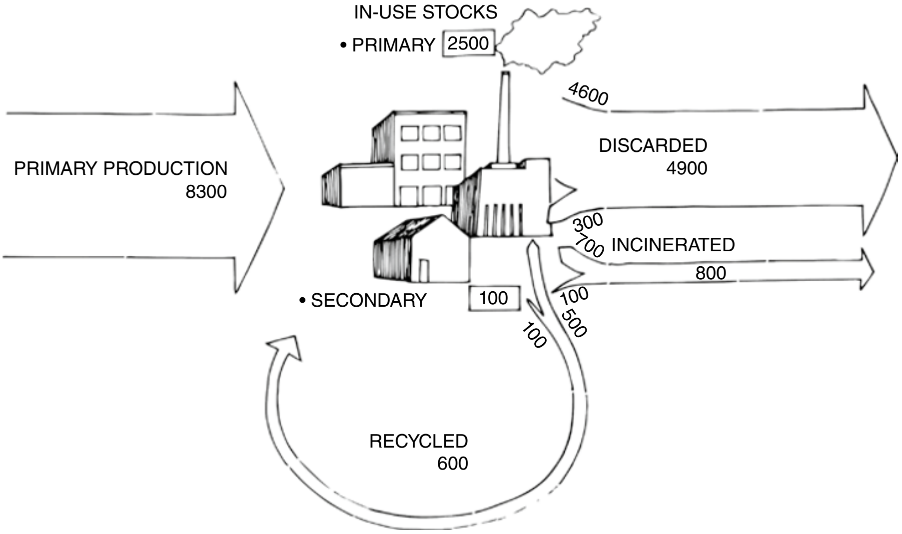


Figure 3.2 A visualization of a material flow analysis for plastics from production to use and to end-of-life, where plastic flows are illustrated by arrows and nodes by figures. *Source:* Figure adapted from Geyer et al. (2017) (Artwork: Cher van den Eng).

Plastic pollution can also be quantified through determining *littering and mismanaged waste values*. Data on mismanaged waste and littering are available on country, region or global level (Hoornweg and Bhada-Tata 2012; The Waste Atlas 2020). When combined with waste composition data, an estimate on mismanaged plastics and hence potential plastic pollution rates are available. This resembles the methodology of Jambeck et al. (2015), who assesses plastic pollution with the population living in coastal areas in combination with mismanaged waste percentages. This study was the first to use this methodology. Following this study are Lebreton et al. (2017) and Schmidt et al. (2017), who use mismanaged waste data on a country level, together with country population data, discharge, and dams to estimate plastic pollution quantities emitted to rivers. Lebreton and Andrady (2019) and Lau et al. (2020) apply this method on a global scale, using future scenarios for plastic generation and disposal. Tramoy et al. (2019) apply the method on a local scale (one catchment) and linked to plastic litter observations within the catchment.

Determining plastic emission rates results in valuable insights in the scope of the problem in terms of total production and use quantities. Furthermore, plastic pollution hotspots can be are located, either spatially (country or region), per sector or in terms of life cycle stage. So far, the plastic pollution hotspots are determined in densely populated areas in countries with a failing waste management system (Jambeck et al. 2015; Schmidt et al. 2017). Here, the end of life phase of plastics seems to contribute in high quantities to environmental plastic pollution. In countries with adequate waste management, littering during use contributes in significant quantities to plastic pollution. MFA models (Kawecki and Nowack 2019) have determined that during the use phase, on-the-go packaging and agriculture to be the main release sources in a country with adequate waste management (Switzerland). Littering rates are found to be often close to about 2% of total plastic production (Jambeck et al. 2015; Kawecki and Nowack 2019). However, persistency seems to be a significant problem when 2% of littering accumulates over the years.

3.2.1.2 Open questions and missing data

3.2.1.2.1 Determining Plastic Pollution Transport Coefficients

In global studies, mismanaged plastic waste is often used to address the littered plastics to the environment, by which all of the plastic mismanaged can potentially end up in oceans and rivers (the 'teflon theory'). However, by assessing mismanaged waste also landfilling in various forms is often included (Hoornweg and Bhada-Tata 2012). What is still unknown is plastic pollution behavior in the environment, mainly the distribution over different ecosystems (terrestrial or aquatic). Of all plastic waste mismanaged, most (macro) plastic pollution is most likely to be littered on land, hence affecting terrestrial ecosystems (Kawecki and Nowack 2019). When these ecosystems act as a sink, these plastics come with risks for terrestrial species and human health. Jambeck et al. (2015) assumed that mismanaged waste would be transported to the ocean with a ratio between 15% and 40%. However, the transport of plastics, such as from land to ocean, depends on various aspects that can instigate plastic movement. This includes topography, proximity to water, rainfall and runoff, urban drainage infrastructure, wind, clean-up efforts, and waste management (van Emmerik and Schwarz 2020). Additionally, leakage from landfills to the environment depends on the type of landfill, where in some cases leakages occur more easily than in others (Yadav et al. 2020). Furthermore, characteristics of plastics, such as shape and size, should be regarded. These mentioned sensitivities of plastic pollution to the environment are required, which can be addressed at local scales for variation, or on type of plastic flows. The missing sensitivity in plastic flows from land to river and to ocean can be a potential explanation of the large gap in estimations of plastic losses and the transport and fate patterns in the environment, as summarized in Table 3.1. A parameter that also takes into account the temporal variation, such as monsoons, high tides, or extreme events, would give valuable sensitivity but is difficult to realize, especially for studies using static MFAs.

3.2.1.2.2 Bias in Sources Due to Available Data

For industrial sectors where a lot of data on plastic usage is available, studies can use this information to assess potential losses properly. For example, data on plastics used in packaging is abundant. Plastic pollution data from industries, electronics, automotive, agriculture, and building and construction are often incomplete, even though a significant amount of plastic production, waste, and pollution are linked to these sectors (Geyer et al. 2017). Packaging receives high attention for many studies, partially due to its single-use character, lowering its value, and increasing the risk of littering. Consumer plastics such as packaging might also be overrepresented in studies with citizen science due to recognition bias (van Emmerik et al. 2020c).

Several studies observe that marine sources are the dominating source of pollution in oceans and remote beaches (Ribic et al. 2012; Jang et al. 2014; Lebreton et al. 2018). Still, it is often referred to as '80% of ocean plastic pollution comes from rivers'. This might be partially a result from scarce available data on marine-based plastic pollution. The aquaculture and fishery sector has little data available in terms of plastic production annually and which polymers are used. Hence, release and loss quantities from marine-based sources to the environment are difficult to grasp in a material flow analysis. Deshpande et al. (2020) succeeded in estimating fishery gear loss for Norway only, with a static MFA, where losses to the ocean are about 2% of total plastic in stock. Combining sector growth estimates and fishing gear lifespan data, a potential loss percentage can be obtained as well. Determining a littering or loss rate from marine-based littering is difficult as well, since scarce littering estimates are available. Several survey studies with fishers have been executed to assess the loss rates from fisheries and aquaculture sector in terms of percentages (Macfadyen et al. 2009; NOAA Marine Debris Programme 2015). These studies mainly focus on trap gear losses, gillnets, and longline fisheries, often for small-scale fisheries. Some of these studies show high loss rates, such as for longline fisheries where losses are ranging from 15% to almost 80% in small-scale artisanal fisheries (Ayaz et al. 2010; Yildiz and Karakulak 2016). Most of these gear types likely accumulate on ocean floors (Matthews and Glazer 2010). Fisheries operating on significant larger scales, using large trawls or purse seine gear, are rarely surveyed and losses from this huge sector are underrepresented. Loss data from plastics from aquaculture is also scarce, and spatial sources can be estimated through identifying aquaculture types and location from satellite imagery (Liu et al. 2020). Furthermore, country production levels can be used for rough littering estimates, as 89% of global aquaculture is located in Asia (FAO 2020). In short, losses of fishing gear in studies that are done are significant and have the most impact on marine life from all types of plastic pollution available due to entanglement (Ryan 2018). Therefore, it is valuable that MFA and littering studies extend their focus and assess the marine-based sources as well.

3.2.1.3 Future Research Suggestions

As described in the past section, studies executing the plastic emission methodology are valuable and can be very efficient methods to determine and subsequently tackle main plastic pollution sources. However, a lack of data can give a bias toward sources with available data, and might therefore give a wrong representation of the true magnitude of plastic pollution sources. Plastic pollution identification, as discussed in section 2.3, can be used to correct this bias, such as with marine-based sources. Additional effort to improve emission estimates of these sources through littering estimates or MFA, would be effective to determine the contribution of this plastic pollution source. The same is the case for calculations and models that determine plastic pollution from rivers to the ocean. It would be valuable when studies can apply assumptions for item dependent plastic transport (section 2.2) and potential transport behavior in the environment. This ‘transfer coefficient’ between ecosystems is important to determine plastic inputs from land to rivers, and from rivers to oceans. It can indicate whether plastics remain to pollute terrestrial systems, estuaries, shorelines, or sediment, and how much is buoyant and transported to the ocean. Within the transfer coefficients, effects can be concluded regarding plastic type (e.g., foils transporting easily through wind), geography (large height variations can mean more gravitational transport) or effect of biota and human population density (Yadav et al. 2020), or distance to nearest water. These plastic pollution emission rates, with the transfer coefficients, can be determined by using transport models, which are discussed in section 2.2.

3.2.2 Approach 2: Plastic Transport Models

3.2.2.1 Methodology Description

Ocean current data from oceanic drifters were used to develop the first global floating particle models in seas and oceans (Maximenko et al. 2012). Through tracking Lagrangian particles in combination with models on the wind-driven oceanic currents and Ekman pumping (the net transport of water as a result of wind-induced surface drag and Coriolis forces), the development of plastic accumulation zones in subtropical gyres was visualized, which were from then on assumed to be the major global plastic pollution sinks (Maximenko et al. 2012). These models have been elaborated with seasonal cycles and particle emissions from coastal areas (van Sebille et al. 2012). Later, this modeling approach was combined with historical observations of plastics to identify exponential growth of the accumulation zones (Lebreton et al. 2018). According to the Lagrangian particle models, plastic in the ocean and especially in the subtropical gyres are to increase exponentially with growing production, consumption, and emissions (Lebreton et al. 2018). Such transport models can be applied for inverse modeling to connect floating debris observations and transport to estimate plastic emission sources and other sinks in the environment, closing the plastic mass budget (Kaandorp et al. 2020). According to this study, only a fraction of emitted plastics to the ocean end up afloat in oceans, which was a conclusion opposing earlier plastic transportation models.

Local currents may deviate from these global, large-scale oceanic currents. For example, currents along coastlines are highly variable and affect plastic pollution transport from land-based sources to the open ocean (Liubartseva et al. 2016; van der Mheen et al. 2020). Other transport variations in ocean currents can affect plastic transport on smaller levels, such as mesoscale eddies (Brach et al.

2018). The studies above focus on the horizontal transport of floating plastic pollution in oceans. Studies on vertical transportation of plastic pollution demonstrate the important role of wind and waves, as they cause a temporary redistribution of plastics from the surface to the water column (Kulkula et al. 2012). Furthermore, other studies have elaborated on the interactions of buoyant plastics and biological growth, called biofouling, and its effect on vertical transport. Biofouling may lead to decreased degradation due to UV blocking (Gerritse et al. 2020) and function as a surface removal process (Fazey and Ryan 2016; Kooi et al. 2017). Additionally, studies have shown vertical transport of microplastics occurring through ingestion by marine life and fecal pellets (Katija et al. 2017).

For riverine macroplastics, van Calcar and van Emmerik (2019) synthesized observations from over twenty rivers, and found that plastics are often not uniformly distributed over the cross-section. Instead, plastics are often concentrated in specific sections (sides or center) of the river, depending on geometry and flow conditions. With these plastic transport models, the main sources of the plastic waste can be estimated through 'backtracking', estimating the best fitting source releases following observations in oceans and rivers through model-based transport pathways. This method is very effective to determine general sources, such as waste management from land, rivers, beaches, or oceanic sources and hence source reduction measures.

3.2.2.2 Open Questions and Missing Data

3.2.2.2.1 Integration of Transport Models

Movement and transport of plastics in the environment is complex, and as observed in local studies, numerous other factors can play an important role. The importance of the role of these local varieties, like flow velocity, estuaries, wind, eddy's, coastlines, and biological interactions, is yet unknown on a global scale. This can result in an inaccurate potential source emission estimate, such as summarized in Table 3.1. Kaandorp et al. (2020) combined the vertical transport with the horizontal models to estimate plastic pollution sinks in the Mediterranean. This resulted in a high percentage of plastic pollution that is beaching or sinking instead of remaining buoyant (~11%). Through this approach, closing the global environmental plastic mass budget is coming closer. Additionally, studies on local scale are required for calibration of the global models, where global models need to adapt upon. The importance of calibration is shown on a basin scale for plastic transport from rivers to ocean (Tramoy et al. 2019).

Except for local deviations in oceanic transport patterns, plastic particle characteristics also have to be taken into account. Plastic item characteristics play a key role in transport and fate of plastics, and dominate in whether the particles sink, beach, or are buoyant, where the latter group can potentially be transported over long distances. Not all plastic types afloat in rivers will be transported to oceans. Plastics can sink to the riverbed, beach on riverbanks, get stuck in biomass along rivers or in hydraulic structures, and in riverine vegetation (van Emmerik et al. 2019a; van Emmerik and Schwarz 2020). One of the simplest integrations into plastic transport models is polymer type, which affects product density and hence transportation potential. For example, only low-density polymers (density >1 g/cm^3) are able to remain afloat for longer periods of time (Schwarz et al. 2019). Also. degradation rates depend on polymer type (Gerritse et al. 2020). Additionally, shape (such as fiber, flexible or hard plastics) and size play a key role in transport pathways. For example, flexible plastics tend to accumulate in higher quantities in riparian vegetation or hydraulic infrastructure (Williams and Simmon 1999; Honingh et al. 2020).

At last, studies suggest that the role of rare events can cause 'super littering', where high quantities of plastic pollution are transported in a very short period of time (Maximenko et al. 2012; Eriksen et al. 2016; Roebroek et al. 2021). These events include heavy or long rainfall resulting in floods, storms, high tides, or earthquakes and tsunamis. The monitoring of these events can result in important data on transport of littered plastics but also on the significance of these potential super littering contributions.

3.2.2.3 Suggestions for Future Research

Integration of important parameters assessed for plastic transport from local scale studies to global scale studies can result in additional valuable data on transport of plastics through the environment. These insights can aid with determining potential plastic pollution sinks. Additionally, plastic particle characteristics are potentially another complicating dimension in plastic transport, which can be included in models to observe the effects on pollution source and sink determination. Besides transport within the environment, these characteristics can also aid in determining transport coefficients of plastic pollution sources to the environment, as described earlier in section 2.1.3,. Another local factor that should be included in models is flow velocity, which can result in retention of buoyant plastic pollution, for example in city areas with canals or small rivers (Tasseron et al. 2020). Subsequently, study efforts have to be used to couple river plastic emission models directly to marine transport models, including estuary effects, to calibrate both river emission data and marine transport models (Tramoy et al. 2019).

3.2.3 Approach 3: Plastic Pollution Identification

3.2.3.1 Methodology Description

Observational data of plastic pollution in the environment can be valuable in terms of quantity, where mass or number of objects are the main data points. This type of plastic pollution identification is purely quantitative and does not give additional information on where the plastic pollution came from and how it ended up there. However, this information can be extracted, as the observed plastic pollution exists of various plastic items varying in such as polymer type, shape, size, item type, and state of degradation. Identifying and characterizing these individual plastic items can provide important insights in their emission sources, pathways, potential sinks, and associated risks. Studies have observed that polymer composition in different terrestrial and aquatic ecosystems can vary considerably (Schwarz et al. 2019). Other comparative studies show that the most abundant plastic item or polymer category is different for rivers within and across countries (van Calcar and van Emmerik 2019), which in turn can be related to local consumption and waste management practices. Plastic item identification data contain crucial supplementary information to complement plastic transport and emission estimates. Quantifying the total flux of plastic from river mouths into the ocean leaves the question where and how this leaked into the environment in the first place. Plastic pollution is generally assumed to travel from land to ocean. However, plastics from the ocean can also enter an estuary during flood tide and get (temporarily) trapped in this system, which could imply marine sources (Galgani et al. 2015; Pasquini et al. 2016; Tramoy et al. 2019). Furthermore, abundance of specific items can be directly associated with risks, as this might vary per item type. As mentioned earlier, fishing gear leads to high risk of entanglement (Ryan 2018). Other plastics might be more likely to be ingested, leach potentially toxic additives, accumulate in such as mangrove forests, or blocking hydraulic infrastructure (Honingh et al. 2020). Plastic characteristics contain clues about the sources (e.g., consumers, industry, fishers) but also aid in determining transport mechanisms (e.g., wind, surface runoff, direct littering, transport through sewage). Here, we provide a brief overview of the possible item identification and characterization methods, and discuss what insights may be obtained from specific analyses. The different item characteristics are summarized and illustrated in Figure 3.3.

3.2.3.1.1 Item Category

One of the main characteristics of plastic litter is the item category, or type of item. Plastic items are identified by how they were used before littering. Various protocols are available to determine the plastic item categories during surveys and monitoring efforts, with different levels of detail (Vriend et al. 2020). The OSPAR and NOAA protocols are the most frequently used item lists of beach litter, which contain very specific categories such as “bottle”, “lid”, “fish line” and more. Similar (Bruge et al. 2018) or adapted

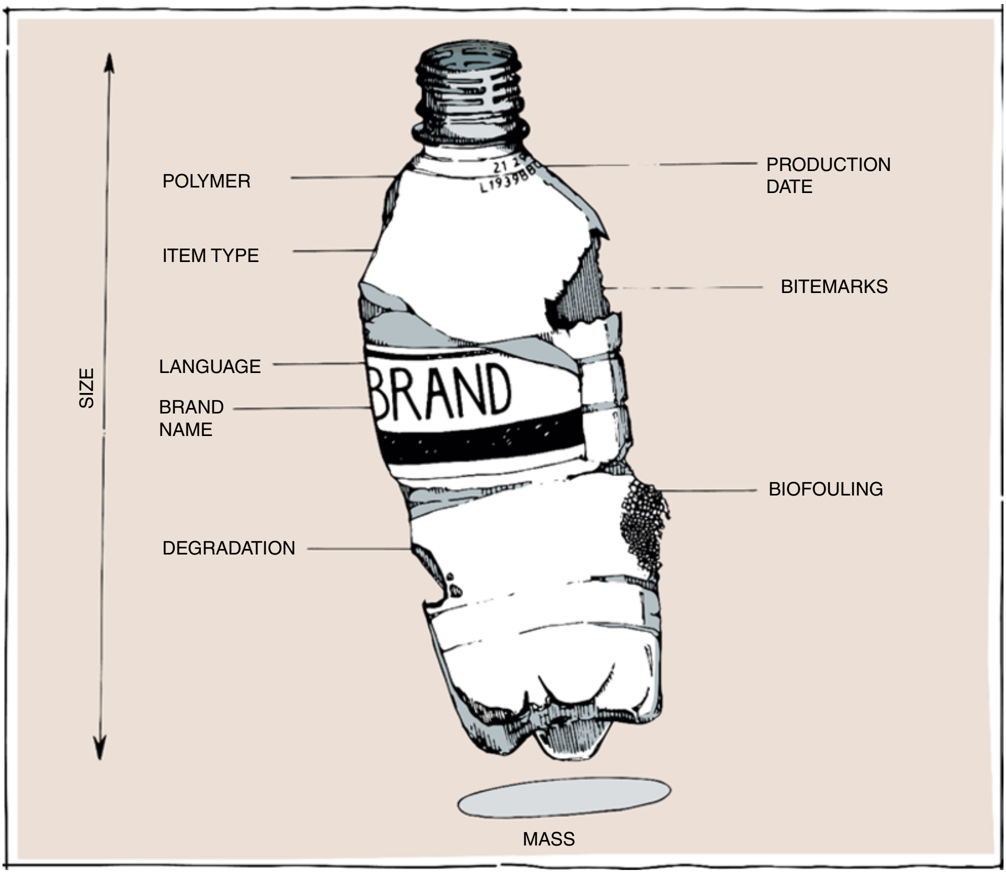


Figure 3.3 Illustration of a plastic bottle which can be identified when littered in the environment. From the item several characteristics can be registered, which are summarized around the item (Artwork: Cher van den Eng).

(González-Fernández and Hanke 2017) lists are also used to characterize riverine plastics, where over 100 item categories can be included (van Emmerik et al. 2020b). The advantage of a high level of detail is that plastic litter can directly be linked to specific sources, such as fishing activities or recreational areas. However, detailed classification methods risk being too complicated for observers, leading to misclassification (Rambonnet et al. 2019). Simpler protocols therefore only categorize plastics in general, and some use a sub-set of specific categories such as "cigarettes" (Kiessling et al. 2018).

3.2.3.1.2 Release Location

A commonly used method to classify items is by assumed release location, or source. This source classification is to be executed following item identification. A source division that is applied for oceanic plastic pollution is through identifying where the litter entered the environment, which can be either land or marine based (Galgani et al. 2015). Items related to oceanic activities, such as fishnets, are quite clearly marine based. Abandoned, Lost or Discarded fishing gear (ALDFG) is included in the source category of marine-based sources, which also includes aquaculture gear and material from maritime shipping (Galgani et al. 2015). It is more difficult to determine the emission source for other items, as they are used in both terrestrial and marine environments (e.g., crates, jugs, bottles, toothbrushes). In remote oceanic environments, where land-based plastic input is less likely, debris from marine sources tends to dominate (Faris and Hart 1994; Macfadyen et al. 2009; Ribic et al. 2012; Galgani et al. 2015; Lebreton et al. 2018).

3.2.3.1.3 Polymer Type

An important property of plastic items is the polymer type. This information can be linked to plastic production and waste handling data, per sector, as these data are mainly collected at polymer levels (Geyer et al. 2017; Plasticseurope 2019). Additionally, data on the abundance of specific polymers in a certain area can be used to determine the mass balance for different polymers, as polymer characteristics affect transport potentials (Schwarz et al. 2019). Additives, which can be supplemented with a plastic polymer to form a product, can also have a significant effect (Turner and Filella 2020). Additives can make up to 50 wt% of a plastic item beside a polymer (Hahladakis et al. 2017). Determining the polymer type is not always easy, specifically not under field conditions. Plastic items can have the polymer type printed, but when items are bio-fouled, degraded or fragmented, this may not be visible. The polymer type can sometimes be inferred from the item category (e.g., most transparent bottles are PET; PVC is mostly rigid and brittle), although in some cases lab analysis may be required, which are potentially expensive and time-consuming. The latter includes using Raman spectroscopy or Fourier transform infrared spectroscopy (FTIR) (Reisser et al. 2013; Lebreton et al. 2018). Alternative field protocols can use polymer categories to allow for fast characterization in the field. Examples include the CrowdWater citizen science app, which uses seven polymer categories, where item shape and polymer are combined (van Emmerik et al. 2018). Although the data is not highly detailed, it can provide adequate information for source identification and waste management practices.

3.2.3.1.4 Geometry (and Other Numbers)

More detailed analyses of plastic pollution include determining the item mass, shape, and size. Item mass, and mass distributions, are crucial to establish plastic mass balances, transport, and transport into the ocean (van Emmerik et al. 2018; Schwarz et al. 2019). Together with the shape and size distribution, these data give insight in the potential retention of plastics in a specific ecosystem, and the relative contribution of certain size classes. Understanding the contribution of the total mass of each size class may support prioritizing research, and clean-up activities focused on specific size classes. Additionally, geometrical data can give source insights as well. For example, foamed particles are often made of expanded polystyrene, or Styrofoam. In turn, these can be linked to aquaculture buoys, as these dominantly are made of expanded polystyrene (Jang et al. 2014). Another example includes fiber particles, which are likely to originate from textiles or fishery equipment.

3.2.3.1.5 Language

Plastic items, especially packaging related, often have written text printed or molded on the item. The language used can be linked to the location of production, consumption or leakage into the environment. For example, through language analysis, items in the North Pacific Ocean were hypothesized to be linked to the 2011 tsunami in Japan (Maximenko and Hafner 2014; NOAA Marine Debris Programme 2015; Lebreton et al. 2018). One should be careful however when interpreting results from language-based analysis. Beached plastics may have been leaked into the ocean from shipping, which could bring plastic items from anywhere to anywhere. Moreover, “foreign” items in river systems may be either leaked locally through tourists or have traveled downstream after being littered in an upstream country.

3.2.3.1.6 Brand

Some item identification protocols also register visible brands. This includes the globally used Litterati app, which is mainly used by citizens scientists to identify plastics in riverine systems. Here, brand information may help to identify specific plastic leakage locations, related to stores or restaurants. In the ocean, brand identification can contribute to source estimations, as some brands are unique to a country, hence the product can be linked to the country of origin. Again, one has to be careful as it can be leaked from a ship located at a foreign port, or in the open ocean. Brand data does not directly contribute to calculating mass balances, but may contribute to increasing awareness among producers and consumers. Targeted data collection has for example resulted in bans of specific items, change in design of food packaging, and support for the introduction of item deposit systems (Elliott et al. 2020).

3.2.3.1.7 Biofouling, Degradation, and Bitemarks

Depending on the location and matrix, items may experience biofouling. Quantifying and qualifying the bio-fouling on items can be used to determine the retention time, and the interaction with the ecosystem (Hollein et al. 2014). Similar information can be obtained by investigating the state of degradation and bitemarks on the items. Recent research showed the differences in degradation rates of (bio)degradable plastics in terrestrial and marine environments (Napper and Thompson 2019). UV degradation is found to be the most important degradation mechanism, which is affected by the amount of sunlight available in the environment. Biofouling can affect the level of UV exposure received (Gerritse et al. 2020). Also, beaches and buoyant plastics have higher UV exposure than sediments. Hence, the rate of degradation may therefore indicate the environmental transportation of the analyzed item. Bitemarks on plastic debris can be used to determine its interaction with specific species, contributing to improved risk assessments of plastics in the environment (Eriksen et al. 2016).

3.2.3.1.8 Date Stamps

Like polymer types, a plastic item can include date stamps. These may either be production dates or dates of expiration. Although it is impossible to reconstruct an item's journey based on a single date, it does provide an estimate of the retention time in the system. In addition to explicit dates, determining the time of production may be used to better understand transport processes. In the Seine, items produced in the 1970s were found to be ubiquitous along the riverbanks, suggesting that macroplastics can be retained within river systems for nearly half a century (Tramoy et al. 2020). The same is the case for oceanic environments wherein the North Pacific Subtropical Gyre, 50 items had a date stamp: 1 in 1977, 7 in the 1980s, 17 in the 1990s, 24 in the 2000s, and 1 from 2010 (Lebreton et al. 2018).

3.2.3.2 Open Questions and Missing Data

Littered plastic items can contain clues about origin, transport through the environment, and the risks it poses on the environment. Beside oceanic beaches, in freshwater systems, terrestrial environments, open oceans, and estuarine zones there is still a lack of studies that allows for more detailed analysis, such as assessments and comparisons between sites (Pedrotti et al. 2016). Especially for oceanic environments, the labor and cost-intensive sampling options related to the vast and remote large oceanic study sampling area can pose a significant barrier for this methodology.

Especially for identification in the open ocean, additional barriers occur. Linking marine-based plastic debris to a country of origin remains challenging as open oceans are no man's land (UNCLOS 1982). Furthermore, buoyant plastic is transported through sea surface currents and therefore not retrieved where they are lost. During monitoring and observations, it could occur that the majority of the items samples contain little to no explicit clues, such as logos, language, or date stamps. This is a possible result of fragmentation and degradation occurring over time in oceanic environments. Hence, a significant number of buoyant plastics can remain without any identification (Lebreton et al. 2018).

Despite these limits, item identification and characterization demonstrates to provide crucial information to tackle the global plastic pollution challenge. Recent studies in urban water systems demonstrated the valuable link between plastic identification data and negative impacts (e.g., soft plastics increase flood risk, Honingh et al. (2020), fishing gear entangles individuals (Gall and Thompson 2015). Such data can also be used to identify plastic pollution hotspots (foam and soft plastics around the market, Tasseron et al. 2020). It is optimistic to expect that observation and monitoring efforts will all include detailed characterization of plastic litter. We emphasize that there is no perfect protocol, and optimizing monitoring strategies always includes the trade-off between available resources and the research questions to be answered (Vriend et al. 2020). For any observation and monitoring effort, it is important to ensure that the selected protocol links back to the research question. If that question can be answered by only collected quantitative data on plastic abundance, no further characterization is required. The saved resources can in turn be allocated to increasing the temporal and spatial coverage of data collection. If the research question relates to risks or identifying sources, it is absolutely necessary to characterize the sampled litter in more detail.

3.2.3.3 Suggestions for Future Research

Item identification protocols vary between studies and between ecosystems, such as beaches or sediments. Future efforts may focus on the harmonization of methods, to facilitate better transferability of data over time and space. Item identification can be a valuable addition to transport and emission estimates, given that the collected data is consistent. There are always practical reasons to use a tailor-made protocol, such as resources limitations or specific questions that need to be answered (Vriend et al. 2020). However, data collected at different levels of detail can still be compared as long as the overall method is aligned.

A promising new method is the Litter ID method (Strietman et al. 2020), which analyses litter together with stakeholders and citizens. All collected litter is jointly separated into predetermined item categories. After sorting, all items are weighed and further analyzed per category. The in-depth analysis includes an interactive approach that may result in additional anecdotal evidence about potential sources and transport pathways. For example, all found plastic bottles are generally reported as a single number by the observers. However, by joint analysis additional patterns can emerge. Stakeholders may recognize the brands, shapes and colors, pointing toward local sources. On the other hand, if items are not recognized at all, this may indicate remote sources. Future research may further expand on this method, especially in other domains, such as the terrestrial and riverine environment. Once data from land to ocean can be coupled, an improved estimate of sources, sinks and pathways can be made.

Finally, an important challenge is international collaboration. The OSPAR Commission has demonstrated the value of a consistent monitoring protocol for beach litter (OSPAR Commission 2010), which now allows the comparison of long-term data series around the North Atlantic Ocean. For rivers, the RIMMEL project made a first step to harmonize quantitative and qualitative data collection of floating macroplastic (González-Fernández and Hanke 2017). Similar efforts should be made at the global scale, and for other environmental compartments, such as rivers, estuaries, and terrestrial ecosystems.

3.3 Discussion

As described in Chapter 3.2, three methods were identified to study plastic pollution sources to the environment. Most of the studies discussed are executing one of three methods, and explain the plastic pollution problem using the selected approach. Using the three methods independently has resulted in significant knowledge gain in a short period of time. For example, because the estimates of plastic pollution from land and rivers to the ocean were orders of magnitude higher than observed in surface waters (Table 3.1), additional studies discovered new environmental plastic sinks such as the deep sea (Woodall et al. 2014). However, a fully closed environmental plastic mass budget is still to be developed and the plastic pollution problem is still to be solved. Most studies on plastic pollution, using one method only, are still individual and isolated attempts, and synergies between studies are rare. Hence, the field of plastic pollution can be visualized through the metaphor of individual islands in an ocean of plastic pollution research (Figure 3.4a). When exploring these methodologies, it is evident that the plastic pollution problem is too complex and cannot be solved using only one of the three methods. If we want to solve the environmental plastic problem, combining multiple approaches is required to determine efficient and effective reduction measures and actions. A synergy strategy is required to effectively match existing knowledge from the studies to identify open questions and, at last, solve the plastic pollution problem. To describe the various strategies to stimulate synergies, also metaphors of islands are used (Figure 3.4b–d).

3.3.1 Strategy 1 (Figure 3.4b): The Ferry Method—Input–Output Data Sharing

The first strategy is a highly feasible approach to link together existing studies using different methods. This ‘ferry’ strategy is already executed in some studies, for example, calibrating global

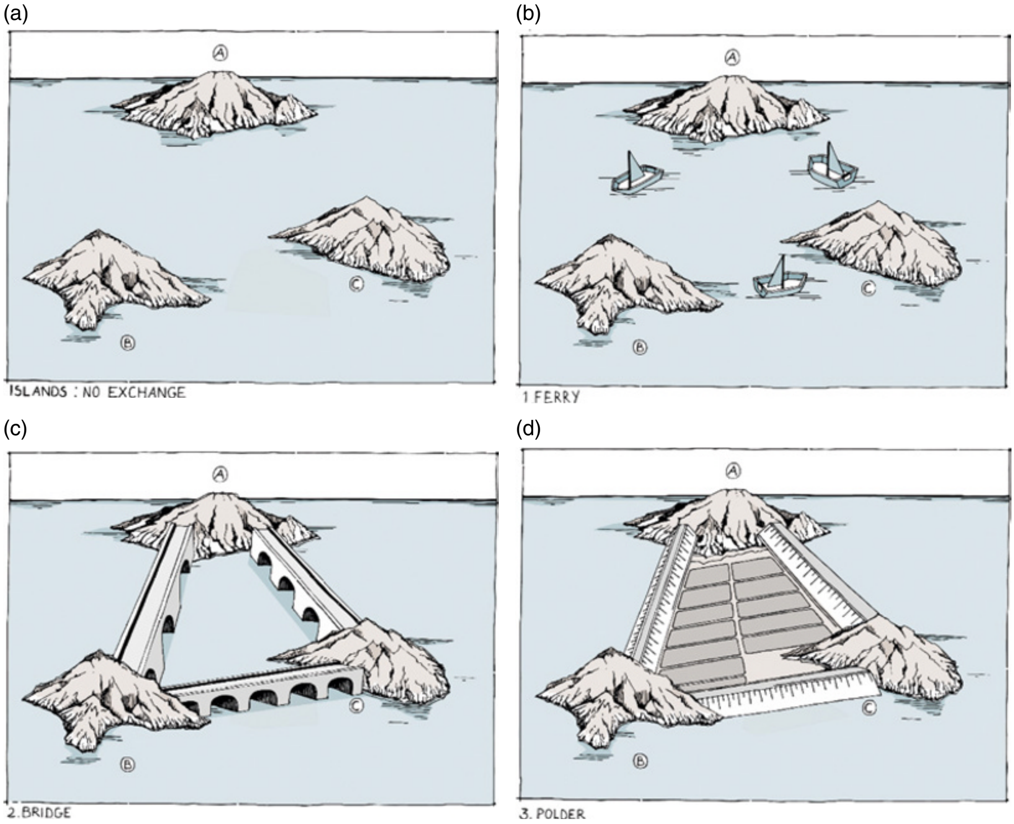


Figure 3.4 The scientific field of plastic pollution research and potential synergies, visualized through the metaphor of individual islands in an ocean of plastic pollution research. a) The situation as it is, where study methods are used individually. b) Input-output data exchange between studies, visualized by a ferry. c) Hard connections between methodologies, visualized by a bridge. d) a universal plastic litter model, where all studies are connected. Visualized by a drained landscape (Artwork: Cher van den Eng).

plastic littering studies (Jambeck et al. 2015) at one river basin (Tramoy et al. 2019). Other examples include using mismanaged plastic waste estimates (Lebreton and Andrady 2019) to model plastic mobilization through rivers (Roebroek et al. 2021). For plastic pollution studies, output from models and calculations are often open source and data sharing is possible through well-established contacts. However, using input-output data sharing can be unsuitable for integration, and often do not include feedback loops between models. Level of detail and measured parameters which can seem irrelevant in one approach can be important for another approach, and hence crucial information can be missing for input-output data sharing. Furthermore, assumptions taken in one study can deviate from another, resulting in a suboptimal result when data is shared. In short, the ferry method approach is valuable, especially for first explorations whether a match is possible between approaches, which would be required for any hard connections between methodologies.

3.3.2 Strategy 2 (Figure 3.4c): The Bridge Method—Feedback between Methodologies

As discussed in the first strategy, it is a challenge to connect data from existing methodologies due to varying assumptions, level of scale and detail or chosen parameters. Through input-output data sharing, these variations can be overcome as no feedback is given between methods. However, when connecting studies in such a way that allows for feedback between methodologies, as used in the 'bridge method', the methodologies can 'learn' from one another and improve simultaneously. One example of a study using feedback between methodologies is through inverse modeling of oceanic plastic transport, where the plastic mass budget could be closed (Kaandorp et al. 2020). Although the results and outcome of this strategy are way more valuable, feasibility is lower and effort required higher compared to input-output data sharing. Calculations and models in plastic pollution studies are often designed for the study's individual approach and purpose, making it inflexible and too specific for establishing a connection with feedback between methodologies. This challenge is to be tackled by studies designed to adapt and prepare existing models and data for use in other methods. Additional fieldwork or significant adaptations are required when it is discovered that models or sampling methods miss crucial data for a hard connection strategy. When establishing connections with feedback, also the insight in other methodologies will increase, and hopefully, missing information and different assumptions will be a problem from the past. The connected methodologies will become available and lead to new knowledge to answer the open research questions. Additionally, existing efforts and details in individual studies are not lost but are used. This is very useful for tackling the open research questions without losing important information from individual studies.

3.3.3 Strategy 3 (Figure 3.4d): The Polder Method—A Universal Plastic Pollution Model

A universal plastic pollution model might be a point on the horizon, where all individual studies are integrated in one universal model to illustrate plastic pollution on a global level without losing any valuable small scale data. However, the feasibility of the universal plastic litter model would require high effort, labor, maintenance and management. Not only feedback between all three methodologies is required for this strategy, full integration has to be in place. During integration of studies, a selection has to be executed, and details simplified, extrapolated or left out. Similar to the previous strategy, a slight variation in study design, approach or methodology might already result in problems connecting studies. For a universal model, this can result in a loss in level of detail. Furthermore, the added value of a universal plastic litter model to local scale plastic pollution problems should be defined as well. Although a universal model is the most desirable outcome in terms of closing the global plastic mass budget in the environment, the goal of such a large and complex operation might not contribute most efficiently to solving the environmental plastic pollution problems.

In short, the three strategies that are presented above require different levels of integration of studies and approaches, but some level of integration between different model-based and observation-based studies is always required. Future studies should recognize that for solving the plastic pollution problem, a smooth exchange between their study effort and existing studies should be ensured. This might require collecting additional data, inputs or exploring alternative modeling approaches. Additionally, research questions and study efforts can focus specifically on integration efforts of existing studies, also to identify potential gaps that can occur between methodologies. The strategies that are mentioned here are not silver bullets. This is presented by the trade-offs mentioned between feasibility and how useful the methodological integrations can be in the light of the open research questions. However, the strategies can also be combined, and to use the metaphors available, while some islands are connected with a ferry, others might be connected by bridges to a partially reclaimed land.

3.4 Conclusions

In this review study, different scientific methodological approaches to the plastic pollution problem are identified and reviewed. The three approaches identified are as follows: plastic emission rates, plastic transport models, and pollution identification. All three methods give important insights in the sources, sinks, and pathways of plastic pollution in the environment, including for land, rivers, and oceans. What method or approach to use strongly depends on questions to be answered by the study. As more research is done, the larger question on how to solve the global plastic pollution problem is still to be tackled. In this review study, it was found that integration of methods is required to solve the plastic pollution problem. Future efforts should focus on integration of studies and approach and provide possibilities for a smooth exchange between approaches. Three strategies for future and better collaboration between studies are presented, where neither strategy is found to be a silver bullet but rather represents a trade-off between required resources, integration, and effectiveness.

Acknowledgments

We thank Cher van den Eng for providing the artwork for Figures 3.2–3.4. We thank Eline Langeveld, Paul Vriend, Louise Schreyers and Rose Pinto for providing valuable feedback on an earlier version of this chapter.

References

Aretoulaki, E., Ponis, S., Plakas, G., and Agalianos, K., 2020. A systematic meta-review analysis of review papers in the marine plastic pollution literature. *Marine Pollution Bulletin*, 161, 111690.

Ayaz, A., Ünal, V., Acarli, D., and Altinagac, U., 2010. Fishing gear losses in the Gökova Special Environmental Protection Area (SEPA), eastern Mediterranean, Turkey. *Journal of Applied Ichthyology*, 26(3), 416–419.

Bai, M., and Li, D., 2020. Quantity of plastic waste input into the ocean from China based on a material flow analysis model. *Anthropocene Coasts*, 3(1), 1–5.

Borrelle, S. B., Ringma, J., Law, K. L., Monnahan, C. C., Lebreton, L., McGivern, A., . . . and Eriksen, M., 2020. Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. *Science*, 369(6510), 1515–1518.

Blettler, M. C., Abrial, E., Khan, F. R., Sivri, N., and Espinola, L. A., 2018. Freshwater plastic pollution: Recognizing research biases and identifying knowledge gaps. *Water Research*, 143, 416–424.

van Calcar, C. J., and van Emmerik, T. H. M., 2019. Abundance of plastic debris across European and Asian rivers. *Environmental Research Letter*, 14: 124051.

Carpenter, E. J., and Smith, K. L., 1972. Plastics on the Sargasso Sea surface. *Science*, 175(4027), 1240–1241.

Cózar, A., Echevarría, F., González-Gordillo, J. I., Irigoien, X., Úbeda, B., Hernández-León, S., . . . and Fernández-de-Puelles, M. L., 2014. Plastic debris in the open ocean. *Proceedings of the National Academy of Sciences*, 111(28), 10239–10244.

Deshpande, P. C., Philis, G., Brattebø, H., and Fet, A. M., 2020. Using Material Flow Analysis (MFA) to generate the evidence on plastic waste management from commercial fishing gears in Norway. *Resources, Conservation and Recycling: X*, 5, 100024.

Dunlop, S. W., Dunlop, B. J., and Brown, M., 2020. Plastic pollution in paradise: Daily accumulation rates of marine litter on Cousine Island, Seychelles. *Marine Pollution Bulletin*, 151, 110803.

Egger, M., Sulu-Gambari, F., and Lebreton, L. (2020). First evidence of plastic fallout from the Great Pacific Garbage Patch. *Scientific Reports*, 10, 7495.

Elliott, T., Gillie, H., and Thomson, A., 2020. European Union's plastic strategy and an impact assessment of the proposed directive on tackling single-use plastics items. In: Letcher, T.M. (Ed.), *Plastic Waste and Recycling*. Academic Press, pp. 601–633.

van Emmerik, T., Kieu-Le, T. C., Loozen, M., van Oeveren, K., Strady, E., Bui, X. T., . . . and Schwarz, A., 2018. A methodology to characterize riverine macroplastic emission into the ocean. *Frontiers in Marine Science*, 5, 372.

van Emmerik, T., Strady, E., Kieu-Le, T. C., Nguyen, L., and Gratiot, N., 2019a. Seasonality of riverine macroplastic transport. *Scientific Reports*, 9(1), 1–9.

van Emmerik, T., Loozen, M., Van Oeveren, K., Buschman, F., and Prinsen, G., 2019b. Riverine plastic emission from Jakarta into the ocean. *Environmental Research Letters*, 14(8), 084033.

van Emmerik, T., and Schwarz, A., 2020. Plastic debris in rivers. *Wiley Interdisciplinary Reviews: Water*, 7(1), e1398.

Van Emmerik, T., Roebroek, C., De Winter, W., Vriend, P., Boonstra, M., and Hougee, M., 2020a. Riverbank macrolitter in the Dutch Rhine–Meuse delta. *Environmental Research Letters*, 15(10), 104087.

van Emmerik, T., Van Klaveren, J., Meijer, L. J., Krooshof, J. W., Palmos, D. A. A., and Tanchuling, M. A., 2020b. Manila river mouths act as temporary sinks for macroplastic pollution. *Frontiers in Marine Science*, 7, 770.

van Emmerik, T., Seibert, J., Strobl, B., Etter, S., Den Oudendammer, T., Rutten, M., . . . and van Meerveld, I., 2020c. Crowd-based observations of riverine macroplastic pollution. *Frontiers in Earth Science*, 8, 298.

Eriksen, M., Lebreton, L. C., Carson, H. S., Thiel, M., Moore, C. J., Borerro, J. C., . . . and Reisser, J., 2014. Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. *PloS One*, 9(12), e111913.

Eriksen, M., Thiel, M., and Lebreton, L., 2016. Nature of plastic marine pollution in the subtropical gyres. In: Takada, H., Karapanagioti, H. (Eds.), *Hazardous Chemicals Associated with Plastics in the Marine Environment*. The Handbook of Environmental Chemistry, Vol. 78. Springer, Cham, pp. 135–162.

FAO. 2020. *The State of World Fisheries and Aquaculture 2020: Sustainability in Action*. Rome, FAO. https://doi.org/10.4060/ca9229en

Fazey, F. M., and Ryan, P. G., 2016. Biofouling on buoyant marine plastics: An experimental study into the effect of size on surface longevity. *Environmental Pollution*, 210, 354–360.

Galgani, F., Hanke, G., and Maes, T., 2015. Global distribution, composition and abundance of marine litter. In *Marine Anthropogenic Litter*. Springer, Cham, pp. 29–56.

Gall, S. C., and Thompson, R. C., 2015. The impact of debris on marine life. *Marine Pollution Bulletin*, 92(1–2), 170–179.

Gerritse, J., Leslie, H. A., Caroline, A., Devriese, L. I., and Vethaak, A. D., 2020. Fragmentation of plastic objects in a laboratory seawater microcosm. *Scientific Reports*, 10(1), 1–16.

González-Fernández, D., and Hanke, G., 2017. Toward a harmonized approach for monitoring of riverine floating macro litter inputs to the marine environment. *Frontiers in Marine Science*, 4, 86.

Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E. and Purnell, P., 2018. An overview of chemical additives present in plastics: migration, release, fate and environmental impact during their use, disposal and recycling. *Journal of Hazardous Materials*, 344, pp.179–199.

Honingh, D., van Emmerik, T., Uijttewaal, W., Kardhana, H., Hoes, O., and van de Giesen, N., 2020). Urban river water level increase through plastic waste accumulation at a rack structure. *FrEaS*, 8, 28.

Hoornweg, D., and Bhada-Tata, P. (2012). *What a Waste: A Global Review of Solid Waste Management*. Urban Development Series; Knowledge Papers no. 15. World Bank, Washington, DC.

Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., . . . and Law, K. L., 2015. Plastic waste inputs from land into the ocean. *Science*, 347 (6223), 768–771.

Jang, Y. C., Lee, J., Hong, S., Lee, J. S., Shim, W. J., and Song, Y. K., 2014. Sources of plastic marine debris on beaches of Korea: more from the ocean than the land. *Ocean Science Journal*, 49(2), 151–162.

Kaandorp, M. L., Dijkstra, H. A., and van Sebille, E., 2020. Closing the Mediterranean Marine Floating Plastic Mass Budget: Inverse Modeling of Sources and Sinks. *Environmental Science and Technology*, 54(19), 11980–11989.

Katija, K., Choy, C. A., Sherlock, R. E., Sherman, A. D., and Robison, B. H., 2017. From the surface to the seafloor: How giant larvaceans transport microplastics into the deep sea. *Science Advances*, 3(8), e1700715.

Kawecki, D., Scheeder, P. R., and Nowack, B., 2018. Probabilistic material flow analysis of seven commodity plastics in Europe. *Environmental Science and Technology*, 52(17), 9874–9888.

Kawecki, D., and Nowack, B., 2019. Polymer-specific modeling of the environmental emissions of seven commodity plastics as macro-and microplastics. *Environmental Science and Technology*, 53(16), 9664–9676.

Kooi, M., Nes, E. H. V., Scheffer, M., and Koelmans, A. A., 2017. Ups and downs in the ocean: effects of biofouling on vertical transport of microplastics. *Environmental Science and Technology*, 51(14), 7963–7971.

Kukulka, T., Proskurowski, G., Morét-Ferguson, S., Meyer, D. W., and Law, K. L., 2012. The effect of wind mixing on the vertical distribution of buoyant plastic debris. *Geophysical Research Letters*, 39(7), L07601.

Lau, W. W., Shiran, Y., Bailey, R. M., Cook, E., Stuchtey, M. R., Koskella, J., . . . and Thompson, R. C., 2020. Evaluating scenarios toward zero plastic pollution. *Science*, 369(6510), 1455–1461.

Lavers, J. L., Dicks, L., Dicks, M. R., and Finger, A., 2019. Significant plastic accumulation on the Cocos (Keeling) Islands, *Australia. Scientific Reports*, 9(1), 1–9.

Lebreton, L. C., Van Der Zwet, J., Damsteeg, J. W., Slat, B., Andrady, A., and Reisser, J., 2017. River plastic emissions to the world's oceans. *Nature Communications*, 8, 15611.

Lebreton, L., Slat, B., Ferrari, F., Sainte-Rose, B., Aitken, J., Marthouse, R., . . . and Noble, K., 2018. Evidence that the Great Pacific Garbage Patch is rapidly accumulating plastic. *Scientific Reports*, 8(1), 1–15.

Lebreton, L., and Andrady, A., 2019. Future scenarios of global plastic waste generation and disposal. *Palgrave Communications*, 5(1), 1–11.

Lippiatt, S., Opfer, S., and Arthur, C., 2013. Marine debris monitoring and assessment: recommendations for monitoring debris trends in the marine environment. *Frontiers in Marine Science*, 6:447. doi: 10.3389/fmars.2019.00447.

Liro, M., Emmerik, T. V., Wyżga, B., Liro, J., & Mikuś, P. (2020). Macroplastic storage and remobilization in rivers. *Water*, 12(7), 2055.

Liu, Y., Wang, Z., Yang, X., Zhang, Y., Yang, F., Liu, B., and Cai, P., 2020. Satellite-based monitoring and statistics for raft and cage aquaculture in China's offshore waters. *International Journal of Applied Earth Observation and Geoinformation*, 91, 102118.

Liubartseva, S., Coppini, G., Lecci, R., and Clementi, E., 2018. Tracking plastics in the Mediterranean: 2D Lagrangian model. *Marine Pollution Bulletin*, 129(1), 151–162.

Macfadyen, G., Huntington, T., and Campell, R., 2009. *Abandoned, Lost or Otherwise Discarded Fishing Gear*. UNEP Regional Seas Reports and Studies, No. 185; FAO Fisheries and Aquaculture Technical Paper No. 523. Rome, UNEP/FAO, p. 115.

Matthews, T. R., and Glazer, R. A., 2010. Assessing opinions on abandoned, lost, or discarded fishing gear in the Caribbean. In Proceedings of the Gulf and Caribbean Fisheries Institute (Vol. 62). Gulf and Caribbean Fisheries Institute, Harbor Branch Oceanographic Institution, Inc. Fort Pierce, FL, pp. 12–22.

Maximenko, N., Hafner, J., and Niiler, P., 2012. Pathways of marine debris derived from trajectories of Lagrangian drifters. *Marine Pollution Bulletin*, 65(1–3), 51–62.

Maximenko, N., and Hafner, J., 2014. *Story of Marine Debris from the 2011 Tsunami in Japan in Model Simulations and Observational Reports*. International pacific Research Center, University of Hawaii, 20.

Meijer, L. J., van Emmerik, T., van der Ent, R., Schmidt, C., and Lebreton, L. (2021). More than 1000 rivers account for 80% of global riverine plastic emissions into the ocean. *Science Advances*, 7(18), eaaz5803.

van der Mheen, M., van Sebille, E., and Pattiaratchi, C., 2020. Beaching patterns of plastic debris along the Indian Ocean rim. *Ocean Science*, 16(5), 1317–1336.

Moore, C. J., Moore, S. L., Leecaster, M. K., and Weisberg, S. B., 2001. A comparison of plastic and plankton in the North Pacific central gyre. *Marine Pollution Bulletin*, 42(12), 1297–1300.

Napper, I.E. and Thompson, R.C., 2019. Environmental deterioration of biodegradable, oxo-biodegradable, compostable, and conventional plastic carrier bags in the sea, soil, and open-air over a 3-year period. *Environmental Science and Technology*, 53(9), 4775–4783.

NOAA, 2015. Detecting Japan tsunami marine debris at sea: a synthesis of efforts and lessons learned. https://marinedebris.noaa.gov/sites/default/files/JTMD_Detection_Report.pdf (accessed August 20, 2021).

Nurhati, I.S. and Cordova, M.R., 2020. Marine plastic debris in Indonesia: baseline estimates (2010–2019) and monitoring strategy (2021–2025). *Marine Research in Indonesia*, 45(2).

Olivelli, A., Hardesty, B.D. and Wilcox, C., 2020. Coastal margins and backshores represent a major sink for marine debris: insights from a continental-scale analysis. *Environmental Research Letters*, 15(7), 074037.

OSPAR Commission (2010). *Guideline for Monitoring Marine Litter on the Beachers in the OSPAR Maritime Area*. London: OSPAR commission.

Pasquini, G., Ronchi, F., Strafella, P., Scarcella, G., and Fortibuoni, T., 2016. Seabed litter composition, distribution and sources in the Northern and Central Adriatic Sea (Mediterranean). *Waste Management*, 58, 41–51.

Pedrotti, M.L., Petit, S., Elineau, A., Bruzaud, S., Crebassa, J.C., Dumontet, B., Martí, E., Gorsky, G., Cózar, A., 2016. Changes in the floating plastic pollution of the mediterranean sea in relation to the distance to land. *PLoS One*, 11, 1–14.

Peake, L., 2020. Plastic waste in the United Kingdom. In: Letcher, T.M. (Ed.), *Plastic Waste and Recycling*. Academic Press, pp. 585–600.

PlasticsEurope, 2019. *Plastics, the Facts*. PlasticsEurope. https://plasticseurope.org/wp-content/uploads/2021/10/2019-Plastics-the-facts.pdf

Reisser, J., Shaw, J., Wilcox, C., Hardesty, B. D., Proietti, M., Thums, M., and Pattiaratchi, C., 2013. Marine plastic pollution in waters around Australia: characteristics, concentrations, and pathways. *PloS One*, 8(11), e80466.

Ribic, C. A., Sheavly, S. B., Rugg, D. J., and Erdmann, E. S., 2012. Trends in marine debris along the US Pacific Coast and Hawai'i 1998–2007. *Marine Pollution Bulletin*, 64(5), 994–1004.

Roebroek, C. T. J., Harrigan, S., van Emmerik, T., Baugh, C., Eilander, D., Prudhomme, C., and Pappenberger, F., (2021). Plastic in global rivers: are floods making it worse? *Environmental Research Letters*, 16(2), 025003.

Ryan, P. G., and B. P. Watkins. 1988. Accumulation of stranded plastic objects and other artefacts at Inaccessible Island, Central South Atlantic Ocean. *South African Journal of Antarctic Research*, 18: 11–13

Ryan, P. G., 2018. Entanglement of birds in plastics and other synthetic materials. *Marine Pollution Bulletin*, 135, 159–164.

Van Sebille, E., England, M. H., & Froyland, G. 2012. Origin, dynamics and evolution of ocean garbage patches from observed surface drifters. *Environmental Research Letters*, 7(4), 044040.

Van Sebille, E., Wilcox, C., Lebreton, L., Maximenko, N., Hardesty, B. D., Van Franeker, J. A., . . . & Law, K. L. 2015. A global inventory of small floating plastic debris. *Environmental Research Letters*, 10(12), 124006.

Schmidt, C., Krauth, T., and Wagner, S., 2017. Export of plastic debris by rivers into the sea. *Environmental Science and Technology*, 51(21), 12246–12253.

Schwarz, A. E., Ligthart, T. N., Boukris, E., and Van Harmelen, T., 2019. Sources, transport, and accumulation of different types of plastic litter in aquatic environments: a review study. *Marine Pollution Bulletin*, 143, 92–100. doi: 10.1016/j.marpolbul.2019.04.029

Sherman, P., and Van Sebille, E., 2016. Modeling marine surface microplastic transport to assess optimal removal locations. *Environmental Research Letters*, 11(1), 014006.

Strietman, W. J., van den Heuvel-Greve, M. J., van den Brink, A. M., de Groot, G. A., Skirtun, M., Rebolledo, E. B., and Koffeman, K. J., 2020. Results of a source analysis of littering in Griend; results from a detailed source analysis of litter collected on the Wadden Island Griend, which was studied with local stakeholders during a liter ID session. (No. 2020–057). Wageningen Economic Research.

Tasseron, P., Zinsmeister, H., Rambonnet, L., Hiemstra, A.F., Siepman, D. and van Emmerik, T., 2020. Plastic hotspot mapping in urban water systems. *Geosciences*, 10(9), 342.

Thompson, R. C., 2006. Plastic debris in the marine environment: consequences and solutions. *Marine Nature Conservation in Europe*, 193, 107–115.

Tramoy, R., Gasperi, J., Colasse, L., and Tassin, B., 2020. Transfer dynamic of macroplastics in estuaries—New insights from the Seine estuary: Part 1. Long term dynamic based on date-prints on stranded debris. *Marine Pollution Bulletin*, 152, 110894.

Turner, A. and Filella, M., 2020. The influence of additives on the fate of plastics in the marine environment, exemplified with barium sulphate. *Marine Pollution Bulletin*, 158, 111352.

Vriend P, Roebroek CTJ and van Emmerik T, 2020. Same but different: a framework to design and compare riverbank plastic monitoring strategies. *Frontiers in Water*, 2: 563791. doi: 10.3389/frwa.2020.563791

The Waste Atlas 2020. http://www.atlas.d-waste.com/ (accessed December 5, 2020).

Williams, A. T., and Simmons, S. L., 1999. Sources of riverine litter: the river Taff, South Wales, UK. *Water, Air, and Soil Pollution*, 112(1–2), 197–216.

Woodall, L. C., Sanchez-Vidal, A., Canals, M., Paterson, G. L., Coppock, R., Sleight, V., . . . and Thompson, R. C., 2014. The deep sea is a major sink for microplastic debris. *Royal Society Open Science*, 1(4), 140317.

Yadav, V., Sherly, M. A., Ranjan, P., Tinoco, R. O., Boldrin, A., Damgaard, A., and Laurent, A., 2020. Framework for quantifying environmental losses of plastics from landfills. *Resources, Conservation and Recycling*, 161, 104914.

Yıldız, T., and Karakulak, F. S., 2016. Types and extent of fishing gear losses and their causes in the artisanal fisheries of Istanbul, *Turkey. Journal of Applied Ichthyology*, 32(3), 432–438.

4

Collection and Characterization of Microplastics Debris in Marine Ecosystems

Jun-Li Xu[1], *Ming Zhao*[1,2], *Brijesh Kumar Tiwari*[2], *and Aoife A. Gowen*[1]

[1] *School of Biosystems and Food Engineering, University College Dublin, Belfield, Dublin, Ireland*
[2] *Department of Food Chemistry and Technology, Teagasc Food Research Centre, Ashtown, Dublin, Ireland*

4.1 Introduction

Global plastic production has increased remarkably over the past decade, reaching 359 million metric tons in 2018 (Giacomucci et al. 2020; PlasticsEurope 2019). Plastic debris is currently found in the marine environment in different sizes, ranging from micrometer to meter. Microplastics (MPs) are usually defined as plastic debris or a polymeric matrix with regular or irregular shape and with size ranging from 1 μm to 5 mm (Hartmann et al. 2019; Kershaw et al. 2019). The occurrence and abundance of MPs in the marine environment were first reported in the 1970s (Carpenter and Smith 1972; Silva et al. 2018b), while in recent years, MP particles have been reported by numerous researchers in all environmental compartments worldwide, ranging from the Arctic Sea ice to agricultural lands.

Although the impact of MPs on public health and aquatic ecosystems remains poorly understood, the ubiquity of MPs in the oceans has become a serious concern. An increasing number of studies that investigated the potential effects or associated risks of MPs, not only in marine environments but also in freshwater environments, have been published (Zarfl 2019). The small size of MP enables its ingestion by several marine species from different trophic levels and with different feeding strategies, resulting in direct physical damage (i.e. sheer mechanical harming potential in the gastrointestinal tracts) and potential toxicity effects due to plastic additives or unbound monomers (Wright et al. 2013; Zhu et al. 2019). Up to now, many research questions in this field have emerged or remained open. For example, knowledge on aging, weathering, and fragmentation of MPs and the impact of particle degradation products on health and the environment is lacking.

Analytical procedures for MPs in environmental samples include sampling, separation, purification, extraction, identification, and quantification. A standardized or unified procedure for routine analysis of MPs, however, is still lacking, and methodologies used in different studies vary widely leading to incomparable data between different studies (Renner et al. 2018). Method development in MP analysis is a relatively young exercise that builds upon the experience from related fields such as analytical chemistry, material science, and nanoscience. In this chapter, we will explore the key procedures for sampling, collection, identification, and quantification of the abundance of MP particles in the marine environment. We will focus particularly on the more commonly used techniques and strategies recently applied for MP analysis. Special emphasis will be given to challenges in the current practices for identifying environmental MP from complex matrices and possible solutions.

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

4.2 MP Sampling

In marine ecosystems, MP debris exists ubiquitously in seawater, sediments, macrophytes (e.g. macroalgae and seagrasses), plankton (e.g. phytoplanktons including microalgae and photosynthetic bacteria; zooplanktons including zooflagellates, foraminifera, radiolarians, some dinoflagellates, and marine micro animals), shellfish (e.g. mollusks and crustaceans), and fish species.

4.2.1 Seawater

The presence of microplastics was found on both the surface and subsurface of seawater (Amélineau et al. 2016; Castillo et al. 2016; Cózar et al. 2014; Kanhai et al. 2018). MPs derived from plastics that are less denser than seawater are buoyant but finally sink after entanglement and biofouling (Ioakeimidis et al. 2014), while denser polymers (e.g. nylon, poly(ethylene terephthalate) [PET], and poly(vinyl chloride) [PVC]) merge into the subsurface of seawater column (Castillo et al. 2016). MPs from surface water have been sampled from the Atlantic, Pacific, Indian, and Arctic oceans and gulf areas (Amélineau et al. 2016; Castillo et al. 2016; Kanhai et al. 2018) primarily using a Neuston-net or a Manta trawl with 100–390 μm mesh sizes (Hidalgo-Ruz et al. 2012; Isobe et al. 2014; Ivar do Sul et al. 2013) attached to a research vessel and submerged for ca. 0.25 m beneath the surface. Normally, the net should be towed for approximately 10–15 minutes at a speed of 2–3 knots. A flow meter fitted to the mouth of the net was used to measure the volume of water passing through the net during sampling. By using a manta trawl, the trawling time varied between 20 and 50 minutes depending on the bio productivity of the region; the skimmed area was estimated using the recorded vessel speed. A sampling of subsurface seawater has been reported from a continuous intake at the depth of ca. 8.5 m using a rotary positive displacement pump at an optimal flow rate ca. 85 L/min; sea water was transported in the laboratory via stainless steel pipes with a stainless steel primary filter (2.5 mm pore size; Kanhai et al. 2018).

4.2.2 Beach Sediment

Dry sediment samples can be collected from sandy beaches from the intertidal to the supralittoral zones. However, the distribution of MPs was less known earlier as they are mainly driven by particle aggregation or animal activities (Hidalgo-Ruz et al. 2012). Generally, MPs are more abundant in the subtidal zone sediments than on dry sandy beaches or in estuarine habitats (Browne et al. 2011; Ismail et al. 2009). They may be retained on the surface and/or buried underneath sands in various depths of sediment during the accretion periods (Browne et al. 2010; Carson et al. 2011; Martins and Sobral 2011; Rusch et al. 2000). Therefore, sampling should ideally be performed at variable depths (0–32 cm) below the sediment surface (Hidalgo-Ruz et al. 2012).

4.2.3 Macrophytes

MPs can also be trapped on the surfaces of macrophytes' blades (Gutow et al. 2016; Seng et al. 2020; Sundbaek et al. 2018) or encrusted in the epibionts on the seagrasses (Goss et al. 2018). Macrophytes are collected from the subtidal reef flats 2–3 m-depth during low tide of less than 1 m depth using scuba. At least 20 blades of each macrophyte species are harvested by cutting at the blade base for at least 1 m in length. Collected blades from various species and different collecting areas are kept in individual bags to avoid cross-contamination prior to lab analysis (Seng et al. 2020).

4.2.4 Plankton

Adsorption and aggregation of MPs have been observed in scanning electron microscopic images of microalgae (Wang et al. 2020; Zhang et al. 2017). The plastic particles adsorbed on the surface of microalgae by wrapping around caveolae on the surface of the microalgae cells (5–1000 μm diameter). MP debris can also be embedded in the cell wall of microalgae and even cause physical damage to the cells. Zooplankton species (<31 μm diameter) are well known to ingest minute MPs (7.3–30.6 μm) (Cole et al. 2014). Research on the abundance of MPs associated with plankton, over large areas of the ocean is particularly challenging. A 5-year research data of a designed instrument unit – Continuous Plankton Recorders (CPR) by the Sir Alastair Hardy Foundation for Ocean Science (SAHFOS) recorded the abundance of MPs associated with the plankton samples of the gyres and coastal lines of the Northwest Atlantic. The CPR instrument was specifically designed to be towed from merchant ships to capture plankton samples from 10 m over very large areas of the ocean. Sample planktons were constantly collected using a continuously moving band of silk screen with the mesh size of 280 μm and towed behind the vessels; filtered plankton samples along with any MPs loaded with the filter silk were sent to the laboratory (Crawford and Quinn 2017).

4.2.5 Shellfish and Fish Species

MPs (ca. 0.0001–5 mm in length) are found in many shellfish and fish species (Alnajar et al. 2021; Convernton et al. 2019; Jahan et al. 2019; Marić et al. 2018; Ohkubo et al. 2020; Ory et al. 2018a. 2018b; Phuong et al. 2018a, 2018b; Rochman et al. 2016) due to direct or indirect ingestion, adherence, bioaccumulation, and cross-contamination at all trophic levels of the marine food web. Sediment-dwelling blue mussels (*Mytilus edulis*), for instance, are frequently used in research on MPs (Browne et al. 2008; Van Cauwenberghe et al. 2015). Mussels, oysters, clams, scallops, crabs, lobsters, and shrimps were collected from estuaries and coastal areas of North South America, North-South West of Australia, and the Atlantic, Pacific, and Mediterranean seas and have been studied for the abundance of MPs associated with them (Convernton et al. 2019; Jahan et al. 2019; Waite et al. 2018; Walkinshaw et al. 2020). Microplastic ingestion in shellfish was not found to be species-specific, and the particles were mainly located in epithelial cells; hepatopancreatic tissues and gills of mollusks; and in the stomachs, ovary, hepatopancreas, gills and hemolymph of crustaceans (Farrell and Nelson 2013; Gaspar et al. 2018; Walkinshaw et al. 2020). Most MP fibers were found localized in the gastrointestinal tracts and adhered on the gills of many different edible demersal, pelagic, and reef fish species sampled across the globe (Walkinshaw et al. 2020), as well as in their pseudo feces and feces.

Shellfish and fish species can be sampled using a water column trawl net with a 50-mm mesh size at selected sampling locations (Goswami et al. 2020) or acquired from shellfish and fish farms or fish markets but without knowing the sampling details. Post-sampling, live shellfish and fish have various gut evacuation times: 10–52 hours for fish and 30 minutes to 150 hours for crustaceans (Lusher et al. 2017; McGaw and Curtis 2013; Santos and Jobling 1992). MP debris can be evacuated from the GI tracts of fish or shellfish during this period. Therefore, collected samples should be stored and frozen at −20 °C prior to analysis. To avoid cross-contamination, samples of different species collected from different sampling sites should be separately placed in sealed glass jars or freezer bags during transportation to the laboratory.

4.3 Sample Processing

4.3.1 Physical Separation

Physically separating the MPs from seawater and sediment samples relies mainly on density separation, sieving, and filtration. Densities of MP debris range from 0.9 to 2.4 g/cm^3 based on data from 42 studies with values for a majority of plastics (e.g. polystyrene (PS), polyamide (PA), acrylic, poly (oxymethylene), poly(vinyl alcohol), polyvinyl chloride (PVC), poly(methyl acrylate) (PMA), polyethylene (PE) and poly(ethylene terephthalate) (PET)) in the range of 1–1.6 g/cm^3. The densities of polyethylene (PE) and polypropylene (PP) are in the range of 0.9–1 g/cm^3 and those of polyester and alkyd are around 1.2–2.3 g/cm^3 (Hidalgo-Ruz et al. 2012). Low-density MP debris (i.e. PE, PP, PS, PA, PVC, and PET) float in the supernatant of a mixture of sediment or seawater with concentrated saline solutions (e.g. NaCl of 1.2 g/cm^3 or $Na_6O_{39}W_{12}$ of 1.4 g/cm^3; Andrady 2011; Hidalgo-Ruz et al. 2012). Different salt solutions have been used in a density separation process, as shown in Table 4.1. A novel instrument, namely Munich Plastic Sediment Separator (MPSS), also demonstrated successful density separation of MP particles of 5–1 mm and even <1 mm (Imhof et al. 2012).

MP debris in sediment and seawater can also be separated using a cascade of sieves with mesh sizes ranging from 0.038 to 4.75 mm, with the MP debris retained on each sieve tier sorted in different sizes. The supernatant obtained after density separation can also be similarly sieved using a mesh size of 380 μm or 500 μm followed by vacuum filtration through a filter paper with the pore size of 1 or 2 μm. The materials retained at each step of separation using sieves or filters can be transferred into Petri dishes or glass slides for further visual sorting using microscopy or spectroscopy.

Visual sorting is commonly used to separate MP debris attached to or embedded in macrophytes. These MPs can be imaged on the microphyte blade surface and identified by structure, color, and thickness of the fragment or fibers in stereomicrographs (Lim et al. 2014; Mohamed Nor and Obbard 2014). In visual sorting of MP debris in plankton samples collected with the CPR, plankton with microplastics collected on the filter silk is examined under a dissecting microscope.

Table 4.1 Summary of density separation methods used to separate microplastics from marine sediment.

Method	Density (g/L)	MP recovery (%)	Reference
NaCl	1.2	PE, chlorinated PE, chlorosulfonated PE (80–100%)	Fries et al. (2013)
NaI	1.6	PS, Nylon (93–98%)	Claessens et al. (2013)
NaBr	1.37	PE, HDPE, PS, PVC, PET, Nylon (88–98%)	Quinn et al. (2017)
$ZnBr_2$ (25%)	1.7	PE, HDPE, PS, PVC, PET, Nylon (90–98%)	Courtene-Jones et al. (2017)
$ZnCl_2$	1.37	PE, PP, PS, polyester-PET, PVC, Nylon 6 (>97%)	Maes et al. (2017)
$CaCl_2$	1.30–1.35	PE (60–100%)	Stolte et al. (2015)
Castor oil	~1	PP, PS, PMMA, and PETG (95–99%)	Mani et al. (2019)
Sodium polytungstate	1.2	PP, PE	Corcoran et al. (2009)
K_2CO_3	1.54	PVC (~92%)	Gohla et al. (2020)

Note: Microplastics (MP), polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (polyester-PET), poly(vinyl chloride) (PVC), polyamide (nylon 6), poly(methyl methacrylate) (PMMA), glycol-modified poly(ethylene terephthalate) (PETG).

Zooplankton samples (in 1–2 hours of collection) retained on the plankton mesh or the CPR filter silk can also be removed and transferred into a vial of 0.22 μm Millipore filtered seawater to achieve complete gut depuration in 24 hours (Cole et al. 2014). To observe the interaction and ingestion of MP debris by zooplankton species (i.e. *Acartia clausi*, *Calanus helgolandicus*, *Temora longicornis*, *Doliolidae tunicata*, *Euphausiidae*, *Bivalvia [larvae]*, *Brachyura [megalopa]*, *Caridea [larvae]*, and *Oxyrrhis marina*), the specimens were exposed to fluorescent polystyrene beads for 1 or 24 hours, and then microscopy was used to assess MP ingestion by zooplankton species (Cole et al. 2014).

4.3.2 Chemical Digestion

To isolate MPs ingested by marine biota or embedded within their tissues, digestion using acid, alkaline, oxidizing agents, and enzymes, is commonly employed to remove tissue and organic matter from the sample. Prior to digestion, frozen samples should be defrosted. The surface of both fresh and defrosted samples was rinsed in order to remove the externally adhered microplastics. For larger marine biota such as fishes, mollusks, crabs, and lobsters, dissection to collect their GI tracts, gills, and normal tissues for digestion is convenient; with smaller organisms and plankton, it is more common to digest the whole organism (Lusher et al. 2017). However, the MP debris can also be degraded or damaged by digestion. Many previous studies have been conducted to find the sensitivity of plastic polymers to different digestion reagents, as shown in Table 4.2. Compared with hydrochloric acid (HCl) and perchloric acid ($HClO_4$), nitric acid (HNO_3) is more effective in digesting >98% tissue or organic matter. Several studies have successfully used 65–100% nitric acid to digest all soft tissues from blue mussels, oysters, lugworms, zebra fishes, euphausiids copepods, and manilla clams (Claessens et al. 2013; Desforges et al. 2015; Santana et al. 2016; Van Cauwenberghe et al. 2015). To approach complete digestion, 69–71% nitric acid or 100% nitric acid for 2–4 hours at 90 °C has been used with blue mussels, manilla clams, and zebrafish (Lu et al. 2016; Santana et al. 2016). Furthermore, 100% nitric acid for 30 minutes at 20 °C was used for *Euphausiids* copepods (Desforges et al. 2015) that could effectively isolate MP debris from organic matters. However, MPs can also be obscured by the oily residue obtained in acid digestion (Davidson and Dudas 2016). To avoid the oily residues, some other studies reported the use of an acid mix of 65% HNO_3 and 68% perchloric acid ($HClO_4$) in a ratio of 4:1 (v/v) at room temperature for approx. 12 hours followed by boiling at 100 °C for 10 minutes, to digest soft tissues of blue mussels or brown shrimps (Devriese et al. 2015). However, treatments with strong acid at a high temperature can reduce the recovery rates of certain MP polymers such as PA, PE, PS, and PET due to either their relatively higher pH sensitivity or lower thermal resistance than other plastic polymers (Dehaut et al. 2016; Lusher et al. 2017).

Dehaut et al. (2016) compared the digestion effectiveness of 10% (w/w) potassium hydroxide (KOH) at ca. 22 °C for 3 weeks, 10 M sodium hydroxide (NaOH) at 60 °C for 24 hours, an oxidizing solution composed of 0.27 M peroxodisulfate potassium ($K_2S_2O_8$), and 0.24 M NaOH at 65 °C for 24 hours. Results indicated that alkaline digestion methods, especially using a KOH 10% solution with incubation at 60 °C for 24 hours, achieved good digestion without significant degradation of the polymers in MPs (i.e. high- and low-density polyethylene [HDPE and LDPE], polylauryllactam [PA-12], polycaprolactam [PA-6], polycarbonate [PC], PET, poly(methyl methacrylate) [PMMA], PP, PS, crosslinked polystyrene [PSXL], poly tetrafluoroethylene [PTFE], polyurethane [PUR] and unplasticized polyvinyl chloride [uPVC], and expanded polystyrene [ePS] with the exception of cellulose acetate [CA]). Digestion of fish tissue using a mixture of 9% sodium hyperchlorite (NaClO, alkaline) and 65% HNO_3 (1:10 v/v) with ultrasonication has also been successfully used (Collard et al. 2015). Another successful method that considerably shortens the digestion time of fish gut tissue used 1 M NaOH, 65% HNO_3, followed by density separation using sodium iodide

Table 4.2 Summary of chemicals used for digestion of marine organisms to extract microplastics.

Chemicals	Processing	Organism	Efficiency (%)	MP recovery (%)	Reference
HNO_3 (22.5 M)	RT (overnight) + boiling (15 min)	Mussel			Santana et al. (2016)
HNO_3	70 °C (2 h)	Zebrafish (liver, gut, gill)		PS	Lu et al. (2016)
HNO_3 (69–71%)	90 °C (4 h)	Manila Clam			Davidson and Dudas (2016)
HCl (12.1 M)	80 °C (1–3 h)	Copepod, Euphausiid			Desforges et al. (2015)
1:1 v/v of HCl (12.1 M) and HNO_3 (15.9 M)	80 °C (1–3 h)	Copepod, Euphausiid	Most digested		Desforges et al. (2015)
HNO_3 (100%)	80 °C (1–3 h)	Copepod, Euphausiid	~100	PS (>90%) and Nylon (98%)	Desforges et al. (2015)
H_2O_2 (0.9 M)	80 °C (1–3 h)	Copepod, Euphausiid			Desforges et al. (2015)
1:1 v/v of HCl (12.1 M) and H_2O_2 (0.9 M)	80 °C (1–3 h)	Copepod, Euphausiid			Desforges et al. (2015)
HNO_3 (69%)	RT (overnight) + boiling (2 h)	Blue mussel, Lugworm			Van Cauwenberghe et al. (2015)
HNO_3 (69%)	RT (overnight) + boiling (2 h)	Blue mussel, Oyster			Van Cauwenberghe and Janssen (2014)
HNO_3 (65%) + $HClO_4$ (68%) (4:1 v:v)	RT (overnight) + boiling (10 min)	Blue mussel		Synthetic fiber	De Witte et al. (2014)
HNO_3 (65%) + $HClO_4$ (68%) (4:1 v:v)	RT (overnight) + boiling (10 min)	Brown shrimp		Synthetic fiber	Devriese et al. (2015)
KOH (10%)	60 °C (24 h)	Mussels, crab, seabream	99.6–99.8		Dehaut et al. (2016)
Pepsin (0.5% (w/v)) + HCl (0.063M)	35 °C (2 h)	Mussels, crab, seabream			Dehaut et al. (2016)
HNO_3 (65%)	RT (overnight) + 60 °C (2 h)	Mussels, crab, seabream			Dehaut et al. (2016)

HNO_3 (65%) + $HClO_4$ (65%) (4:1 v:v)	RT (overnight) + boiling (10 min)	Mussels, crab, seabream			Dehaut et al. (2016)
NaOH (10 M)	60 °C (24 h)	Mussels, crab, seabream	98.2–99.7		Dehaut et al. (2016)
$K_2S_2O_8$ (0.27M) + NaOH (0.24M)	65 °C (24 h)	Mussels, crab, seabream	Poor		Dehaut et al. (2016)
H_2O_2 (30%)	RT (7 d)	Sediment		PE (99%), PP (96%), PVC (97%), PET (91%), PS (92%), ePS (68%), PUR (96%)	Nuelle et al. (2014)
H_2O_2 (30%)	55 °C (7 d)	Fish (liver and GI tract)		PE and PS (~70%)	Avio et al. (2015)
NaCl + H_2O_2 (15%)	50 °C (overnight)	Fish (liver and GI tract)		PE and PS (~95%)	Avio et al. (2015)
NaClO (9%) + H_2O (1:3 v:v)	RT (overnight)	Fish (stomach)		PE, PP, PET, PS, and PVC	Collard et al. (2015)
NaClO (9%) + HNO_3 (65 %) (10:1 v:v)	RT (5 min)	Fish (stomach)			Collard et al. (2015)
Proteinase K (500 mg/mL) + Tris-HCl buffer (400 mM) + EDTA (60 mM) + NaCl (105 mM) + SDS (1%) + NaClO (5M)	50 °C (2 h)	Copepod	>97	PS, PE, and Nylon	Cole et al. (2014)
Trypsin + deionized water (0.3125% (v/v))	38–42 °C (30 min)	Blue mussel	~86–88	PET, HDPE, PVC, PP, PS, and PA	Courtene-Jones et al. (2017)
Corolase 7089 + MilliQ water (1% (v/v))	60 °C (1 h)	Blue mussel		PVC, HDPE (98%), PET (97%), and Nylon (85%)	Catarino et al. (2017)
Alcalase + deionized water (0.25% (v/v))	37 °C (overnight)	Blue mussel	>98	PS (~100%)	Rist et al. (2019)
Pancreatic enzyme + Tris-aminomethane)/Tris-HCl buffer (0.1 M)	37.5 °C (overnight)	Smoothcockle	~97	PE (~92%), Nomex (~91%), PET (~92.5%), PLA (~97.5%), PP (~95%), Modacrylic (~93%), ePS (~90.5%), PP (~97%), and LDPE (94% or 98%)	von Friesen et al. (2019)

Microplastics (MP), high- and low-density polyethylene (HDPE & LDPE), polyamide (PA), polycarbonate (PC), poly(ethylene terephthalate) (PET), polypropylene (PP), polystyrene (PS), polyurethane (PUR), polylactic acid (PLA), expanded polystyrene (ePS), polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC).

(NaI) solution (Roch and Brinker 2017) and obtained ≥95% of MP recovery for all tested polymer types (i.e. ePS, HDPE, LDPE, PA, PS, PP, PET, uPVC, and plasticized poly(vinyl chloride) [pPVC]).

An oxidizing agent such as hydrogen peroxide (H_2O_2) can also be used in the digestion of biological tissue to isolate MPs. For instance, 30% hydrogen peroxide (H_2O_2) was used to digest soft tissue of several different bivalve species at 65 °C in an oscillation incubator at 80 rpm for 24 hours and then at 20 °C followed by 24–48 hours at room temperature. MPs were isolated from digestate by floatation in NaCl solution (Li et al. 2015). This is consistent with the observation (Nuelle et al. 2014) that treatment with 30–35% H_2O_2 solution can easily dissolve biogenic materials without significantly degrading or discoloring the MPs. However, some minor visual changes such as changes in the degree of transparency, size, or thickness were observed in the plastic after exposure to H_2O_2, and a 6.2% loss in size for PP and PE particles (<1 mm) was estimated to result from the treatment (Nuelle et al. 2014). Other studies identified H_2O_2 digestion for fish stomach resulting in only about 70% recovery of spiked MPs due to complications from foaming of H_2O_2 (Avio et al. 2015). Use of hypersaline (NaCl) solution for density separation of fish stomach contents followed by 15% H_2O_2 digestion resulted in 95% recovery of spiked microplastics (i.e. PE; Avio et al. 2015).

Compared with acid, alkaline, or oxidized digestion, treatment with enzymes is known to be gentle enough to recover plastic polymers from the tissue without significant chemical changes to the plastic. This approach is desirable, especially for plastics that are pH-sensitive (Cole et al. 2014; Nuelle et al. 2014). Cole et al. (2014) reported using proteinase K (500 mg/mL) mixed with 400 mM Tris-HCl buffer, 60 mM EDTA, 105 mM NaCl, 1% SDS, and 5M NaClO for the digestion of 0.2 g dried plankton-rich seawater sample and obtained >97% of digestion efficiency. MPs ingested by zooplankton could be quantified after digestion without any apparent degradation (Cole et al. 2014). Other proteases including trypsin, collagenase, and papain were investigated with mussel (*Mytilus edulis*) soft tissues containing MPs (i.e. PET, HDPE, PVC, PP, PS, and PA) in the size range of <0.5 mm to 0.5–5.0 mm. These were also successful, again showing no apparent damage to the plastic. Trypsin in the optimal concentration (0.3125%) demonstrated the highest digestion efficiency ((pre-weight - post-weight)/pre-weight × 100) at approx. 88% for frozen, 86% for fresh, and 78% for formaldehyde preserved mussel tissues without changing the overall particle shape, color, and size of plastic polymers (Courtene-Jones et al. 2017). An industrial protease, Corolase 7089, at the minimum concentration of 0.5% (v/v) was reported to completely digest mussel soft tissue at 60 °C within 12 hours of incubation with the recovery rates of approx. 85%, 97%, and 98% for PA (Nylon), PET, and HDPE (<500 μm), respectively (Catarino et al. 2017). Corolase 7089 is obtained from *Bacillus subtilis* cultures, and it is active in water at pH range 6–9 without the need for a buffer medium as other proteases do. Rist et al. (2019) investigated six different proteases (i.e. Alcalase, Neutrase, NovoBate, Peltec, Ronozyme ProAct, and Savinase) and found that Alcalase was very promising for the digestion of soft tissues of blue mussels (*Mytilus edulis*). It achieved high digestion efficiencies (>98%) of mussel soft tissues, when Alcalase was used at a low concentration (ca. 0.25% v/v) and without adding oxidant chemicals (i.e. H_2O_2 or NaClO) as mentioned using proteinase K (Cole et al. 2014). The recovery rate for MP beads (i.e. PS) when using Alcalase (2.5% v/v) for digestion was around 100% (Rist et al. 2019).

The porcine pancreatic enzyme that contains lipase (40 000 Ph. Eur), amylase (25 000 Ph. Eur), and protease (1600 Ph. Eur) as active substances was employed to isolate MPs from bivalve soft tissues. von Friesen et al. (2019) reported using a 5:100 ratio (w/w) of the pancreatic enzyme to tissue, to digest smoothcockle (*Serripes groenlandicus*) tissue. Tris (tris(hydroxymethyl)aminomethane)/Tris hydrochloride solution was added as a buffer to maintain the optimal pH range (pH – 8.0 ± 0.1) for the pancreatic enzymes. The digestion process was carried out at 37.5 °C with shaking at 126 rpm overnight and achieved a digestion efficiency of ca. 97% for soft tissues and >90% recovery rates for all the tested MP particles (>20 μm) including PE, Nomex, PET, poly(lactic acid) (PA), PP, expanded polystyrene (ePS), and LDPE. There were no morphological changes in shape or color observed on the recovered LDPE particles (von Friesen et al. 2019).

To isolate the recovered MP particles from digestion, chemical or enzyme solution is sieved or filtered, and undigested residues are observed directly under the microscope. The larger retained MP particles can be picked up using forceps and placed on slides or petri dishes for further characterization. The filter membranes used are typically made of either polycarbonate (0.8 μm, 10 μm), cellulose acetate (5 μm), cellulose nitrate (5 μm), glass microfiber filter (0.2 μm, 0.7 μm and 1.2 μm) or metal mesh (50 μm, 250 μm)). The invisible micro-sized or transparent MP particles can be removed by soaking the filters or filter membranes in >70% ethanol or methanol solution under ultrasonication at 50 Hz to release the MPs adhering to the filter membranes. This solution is subsequently transferred into glass- or stainless steel centrifuge tubes and centrifuged at 3000–5000 rpm for 5–10 minutes at different temperatures (e.g., 4 or 20 °C). Isolated pellets can be dried at 60 °C for further analysis using spectroscopy or microscopy (Cole et al. 2014; Collard et al. 2015; Davidson and Dudas 2016; Desforges et al. 2015). Figure 4.1 illustrates the schematics of chemical digestion of the marine organisms and the MP isolation process assisted by ultrasonication and centrifugation.

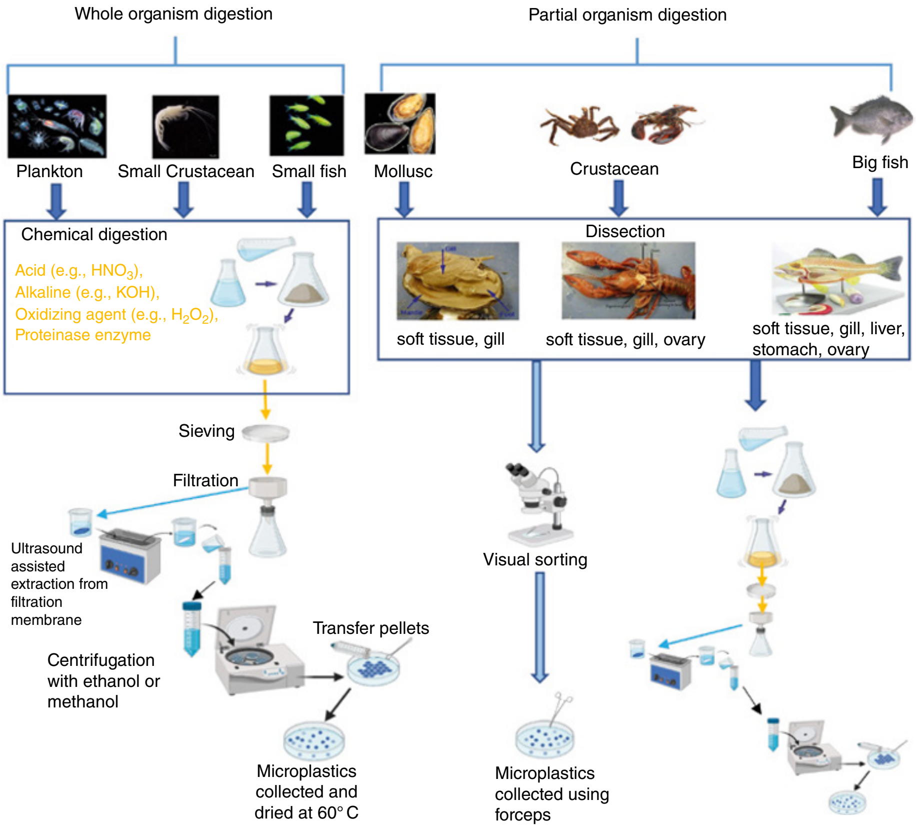


Figure 4.1 The schematics of chemical digestion and MP isolation from marine organisms (assisted by ultrasonication and centrifugation).

4.3.3 Novel Extraction and Isolation

Novel extraction techniques for MP are rarely discussed in the literature except for the use of ultrasonication in assisting extraction. However, use of these techniques can help minimize the generation of contaminants during separation, extraction, and digestion processes. Collard et al. (2015) reported the use of ultrasonication at 50 Hz for 5 minutes to remove small particles retained on a cellulose acetate membrane filter (5 μm porosity). Pulsed ultrasonic extraction was also employed successfully to remove ingested particles from the stomach of small fish – *Japanese medaka,* suspended in ultrapure water (Ghosal et al. 2018) without using any chemicals. Using shorter bursts of ultrasonic energy minimizes potential physical damage to the MPs. Pressurized fluid extraction (PFE) using methanol at 100 °C for pre-extraction followed by dichloromethane at 180 °C was used to recover MPs (i.e. HDPE, PP, PVC, PS, and PET) from the waste solids (Fuller and Gautam 2016). The recovery rate reports are in the range of 85–100% and the whole operation was carried out in less than 20 minutes. PFE will likely be useful, especially with marine sediments or plankton-rich seawater after initial filtration as it can efficiently extract plastic particles (<30 μm) that are not amenable to isolation by floatation and other physical separation procedures. However, PFE extraction could potentially damage the morphology of MP particles due to the high temperature and solvent used.

Wang et al. (2019) demonstrated the use of photocatalytic TiO_2 micromotors to remove MPs from environmental water samples. As self-propelled and micro-scaled devices, photocatalytic micromotors employ H_2O and light to generate H_2 to propel themselves autonomously during the photocatalytic reactions on the particles. These micromotors could attract and remove passive MP particles from water (Eskandarloo et al. 2017; Jurado-Sánchez and Wang 2018). MPs are attracted by micromotors that induce the formation of clusters of MPs during the photochemical reactions, and they can be collected from water by developing assembled chains of the MP particles under an external magnetic field (Wang et al. 2019). Acoustic focusing using piezo elements attached to a microfluidic device with trifurcated microchannel can collect suspended MP particles (i.e. PS, PET, Nylon 6, etc.) in the microchannel by an acoustophoretic force; this acoustic focusing device was able to collect MP particles of 5 μm in diameter (Akiyama et al. 2020).

After MPs are extracted from the surrounding environmental matrices, they need to be characterized and quantified. In recent years, because of growing scientific and public interest in the topic, an increasing number of methods have been proposed for their qualitative, quantitative, or combined analysis from marine samples. Methods development in MP analysis requires a multidisciplinary approach that builds upon the experience from related fields such as nanoscience, analytical chemistry, and materials science. In general, the analysis comprises two steps: the physical characterization of candidate particles (e.g using an optical microscope) followed by chemical characterization (e.g. using chromatography) for identification of plastic types (Shim et al. 2017).

4.4 Characterization and Quantification

4.4.1 Physical Characterization

4.4.1.1 Visual Identification

Visual identification is the simplest, oldest, and most straightforward strategy of MP analysis (Shaw and Day 1994). MPs ranging from 1 to 5 mm, large enough to be discerned by the naked eye, such as plastic pellets, can be easily identified visually depending on the transparency, shape, and color of particles. For instance, Heo et al. (2013) quantified the abundance of small plastic debris on Heungnam beach, in which identification and sorting were performed solely by the naked eye (Heo et al. 2013). Although widely used, the result from visual sorting is not quite reliable, because the accuracy and effectiveness of the approach strongly depend on the observer. In the case of marine samples that normally contain a high level of interfering inorganic and organic materials, the chance of misclassification could be significant. Even with more experienced researchers, a plastic material with colors close to those of natural particles or other materials such as quartz particles, glass pieces, small plant fragments is difficult to discern, and there is a high probability of underestimating or overestimating the counts without the aid of further analytical methods (Zarfl 2019).

4.4.1.2 Microscopic Observation

Identification under a light microscope is employed for smaller MPs usually < 1 mm. Magnified images using microscopy play an important role in characterizing ambiguous and plastic-like particles because they provide detailed surface textures and structural features of objects. However, sub-hundred micron-sized MPs are usually not identifiable microscopically that lead to estimation errors (Renner et al. 2018). The error rate of plastic-like particles using microscopic observation was usually more than 20%, and was as high as 70% for transparent objects which were confirmed with the following spectroscopic analysis (Hidalgo-Ruz et al. 2012; Shim et al. 2017; Song et al. 2015). The misclassification rate often increased with the decreasing particle size, and it was challenging to identify synthetic and natural fibers by using microscopy alone (Song et al. 2015). In addition, subjectivity also contributes to the large observational error. In a study of quantifying MPs of the sediment sample by counting under a microscope, Dekiff et al. (2014) showed discrepancies of 1–4 MP particles in the same sample when counted by three different observers (Dekiff et al. 2014). With the presence of much biogenic organic material, purification is usually recommended in order to discriminate between MPs and other fragments. In this sense, attention has to be paid to the fact that the clarity and color of plastics might change during extraction or purification steps, leading to an increased probability of misjudgments. Taken together, microscopic visual sorting strongly depends on (i) the experience of the observer, (ii) the quality of the magnified images, (iii) sample preparation, and (iv) the complexity of the sample matrix. To facilitate a proper identification, it is recommended to apply additional chemical analytical methods, such as spectroscopy (Löder and Gerdts 2015).

An improvement proposed for visual sorting to identify plastics from other debris involves the "hot needle test" that takes advantage of the thermoplastic properties of many synthetic plastics (Lusher et al. 2017; Silva et al. 2018a). For example, Zhang et al. (2018) introduced a simple and cost-saving method for the identification of MPs by comparing microscope images collected both before and after heating the sample for 3–5 seconds at 130 °C. Melted particles were then identified as thermoplastic polymers (Zhang et al. 2018). Despite being simple and fast, this approach has some limitations: (i) it is destructive, (ii) it cannot provide chemical information in terms of plastic types, (iii) it does not take into consideration that some natural substances such as wax also melt at certain temperatures, and (iv) it does not identify thermoset fragments. The use of polarized-light optical microscopy (PLOM) is a better alternative to visual sorting, particularly in complex biological matrices. PLOM works by placing a particle between crossed polarizers while allowing polarized light to transmit. Isotropic substances appear dark while anisotropic birefringent materials tend to be bright. Several reports have confirmed PLOM as a viable and cost-affordable technique for rapid MP analysis (Abbasi et al. 2019; Collard et al. 2017). More recently, Sierra et al. (2020) demonstrated the strong identification capability of PLOM, as compared with spectroscopic techniques (Sierra et al. 2020). They also pointed out that PLOM identification is inclined to show potential false negatives (particularly non-optically active particles of PVC) and false positives (such as cellulose fibers) findings. Therefore, an additional spectroscopic procedure was suggested in the whole analytical workflow when using PLOM to confirm ambiguous findings.

Another aid to visual sorting under the microscope is the application of a staining dye, reported to be useful in MP quantification (Hengstmann and Fischer 2019; Prata et al. 2019). The use of Nile Red, a lipophilic fluorescent dye that specifically binds to neutral lipids and synthetic polymers in environmental samples and makes them fluoresce under a microscope, was first proposed by Andrady (2010); it has since been adopted in many studies (Dowarah et al. 2020; Karakolis et al. 2019). This method provides rapid staining rates and a strong fluorescence signal. Moreover, Nile red is well known for its higher recovery rates (>96%) for different plastic types including nylon, polyethylene (PE), polystyrene (PS), and polypropylene (PP) with a particle size > 500 μm (Maes et al. 2017). Compared to visual sorting with the naked eye, staining facilitates the identification of some hidden MP particles buried in the complex matrix. Additionally, it can largely reduce misinterpretations since some mineral and organic materials (e.g. wood and algae) are weakly stained or not stained at all. Nevertheless, some limitations are also pointed out. Dye molecules tend to be desorbed from MPs due to the weak affinity of their physical adsorption on the surface. In addition, Nile red is unsuitable for plastic types with low hydrophobicity, such as polycarbonate and poly(vinyl chloride), leading to the underestimation of MPs in a mixed sample. Stanton et al. (2019) examined Nile red's ability to stain a range of MP particles and common natural substances found in environmental samples. In their study, another fluorescent dye that almost exclusively stains biological substances, 4′,6-diamidino-2-phenylindole (DAPI), was applied to assess the extent to which Nile red stained biological materials. Their results showed that the use of Nile red dye alone led to a maximum 100% overestimation of MP particles. Therefore, Stanton et al. (2019) advocated an urgent need for rigorous assessment of the use of Nile red to quantify MP abundance.

4.4.1.3 Electron Microscopy

Scanning electron microscopy (SEM) is commonly used for the identification of MPs from environmental samples (Chen et al. 2020). In this technique, high-resolution images (< 0.5 nm resolution) of a surface are produced by scanning with a high-intensity beam of electrons that interact with atoms in the sample, generating different signals indicative of the surface topography and composition. High-resolution images show clear surface features that facilitate discrimination between MP from other organic particles. Further examination of surface features such as pits, fractures, and grooves allows a better understanding of the mechanical degradation process of MPs. For instance, the action of the wind contributes to fractures on airborne MPs (Cai et al. 2017).

The combination of SEM with energy-dispersive X-ray spectroscopy (SEM-EDS) yields information on the elemental composition of particles making it possible to discriminate carbon-rich MPs from inorganic objects (Dehghani et al. 2017). Although widely used for MP analysis, SEM-EDS is a time-consuming and labor-intensive method with laborious sample pre-treatment. Only a limited number of samples can be analyzed in a given timeframe, making it unsuitable when a large number of particles need to be tested. Moreover, SEM is unable to use the color property of the object, leading to potential misjudgments on the identification and quantification of MPs' abundance in the marine environment.

Dehghani et al. (2017) applied the SEM-EDS to detect MP particles of various morphology (e.g. spherule, hexagonal, irregular polyhedron fibers), sizes, and colors. Their results suggest the presence of additives in plastic polymers or adsorbed debris with Al, Na, Ca, Mg, and Si on the MP surface. Although the chemical composition of representative samples can be obtained from SEM-EDS, visual features can be used by the operator to identify MPs in the sample again leading to erroneous estimates.

Winkler et al. (2019) investigated various sources of MPs found in plastic mineral water bottles that were exposed to mechanical stress by using SEM-EDS. While EDS facilitated elemental analysis, SEM images were employed to quantify MPs' abundance. Specifically, the area and shape of all particles were computed from the SEM images. Winkler et al. (2019) confirmed that SEM-EDS was suitable for the detection and quantification of MP particles in filtered water based on the analysis of high-resolution images. They pointed out the limitations of this technique with different plastics that had only carbon and hydrogen in their structure.

To improve its performance, SEM-EDS can be used in conjunction with other techniques. Wang et al. (2017) applied SEM-EDS combined with light microscopy to characterize MP particles extracted from ocean trawls and fish guts to assess their shape, size, and chemical signatures. Light microscopy facilitated the assessment of morphological properties and quantification of particle size ranges. Their results revealed that it is easy to identify chlorinated plastics, for example, PVC and mineral species due to their unique elemental signatures. By integrating SEM-EDS with optical microscopy, the authors found some ingested MPs by fish were degraded fragments from larger plastic pieces as well as some were manufactured MPs. The surface texture from high-resolution SEM images indicated characteristic cracks consistent with environmental exposure.

SEM-EDS is also applied as a complementary approach to spectroscopic techniques (e.g. Fourier-transform infrared (FTIR) spectroscopy) since it provides significant extra information useful for MP analysis. In a study on the release of fibers from a polyester, polyester-cotton blend, and acrylic fabrics, SEM was used for morphological analysis followed by micro-FTIR for identification of specific plastic types. Li et al. (2016) investigated MP pollution in mussels (*Mytilus edulis*) and initially identified a large amount of uniform transparent spheres as aluminum silicates using micro-FTIR. Yet, SEM-EDS images confirmed the presence of regular holes on the surface. These findings highlight the need to apply different complementary strategies to further valid those plastic-like particles. Taken together, SEM is useful for the evaluation of any modifications on the surface of MP particles, such as pits and cracks which provide information on plastic degradation in the marine environment.

4.4.2 Chemical Characterization

4.4.2.1 Infrared Spectroscopy

Infrared (IR) spectroscopy measures transitions between molecular vibrational energy levels in a measured sample by absorption of IR radiation. In general, vibrational modes observed in infrared spectroscopy arise from bond stretching (which is associated with a change of the bonding length) and bending (which involves a change of the bonding angle). An IR-active bond is a bond that changes its dipole during vibration. For example, C=O, O–H, N–H. Few bonds such as the C–C bond in symmetrical alkene and alkyne are IR inactive transitions. Plastics consist of several, often repeating, functional groups bound to a carbon backbone (see Chapter 2) making IR spectroscopy useful, particularly in MP identification. The infrared energy band is usually divided into three regions: near-infrared (NIR, 12 800–4000/cm), mid-infrared (MIR, 4000–200/cm), and far-infrared (FIR, 200–10/cm).

The broad and overlapping spectral peaks in NIR make spectral interpretation difficult though this radiation allows high penetration depth compared to MIR (Türker-Kaya and Huck 2017). MIR absorption peaks are more straightforward to assign to different functional groups due to the fundamental vibrations of molecular bonds. Therefore, this range produces well-resolved absorption bands (Bevilacqua et al. 2013) and could be more useful in polymer identification. An IR-microscope allows MIR to detect particles down to a diameter of a few micrometers. NIR combined with hyperspectral imaging (HSI) could also potentially identify and quantify plastic types due to the specific overtone vibrations of their C–H bonds (Workman and Weyer 2012). HSI integrates conventional imaging and spectroscopy to attain both spatial and spectral information from the object (Gowen et al. 2007). A hyperspectral image described as $I(x, y, \lambda)$ can be viewed either as a separate spatial image at each individual wavelength λ_i, or as a spectrum at each individual pixel (Xu et al. 2021), as illustrated in Figure 4.2. Few researchers (Karlsson et al. 2016; Serranti et al. 2018) confirmed the possibility of using NIR-HSI for the detection of MPs in the millimeter size range. More recently, Shan et al. (2019) detected common plastics down to the size of 200 μm using this technique. Compared to MIR microscopy, NIR-HSI enables fast collection and less demanding sample preparation to scanning, resulting in an overall short analysis time (Shan et al. 2019), yet it is unfeasible for small/thin MP particles.

4.4.2.2 Mid-infrared MP Characterization

Fourier-transform mid-infrared (FT-MIR) is a common technique for MP identification (Xu et al. 2019), providing fast measurement, as well as a spectral profile with well-defined, characteristic peaks for each polymer. For MP analysis, three different operating configurations: transmittance, reflection, and attenuated total-reflectance (ATR), are widely used in FTIR (see Figure 4.3). In the transmittance mode, the IR beam passes through the sample, and transmitted energy is collected to produce a spectrum. Light passes completely through the sample cross-section maximizing the sensitivity. Hence, even transitions with low extinction coefficients are detectable, an advantage with some polymers due to the enhancement of their very low absorption rates of C–C and C–H vibrational mode transitions. However, where changes in bond dipole moments are strong during the vibrational process as in C–O vibrations, this enhancement leads to detector overflow effects, thereby causing opaque spectral intervals. The transparency of the test sample is the key to obtaining a transmittance spectrum. This mode is not suitable for colored plastics that absorb intensely as insufficient transmitted light reaches the detector.

Some of the aforementioned disadvantages might be reduced to some degree by using the reflectance mode. The ATR mode is one of the most common configurations for MP analysis by FTIR spectroscopy. A reflectance spectrum is acquired when the incident beam passes back through the sample by a combination of diffuse reflectance from the sample surface/subsurface and transfection from an IR reflective substrate. Although reflectance spectra might produce a measurable signal even for thick and partly absorbing materials, the reflected signal tends to be affected by

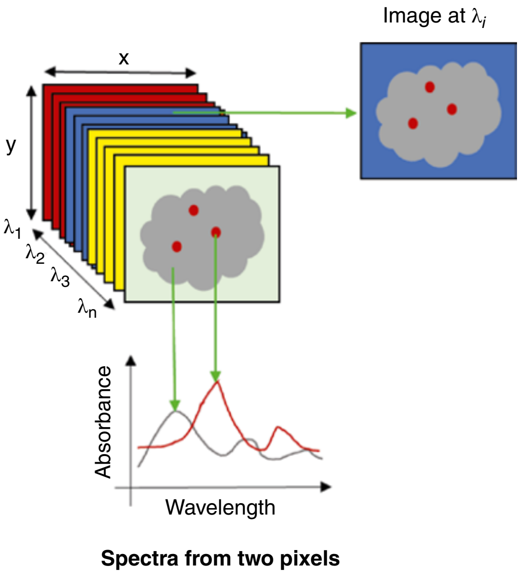


Figure 4.2 Schematic representation of a hyperspectral image.

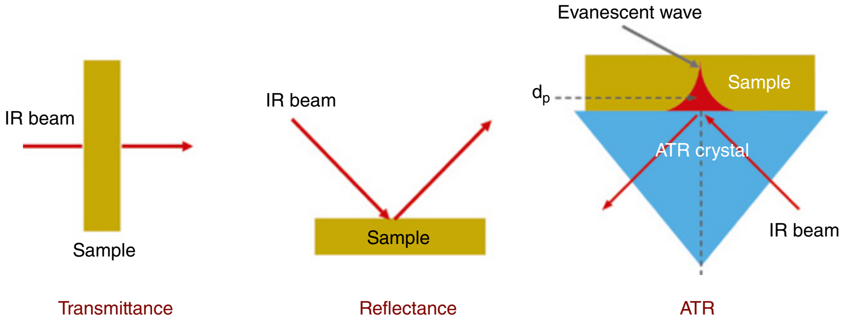


Figure 4.3 Simplified schematic diagram of common FTIR analysis modes.

variations caused by light scattering due to the morphology (size, shape, and refractive index) of the MP particle.

As seen from Figure 4.3, the IR beam travels through an ATR crystal of a high refractive index and interacts with the sample on the surface. Total internal reflection occurs and generates an evanescent wave that extends a short distance (of the order of 1 μm) beyond the surface in the form of waves (called evanescent waves), leading to a slightly attenuated total reflection. Because of the short light penetration depth in ATR configuration, it is ideal for strongly absorbing or thick samples which often produce intense peaks when measured by transmittance. In some instances, MPs extracted from environmental matrices are covered with biofilms as well as other contaminants. Accordingly, the low penetration depth of ATR can be a disadvantage because the IR beam might not pass through the surface layer to reach the MP. In addition, the ATR crystal should be covered by the analyzed particle, thereupon, particles with a size smaller than the crystal are unlikely to generate a desirable spectrum due to the incomplete coverage. There is also the possibility of small particles sticking to the crystal causing spectral aberrations. Transmission and ATR spectra of a plasticized PVC sample (thickness of 130 μm) collected using Nicolet iN10 MX infrared imaging microscope (Thermo Fisher Scientific Inc.) is shown in Figure 4.4. Further details about this instrument can be found in Xu and Gowen (2019). As seen in the figure, ATR-mode spectra de-emphasizes absorption bands with higher wavenumber (e.g. 3500–2500/cm) because the depth of penetration in ATR decreases with the wavenumber decreases.

Vibrational chemical imaging systems were developed to simultaneously acquire spectral and spatial features to allow mapping of the distribution of different chemical species throughout the samples. Chemical imaging of MP is commonly achieved by micro-spectroscopy, that is, integrating an optical microscope with a highly sensitive spectrophotometer. Following three strategies are applied to yield the chemical imaging dataset:

1) point mapping (a spectrum is collected at one position, and a further spectrum is recorded when it moves to the next measurement point on the grid until covering the whole defined area),
2) line imaging (a series of spectra are collected from pixels along a line before moving to the next spatial location), and
3) focal plane array (FPA) mapping which allows fast acquisition of several thousand spectra within an area through one single measurement due to several detectors placed in a grid pattern.

4.4.2.3 Data Analysis for Mid-infrared MP Characterization

For MP characterization based on FT-MIR, the first step is generally to inspect the spectral quality and then decide on suitable strategies for subsequent data processing. In most cases, FT-MIR spectra of MPs are disturbed by physical and chemical interferences, which may potentially reduce the

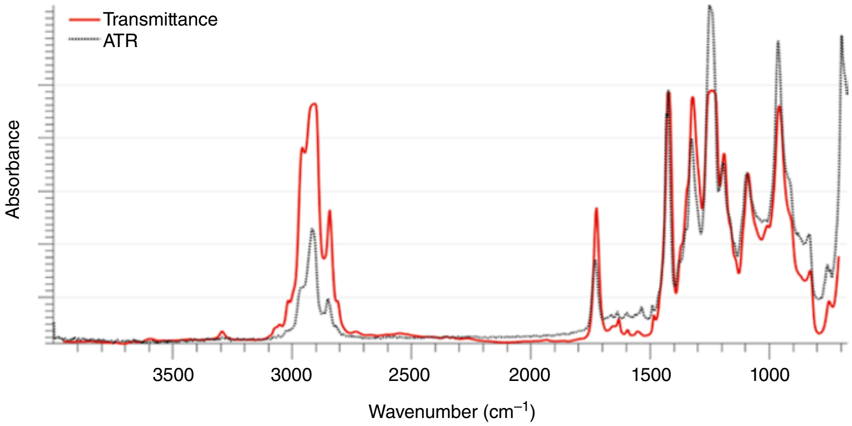


Figure 4.4 Comparison of transmission and ATR techniques based on FTIR spectrum of the plasticized PVC.

accuracy of identification (Renner et al. 2017). Accordingly, employing data-preprocessing techniques to obtain uncontaminated spectral data for subsequent processing is useful (Xu et al. 2020a). Spectral preprocessing eliminates the effects of unwanted signals, such as detector noise, Mie scattering, calibration errors, and enhances subtle differences between different samples. Atmospheric water vapor and carbon dioxide are strongly absorbed in the MIR region, interfering with the detection of weak sample peaks. Water vapor displays a complex set of sharp molecular rotational bands in the regions of 4000–3400/cm and 2000–1400/cm in the FT-MIR spectrum. As a straightforward and practical approach, subtraction of background spectrum is widely used to compensate for water vapor interferences, as expressed in Equation 1

$$A(v)_{\text{Corrected}} = A(v)_{\text{Original}} - k \cdot A(v)_{\text{Water vapor}} \tag{1}$$

where k is an empirical factor that is updated iteratively. However, the correction is unable to remove residuals entirely because the intensity ratios of rotational bands can be easily altered by many complex factors such as pressure, temperature, and airflow. Other common actions to minimize background interference include improving the control of atmospheric conditions or resorting to frequent background calibration.

Characterization of MPs requires high-throughput analysis due to a large number of individual particles within a sample. Since the interpretation of spectral data is a complex and time-consuming procedure, multivariate analysis is sometimes adopted to provide valuable exploration information. Instead of focusing on individual MP, this approach considers the data structure of all samples, as well as few included references. The combination of spectroscopy and multivariate methods of data analysis allows the investigation of intrinsic relationships of samples according to their spectral similarities. A common method for exploratory multivariate characterization of MP is principal component analysis (PCA) (Avio et al. 2015; Pearson 1901). For example, ATR-FTIR spectra (spectral resolution of 8/cm with 160 scans) were collected from eight commonly used plastics: poly(vinyl chloride) (PVC), poly (tetrafluoroethylene) (PTFE), polystyrene (PS), polysulfone (PSU), polypropylene (PP), polyethylene (PE), poly(ethylene terephthalate) (PET), and Nylon 6/6 using Thermo Scientific Nicolet iN10 MX imaging system. PCA model was then developed from 49-pixel spectra of each plastic. The score plot of the first three PCs (explaining the total variance of 86%) is shown in Figure 4.5. Nylon 6/6 is seen far away from the rest of plastics, indicating its distinctive spectral features.

Different strategies might be applied to identify an unknown particle. Some researchers interpret spectra manually based on characteristic peaks of the functional groups (Xu et al. 2019). The mean spectrum of each plastic sample from Figure 4.5 was obtained and plotted in Figure 4.6.

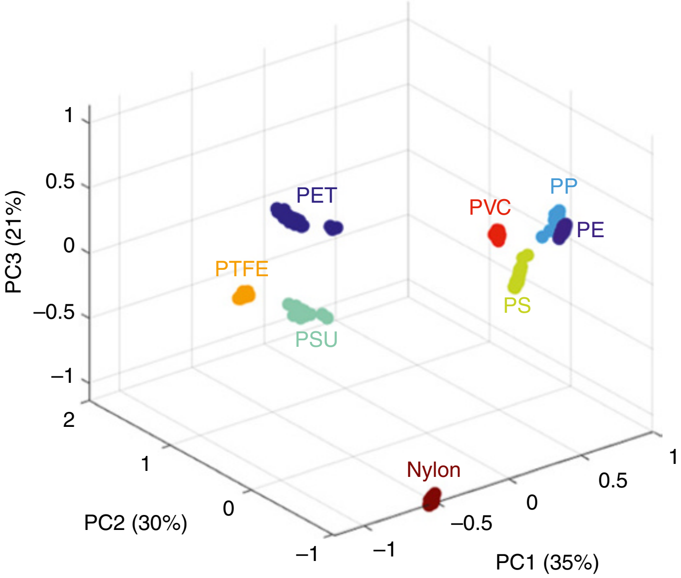


Figure 4.5 Principal component analysis score plot of eight plastics.

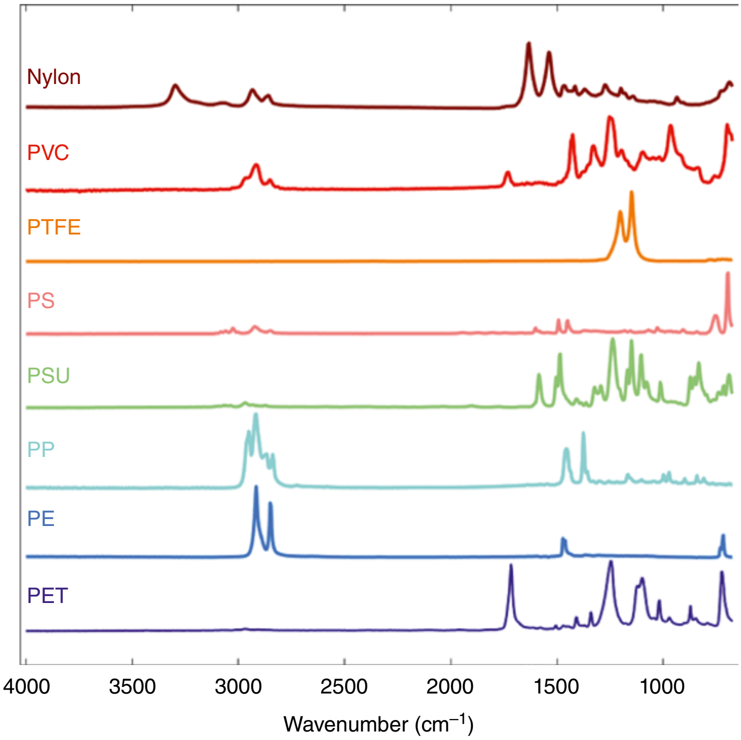


Figure 4.6 ATR-FTIR spectral profiles of the commonly used plastics.

Some band areas represent common vibrations, such as CH stretching (2980–2780/cm), CO stretching (1760–1670/cm), and CH deformation (1480–1400/cm). This visual comparison has the disadvantage of being labor-intensive and subjective. It is a common practice to assign relevant functional bands with the aid of a reference table similar to Table 4.3.

Table 4.3 The assignment for ATR-FTIR spectral features of some plastics.

Sample	Spectral features (per cm)	Peak/band assignment
PVC	2914, 2850	C–H stretch
	1730	C=O stretch
	1430	C–H bend
	1330–1250	C–H stretch
PTFE	1203	Symmetric CF_2 bend
	1147	Asymmetric CF_2 bend
PS	3000–2840	C–H stretch
	1409	C–C aromatic ring stretch
	1247	Asymmetric C–O–C stretch
PSU	2966	C–H stretch
	1585–1502	Aromatic groups
	1238	Asymmetric C–O–C stretch
	1149	C–O stretch
PP	3000–2800	C–H stretch
	1456	C–H bend
	1375	C–H bend
PE	2916–2848	C–H stretch
	1470–1460	C–H deformation
PET	3000–2840	C–H stretch
	1714	C=O stretch
	1340	$C–H_2$ bend
	1247	C–O stretch
Nylon 6/6	3295	N–H stretch
	2935, 2862	C–H stretch
	1632–1535	C=O stretch

Source: Xu et al. (2020b) and Lin et al. (2020).

Another more popular strategy is to compare and identify samples by matching their measured spectra with those in a polymer reference library, For example, Omnic spectral library, Nicodom polymers library, Sadtler Library, and Shimadzu materials library (Xu et al. 2019). Such comparison is usually performed using automated library searching, which is installed in most modern FT-MIR software (Xu et al. 2019). The procedure computes a numeric score that represents the similarity between the reference spectra and the unknown one. A correlation coefficient r is usually used to calculate this score (Wang et al. 2006). Although r allows estimating the level of the spectral similarity between the unknown and reference spectra of the database. There is no consensus regarding how to determine whether or not the score value is adequate to identify an unknown MP sample. It is typical to assign a particle to a specific polymer with an r value > 0.80 since the discrepancy might come from random effects such as the presence of a chemical additive in the plastic or the presence of spectral noise (Mecozzi et al. 2016). Still, it is not advisable to rely blindly on score values. Testing the researching results is strongly recommended for plausibility (Renner et al. 2017). It should also be noted that the discrepancy between different libraries used might result in incomparable results (Cai et al. 2019).

Moreover, environmental exposure often leads to polymer aging and mechanical and oxidative weathering of the plastic surface. Weathering-related changes in infrared spectra have been reported from previous research, largely in the following regions: hydroxyl groups (broad peaks ranging from 3100 to 3700/cm, centered at 3300–3400/cm), alkenes or carbon double bonds (1600–1680/cm), and carbonyls (1690–1810/cm, centered at 1715/cm) (Brandon et al. 2016; Rajakumar et al. 2009). Accordingly, the aging of MP in the environment has the potential to alter the spectral features; therefore, it could influence the accuracy and reliability of library searching results.

4.4.2.4 NIR-HSI for MP Characterization

NIR-HSI is typically used for quality control and process monitoring, which is fast and non-destructive, facilitating real-time and in-line analysis. Compared to MIR, another noticeable advantage of NIR is the deeper penetration of light, making it suitable for particles covered with biofilms or other contaminants. NIR-HSI can be performed directly on the filters which are commonly used to concentrate the digested organismal soft tissue. Since there is no need for particle pre-sorting, this technique limits the risk of losing or incorrectly sorting the particles and reduces the time of analysis, costs, and procedural bias. Combined with chemometrics and machine learning algorithms, it is feasible to detect and identify MPs simultaneously from the spectral image in a short time. One of the earliest studies using hyperspectral imaging to detect polymers in seawater filtrates was carried out by Karlsson et al. (2016). In aid of multivariate analysis, this technique was effective in the determination of the spatial location of plastic debris on the filter and identification of plastic types. Three different wavelength ranges were evaluated, that is, 375–970 nm, 960–1662 nm, and 1000–2500 nm, in which short-wave infrared (SWIR, i.e., 1000–2500 nm) delivered the best result with 100% particle recognition on reference plastic. Karlsson et al. (2016) demonstrated that the near-infrared hyperspectral imaging technique has great potential for MP analysis down to the size of 300 μm.

Serranti et al. (2018) applied NIR-HSI to analyze marine MP litter collected by surface-trawling plankton nets from several parts of the world (i.e. Arctic, Mediterranean, South Atlantic, and North Pacific; Serranti et al. 2018). Hyperspectral images were collected in the SWIR (i.e. 1000–2500 nm) range. Using a combination of 2nd derivative, standard normal variate (SNV), and mean center (MC) algorithms, a classification model was developed adopting a partial least-squares discriminant analysis (PLS-DA) for the reorganization of different types of polymers constituting marine MPs. Their study showed that fragments ranging in the sizes of 1–5 mm were the most abundant, accounting for more than 70%, and PE was the most common polymer type found in the fishing line particles, followed by PP and PS. More recently, Zhu et al. (2020) conducted a series of laboratory assessments based on near-infrared hyperspectral imaging for the identification of MPs enriched on filter substrates. They realized that different plastic types display distinct spectral features at 1150–1250 nm, 1350–1450 nm, and 1600–1700 nm, allowing the use of automatic recognition using spectral angle mapper (SAM) classification (Zhu et al. 2020). Their results confirmed the suitability of using HSI for the detection of three types of MP particles: polyethylene, polypropylene, and polystyrene, down to 100 μm in diameter. They further pointed out that a gold-coated polycarbonate filter showed constant reflectance over 900–1700 nm and a large radiative contrast against loaded plastic particles. Glass fiber filters might also serve as suitable substrates due to their low cost and commercial availability.

4.4.2.5 Raman Microscopy

Raman microscopy (RM) probes molecular vibrations within the MP which can be used for identification of the polymer type and is thus recognized as a well-suited method for MP characterization. In principle, both infrared and Raman spectroscopy monitor the interaction of radiation with molecular vibrations but differ in the manner how the photon energy is transferred to the molecule to change its vibrational state (Xu et al. 2019). The polymer sample is illuminated with a monochromatic laser light source, and the inelastically scattered light from the sample is collected. Raman microscopy (RM) that couples a Raman spectrometer to an optical microscope, allows the collection of spectra from a two-dimensional area at high magnification, expanding its utility for MPs investigation. For example, confocal Raman microscopy has been utilized to produce 3D images of MPs inside living organisms including zooplankton and crab (Ribeiro-Claro et al. 2017). In addition, Raman spectroscopy can be combined with atomic force microscopy (Raman-AFM) to facilitate nanoscale imaging.

Raman spectra of PE and PTFE were collected using an InVia Micro-Raman spectroscopy system (Renishaw, Wotton-under-Edge, Gloucestershire, UK) under 10× objective with a 785 nm excitation laser and 1s exposure time at 100% output power. As demonstrated in Figure 4.7, each Raman spectrum features a series of peaks, showing the scattering intensity on the *y*-axis and the Raman shift on the *x*-axis. Each peak corresponds to a specific molecular bond vibration, including individual bonds such as C–C, C=C, N–O, and C–H. Accordingly, Raman spectra of PE and PTFE are distinctive due to their different chemical structures.

Compared to infrared spectroscopy, the advantages of RM include its high spatial resolution and low sensitivity to water. Theoretically, it is possible to detect particles up to 1 μm size using the technique. Nevertheless, there are not many reports on the identification of MP particles by RM due to demanding sample preparation procedures (e.g. separation and purification) and longer measurement time. RM is less disturbed by water signals, yet the interference of fluorescence is one of the biggest drawbacks, which hampers MP identification. In this sense, some level of preparation (e.g. density separation and purification) is recommended. Pigments or additives, which enable to provide some insight into the composition and possible origin of particles, are normally characterized with strong fluorescence which might mask the spectral features of the polymer.

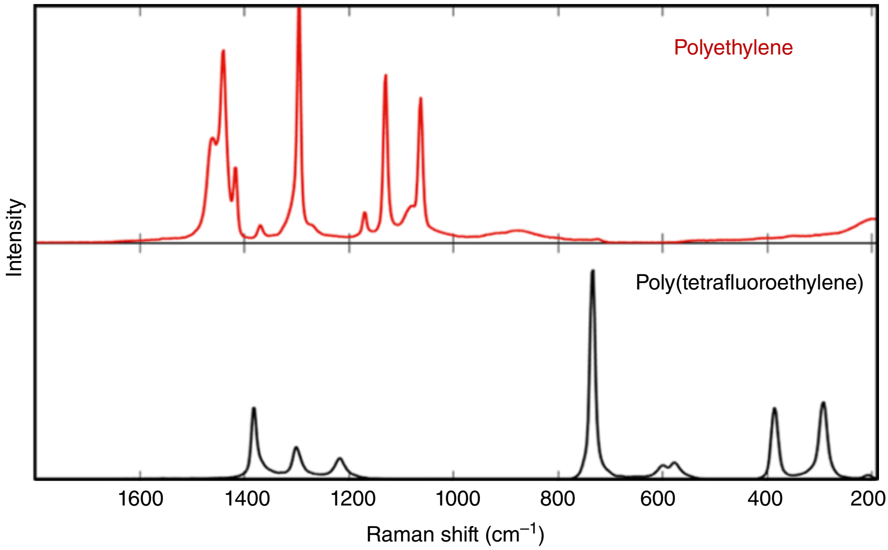


Figure 4.7 Raman spectra of polyethylene and poly(tetrafluoroethylene) plastic films obtained from a 785 nm excitation laser.

4.4.2.6 Chromatography

Chromatographic methods allow qualitative and quantitative identification of individual polymer types. Gel permeation chromatography (GPC) is widely used to measure the molecular weight distribution of MPs, including the high-temperature GPC used with polyolefins that do not dissolve in solvents at ambient temperature. With plastics such as PS soluble at ambient temperatures in chlorinated solvents, GPC is used popularly to assess the average molecular weights (Ceccarini et al. 2018). Promising results were also demonstrated by using pyrolysis gas chromatography-mass spectrometry (Pyr GC-MS), now recognized as a sensitive and well-established method for the mass quantification of polymer types together with their organic additives (Hendrickson et al. 2018; Möller et al. 2020). For Pyr GC-MS analysis, a sample is heated in the absence of oxygen and the evolved volatile pyrolysis products are analyzed using GC-MS. A cold injection system is used to trap the released gaseous compounds subsequently transported to a GC column often in combination with a mass spectrometer. Generally, elucidation of specific polymer pyrolysis products is known and the acquired spectra of the pyrolysis products of unknown MPS are compared to a database of products of known common plastic types. Pyr GC-MS provides information on organic plastic additives (OPAs), which might be toxic as well (Fries et al. 2013). However, this method has several drawbacks. The size of the pyrolysis capsule can accommodate only if very small amount per run is exceedingly small, 1.5 mm (Fries et al. 2013) and 0.5 mg (Eisentraut et al. 2018), respectively. In addition, MPs have to be manually placed into the pyrolysis tube, resulting in the analysis of one particle per run taking approximately 70 minutes, making it rather unsuitable for bulk analysis. Moreover, the MPs need to be large enough to be placed into the tube by tweezer, ruling out the use of small-sized MPs with this technique. No information on the morphology of the plastics can be obtained using this method. Additionally, it is prone to contaminations or even blockages.

More recently, thermal extraction desorption gas chromatography-mass spectrometry (TED-GC-MS) has been proposed to overcome some of the shortcomings of Pyr GC-MS. Higher sample volumes (0.5–100 mg) are used with this technique and account for its higher sensitivity. But the method requires limited pretreatment of the sample other than grinding and mixing to homogenize them. Although measurement time per sample is long (approximately 2.5 hours), a higher throughput might be achieved through full process automatization. Eisentraut et al. (2018) confirmed the suitability of using TED-GC-MS for the identification of microplastic types derived from tire wear in environmental samples. However, like pyrolysis GC, TED-GC-MS is also a destructive approach, and it does not provide sufficient information on the shape and size of MP particles, which could be crucial in the context of assessing the effects of MP on organisms and eco-systems. The bioavailability of MP particles is linked to their size and shape in the ecosystem (de Souza Machado et al. 2018).

4.4.2.7 Thermogravimetric Analysis

Another thermal analysis method used with MPs is thermogravimetry using differential scanning calorimetry (TGA-DSC; Majewsky et al. 2016). The principle behind TGA-DSC is the change of heat capacity during the phase transition of a polymer. It is popular because the technique is widely available, low cost, and straightforward to use. In differential scanning calorimetry (DSC) analysis, the sample MP is heated at a well-defined heating rate (Majewsky et al. 2016). During such temperature change, DSC calculates the heat flow difference between the sample and the reference material. Majewsky et al. (2016) considered TGA-DSC as a potential detection method for the determination of polyethylene (PE) and polypropylene (PP). Nevertheless, few polymers such as PVC, polyamide (PA) could not be recognized due to overlapping phase transition signals. DSC is an especially useful tool for assessing the degree of crystallinity of polymeric material (Rodríguez et al. 2018). However, reference materials are necessary for the identification of polymer types since each plastic product has different DSC characteristics (Huppertsberg and Knepper 2018). In addition, transition temperatures are affected by production parameters including additives, impurities, and branching of polymer chains.

4.4.3 Analytical Quality Assurance

During sampling, pre-treatment, and characterization, there is a high risk of contamination of the samples due to the ubiquity of synthetic polymers. For instance, environmental samples tend to be contaminated by the abraded particles from plastic equipment or airborne polymer fibers (Löder and Gerdts 2015). Special attention needs to be paid to sample collection and storage to avoid contamination. Instead, plastic glass containers should be used for sample storage. The laboratory control sample (LCS) or validation trials should always be included as an integral part of the analytical process. A field blank should be prepared and treated to the same procedures as the actual samples to assess any ambient contamination (Möller et al. 2020). If contamination does occur, it is important to determine whether the laboratory environment can be controlled more easily compared to collection/storage functions in the field. Without further validation studies and blanks, it is not possible to decide if the employed method was reliable, trustworthy, and valid. However, quality assurance/quality control has not been well recognized in past MP research. Möller et al. (2020) reported that even the reported validation of processing and interlaboratory comparisons of protocols are lacking in quality. They further pointed out the lack of regular internal quality control and external proficiency tests.

4.5 Summary and Outlook

The advantages and limitations of each technique in MP analysis, as discussed in this chapter are summarized in Table 4.4. Physical (e.g. size and color) and chemical (e.g. molecular structure) features are the two key characteristics of interest. Microscopy is a straightforward tool for the collection of physical characteristics of MPs, and it is especially well suited for large particles. For small particles with the size of < 1 mm, microscopic analysis in combination with chemical analysis such as vibrational spectroscopic or thermal analysis is generally suggested. Currently, infrared spectroscopy remains the routine method for the identification of the polymer type of MPs in environmental samples, due to the ease of handling and relatively short analytical time. When the size of the MP particle is <20 μm, Raman microscopy should be employed. Automated mapping spectroscopy (e.g. FPA-FTIR) is better suited for laboratory samples of known polymer types. Nevertheless, as Xu et al. (2019) points out several unavoidable obstacles persist in automated mapping spectroscopy (Xu et al. 2019). For instance, the reliability of library matching software in the automated routine is questionable as the likelihood of successful matching greatly depends on the comprehensiveness of the spectral library as well as the robustness of the matching algorithm. FPA-based FTIR imaging allows fast acquisition; however, the analysis time is quite high (10.75 hours for a filter size of 11 mm diameter (Löder et al. 2015). Chromatographic and thermogravimetric analyses are less commonly used for MP analysis and are time-consuming, labor-intensive, destructive, unsuitable for small particles, and unable to provide information on the shape or size of the MP. Overall, techniques for MP analysis can be characterized by trade-offs in precision (in resolution, polymer type identification, and quantification) and the time required to conduct the measurement, as displayed in Figure 4.8.

Several challenges make the collection and characterization of MPs from the complex marine environmental matrices complicated. The need to develop representative sampling designs is

Table 4.4 Advantages and limitations of the commonly used MP identification methods.

Techniques	Advantages	Limitations
Visual identification	• Simple, easy, fast • Cost-effective • Size, color and shape of particles can be detected easily	• Large errors due to subjectivity of the examiner • No chemical information • Time-consuming • Size limitation
Microscopic observation	• Simple, easy • Cost-effective • Size, color, and shape of particles can be detected easily	• Time-consuming • No chemical information • Large errors due to the subjectivity of the examiner
Electron microscopy	• High-resolution (<0.5 nm resolution) • Surface textures of MP particles • Chemical composition of samples can be identified by SEM-EDS	• Time and effort consuming • Sample needs to be well prepared • Expensive instrument
Infrared microscopy	• Reliable and nondestructive methods (except ATR-FTIR) • Smaller particles down to 20 μm can be analyzed by micro-FTIR • FPA-FTIR can identify several thousand particles through one single measurement • Automatic mapping (FPA-FTIR)	• Size limitation • Expensive instrument • Require experienced operators • Sample pre-treatments needed • Sensitivity to water
Raman microscopy	• Can detect with the size 1 μm • Reliable method. • Insensitivity to water • Nondestructive analysis • Non-contact analysis	• Fluorescence distortion • Expensive equipment • Sample pre-treatments needed • Time-consuming and sometime is destructive
Pyr GC-MS	• Polymer types and additives can be analyzed in one run • Shape, size, and color of the samples does not affect result • Reliable	• Time-consuming and destructive. • Morphological characterization is unavailable • Suitable for samples with sizes >100 mm
TED-GC-MS	• Faster than Pyr GC-MS • Higher sensitivity • Limited sample pretreatment	• Destructive • Lacks information on shape, size, and number of MP particles
Differential scanning calorimetry	• Cheap instrument • Easy	• Lacks information on shape, size, and number of MP particles • Destructive

crucial for accurately estimating the abundance of MPs at a given location. From a methodological point of view, estimations of abundance based on several limited samples do not reliably obtain that of the entire area being studied because of the high level of heterogeneity. Therefore selecting appropriate sampling strategies and locations to reliably represent the plastic contamination in a dynamic marine setting such as a beach is undoubtedly challenging (Löder and Gerdts 2015). Another challenge is that in aqueous environments the abundance changes temporally; the sample abundance only presents that at the time of sampling. There is also the possibility of changes

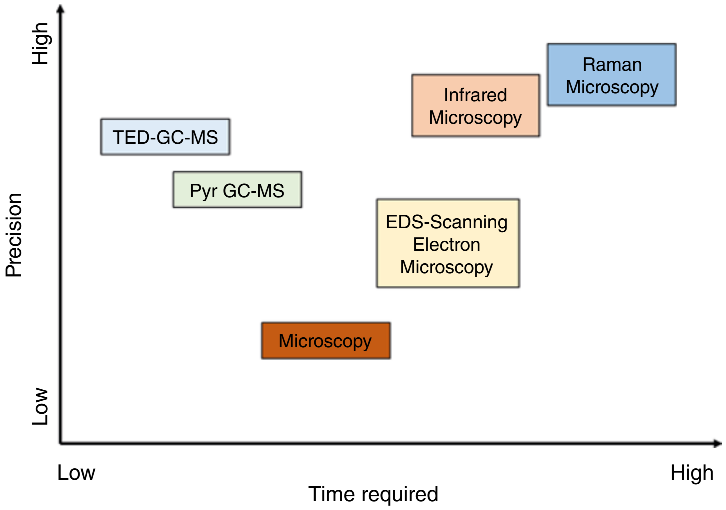


Figure 4.8 Comparison of some commonly used techniques in terms of precision (i.e. degrees of detail) and time required for data acquisition and analysis. *Note:* The relative location of each technique is estimated from the literature data (Elert et al. 2017; Silva et al. 2018b; Zarfl 2019).

suffered by the MP samples during preparation, chemical weathering, natural aging, and biochemical processes, which all have the potential to modify plastic features. Previous reports demonstrated that ultraviolet radiation, thermal oxidation, and humidity could alter the chemical structure of MP through oxidation reactions (see Chapter 8). A general challenge in abundance studies is the lack of a low-cost, high throughput technique to identify enumeration of MPs, allowing a larger number of samples to be processed quickly.

Size fractionation using sieves or filters with different pore sizes should be included prior to chemical analysis, as suggested by Uurasjärvi et al. (2020) who advised the reporting of particle sizes, numbers, and masses per sample in future studies (Uurasjärvi et al. 2020). The standardized application of size fractionation would facilitate better comparisons between different studies. Given a large amount of biological matter (e.g. fish gut contents, tissue, and suspended organic matter) typically encountered in marine environmental samples, and effective rapid digestion procedure is also needed. Additionally, Xu et al. (2020b) recommended the calculation of MP to the non-MP ratio for each sample; this ratio is useful for the comparison of different preparation protocols. This ratio is also beneficial to enhance toxicological research (Anger et al. 2018). Finally, reporting MP prevalence in a sample based on solely the number of particles per unit area or volume is not comprehensive since the size of particles and the relative sample size are also important. Therefore size distributions for each polymer category should be included for consistency and comparability.

4.6 Conclusions

Over all, an accurate and effective MP particle characterization underpins the basic understanding of the spatial and temporal prevalence of plastic contamination in the marine environment. It informs policy and plays an important role in influencing both industry and public opinions. However, the diversity of MPs that persist in the marine environment poses sampling and analytical challenges to achieve reliable quantification. This requires more improvement of existing analytical methods and the development of novel methodologies to reduce the time and effort in analysis without compromising accuracy and reliability. It is anticipated that fully or semi-automated analytical methods that integrate image and spectral analysis methods to capture the physical characteristics and chemical analysis offer a future direction for MP characterization.

References

Abbasi, S., Keshavarzi, B., Moore, F., Turner, A., Kelly, F.J., Dominguez, A.O. and Jaafarzadeh, N. (2019), Distribution and potential health impacts of microplastics and microrubbers in air and street dusts from Asaluyeh County, Iran. *Environmental Pollution*, 244: 153–164.

Akiyama, Y., Egawa, T., Koyano, K. and Moriwaki, H. (2020), Acoustic focusing of microplastics in microchannels: A promising continuous collection approach. *Sensors and Actuators B: Chemical*, 304: 127328.

Alnajar, N., Jha, A.N. and Turner, A. (2021), Impacts of microplastic fibres on the marine mussel, *Mytilus galloprovinciallis. Chemosphere*, 262: 128290.

Amélineau, F., Bonnet, D., Heitz, O., Mortreux, V., Harding, A.M.A., Karnovsky, N., Walkusz, W., et al. (2016), Microplastic pollution in the Greenland Sea: Background levels and selective contamination of planktivorous diving seabirds. *Environmental Pollution*, 219: 1131–1139.

Andrady, A. L., 2010. Using flow cytometry to detect micro-and nano-scale polymer particles. In: Arthur, C. and J. Baker (Eds), Proceedings of the Second Research Workshop on Microplastic Marine Debris, NOAA Technical Memorandum NOS-OR&R-39.

Andrady, A.L. (2011), Microplastics in the marine environment. *Marine Pollution Bulletin*, 62(8): 1596–1605.

Anger, P.M., von der Esch, E., Baumann, T., Elsner, M., Niessner, R. and Ivleva, N.P. (2018), Raman microspectroscopy as a tool for microplastic particle analysis. *TrAC Trends in Analytical Chemistry*, 109: 214–226.

Avio, C.G., Gorbi, S. and Regoli, F. (2015), Experimental development of a new protocol for extraction and characterization of microplastics in fish tissues: First observations in commercial species from the Adriatic Sea. *Marine Environmental Research*, 111: 18–26.

Avio, C.G., Gorbi, S., Milan, M., Benedetti, M., Fattorini, D., d'Errico, G., Pauletto, M., et al. (2015), Pollutants bioavailability and toxicological risk from microplastics to marine mussels. *Environmental Pollution*, 198: 211–222.

Bevilacqua, M., Bucci, R., Magrì, A.D., Magrì, A.L. and Marini, F. (2013), Data fusion for food authentication. Combining near and mid infrared to trace the origin of extra virgin olive oils. *NIR News*, 24(2): 12–15.

Brandon, J., Goldstein, M. and Ohman, M.D. (2016), Long-term aging and degradation of microplastic particles: comparing in situ oceanic and experimental weathering patterns. *Marine Pollution Bulletin*, 110(1): 299–308.

Browne, M.A., Dissanayake, A., Galloway, T.S., Lowe, D.M. and Thompson, R.C. (2008), Ingested Microscopic Plastic Translocates to the Circulatory System of the Mussel, Mytilus edulis (L.). *Environmental Science & Technology*, 42(13): 5026–5031.

Browne, M., Galloway, T. and Thompson, R. (2010), Spatial patterns of plastic debris along Estuarine shorelines. *Environmental Science & Technology*, 44 9: 3404–3409.

Browne, M.A., Crump, P., Niven, S.J., Teuten, E., Tonkin, A., Galloway, T. and Thompson, R. (2011), Accumulation of Microplastic on Shorelines Woldwide: Sources and Sinks. *Environmental Science & Technology*, 45(21): 9175–9179.

Cai, L., Wang, J., Peng, J., Tan, Z., Zhan, Z., Tan, X. and Chen, Q. (2017), Characteristic of microplastics in the atmospheric fallout from Dongguan city, China: preliminary research and first evidence. *Environmental Science and Pollution Research*, 24(32): 24928–24935.

Cai, H., Du, F., Li, L., Li, B., Li, J. and Shi, H. (2019), A practical approach based on FT-IR spectroscopy for identification of semi-synthetic and natural celluloses in microplastic investigation. *Science of the Total Environment*, 669: 692–701.

Carpenter, E.J. and Smith, K.L. (1972), Plastics on the Sargasso Sea surface. *Science*, 175(4027): 1240–1241.

Carson, H.S., Colbert, S.L., Kaylor, M.J. and McDermid, K.J. (2011), Small plastic debris changes water movement and heat transfer through beach sediments. *Marine Pollution Bulletin*, 62(8): 1708–1713.

Castillo, A.B., Al-Maslamani, I. and Obbard, J.P. (2016), Prevalence of microplastics in the marine waters of Qatar. *Marine Pollution Bulletin*, 111(1–2): 260–267.

Catarino, A.I., Thompson, R., Sanderson, W. and Henry, T.B. (2017), Development and optimization of a standard method for extraction of microplastics in mussels by enzyme digestion of soft tissues. *Environmental Toxicology and Chemistry*, 36(4): 947–951.

Ceccarini, A., Corti, A., Erba, F., Modugno, F., La Nasa, J., Bianchi, S. and Castelvetro, V. (2018), The Hidden Microplastics: New Insights and Figures from the Thorough Separation and Characterization of Microplastics and of Their Degradation Byproducts in Coastal Sediments. *Environmental Science & Technology*,52(10): 5634–5643.

Chen, G., Fu, Z., Yang, H. and Wang, J. (2020), An overview of analytical methods for detecting microplastics in the atmosphere. *TrAC Trends in Analytical Chemistry*, 130: 115981.

Claessens, M., Van Cauwenberghe, L., Vandegehuchte, M.B. and Janssen, C.R. (2013), New techniques for the detection of microplastics in sediments and field collected organisms. *Marine Pollution Bulletin*, 70(1): 227–233.

Cole, M., Webb, H., Lindeque, P.K., Fileman, E.S., Halsband, C. and Galloway, T.S. (2014), Isolation of microplastics in biota-rich seawater samples and marine organisms. *Scientific Reports*, 4(1): 4528.

Collard, F., Gilbert, B., Eppe, G., Parmentier, E. and Das, K. (2015), Detection of Anthropogenic Particles in Fish Stomachs: An Isolation Method Adapted to Identification by Raman Spectroscopy. *Archives of Environmental Contamination and Toxicology*, 69(3): 331–339.

Collard, F., Gilbert, B., Compère, P., Eppe, G., Das, K., Jauniaux, T. and Parmentier, E. (2017), Microplastics in livers of European anchovies (*Engraulis encrasicolus*, L.). *Environmental Pollution*, 229: 1000–1005.

Converton, GA, Collicutt, B., Gurney-Smith, H.J., Pearce, C.M., Dower, J.F., and Ross, P.S., Dudas, S. (2019), Microplastics in bivalves and their habitat in relation to shellfish aquaculture proximity in coastal British Columbia, Canada. *Aquaculture Environment Interactions*, 11: 357–374.

Corcoran, P.L., Biesinger, M.C. and Grifi, M. (2009), Plastics and beaches: a degrading relationship. *Marine Pollution Bulletin*, 58(1): 80–84.

Courtene-Jones, W., Quinn, B., Murphy, F., Gary, S.F. and Narayanaswamy, B.E. (2017), Optimisation of enzymatic digestion and validation of specimen preservation methods for the analysis of ingested microplastics. *Analytical Methods*, 9(9): 1437–1445.

Cózar, A., Echevarría, F., González-Gordillo, J.I., Irigoien, X., Úbeda, B., Hernández-León, S., Palma, Á.T., et al. (2014), Plastic debris in the open ocean. *Proceedings of the National Academy of Sciences*, 111(28): 10239–10244.

Crawford, C.B. and Quinn, B. (2017), Microplastic collection techniques. In: Crawford, C.B., Quinn, B. (Eds.), *Microplastic Pollutants*, Elsevier, Amsterdam, Netherlands, pp. 179–202.

Davidson, K. and Dudas, S.E. (2016), Microplastic Ingestion by Wild and Cultured Manila Clams (Venerupis philippinarum) from Baynes Sound, British Columbia. *Archives of Environmental Contamination and Toxicology*, 71(2): 147–156.

de Souza Machado, A.A., Lau, C.W., Till, J., Kloas, W., Lehmann, A., Becker, R. and Rillig, M.C. (2018), Impacts of Microplastics on the Soil Biophysical Environment. *Environmental Science & Technology*, 52(17): 9656–9665.

De Witte, B., Devriese, L., Bekaert, K., Hoffman, S., Vandermeersch, G., Cooreman, K. and Robbens, J. (2014), Quality assessment of the blue mussel (*Mytilus edulis*): comparison between commercial and wild types. *Marine Pollution Bulletin*, 85(1): 146–155.

Dehaut, A., Cassone, A.-L., Frère, L., Hermabessiere, L., Himber, C., Rinnert, E., Rivière, G., et al. (2016), Microplastics in seafood: benchmark protocol for their extraction and characterization. *Environmental Pollution*, 215: 223–233.

Dehghani, S., Moore, F. and Akhbarizadeh, R. (2017), Microplastic pollution in deposited urban dust, Tehran metropolis, *Iran. Environmental Science and Pollution Research*, 24(25): 20360–20371.

Dekiff, J.H., Remy, D., Klasmeier, J. and Fries, E. (2014), Occurrence and spatial distribution of microplastics in sediments from Norderney. *Environmental Pollution*, 186: 248–256.

Desforges, J.-P.W., Galbraith, M. and Ross, P.S. (2015), Ingestion of microplastics by zooplankton in the northeast Pacific Ocean. *Archives of Environmental Contamination and Toxicology*, 69(3): 320–330.

Devriese, L.I., van der Meulen, M.D., Maes, T., Bekaert, K., Paul-Pont, I., Frère, L., Robbens, J., et al. (2015), Microplastic contamination in brown shrimp (Crangon crangon, Linnaeus 1758) from coastal waters of the Southern North Sea and Channel area. *Marine Pollution Bulletin*,98(1–2): 179–187.

Dowarah, K., Patchaiyappan, A., Thirunavukkarasu, C., Jayakumar, S. and Devipriya, S.P. (2020), Quantification of microplastics using Nile Red in two bivalve species Perna viridis and Meretrix meretrix from three estuaries in Pondicherry, India and microplastic uptake by local communities through bivalve diet. *Marine Pollution Bulletin*, 153: 110982.

Eisentraut, P., Dümichen, E., Ruhl, A.S., Jekel, M., Albrecht, M., Gehde, M. and Braun, U. (2018), Two birds with one stone – fast and simultaneous analysis of microplastics: microparticles derived from thermoplastics and tire wear. *Environmental Science & Technology Letters*,5(10): 608–613.

Elert, A.M., Becker, R., Duemichen, E., Eisentraut, P., Falkenhagen, J., Sturm, H. and Braun, U. (2017), Comparison of different methods for MP detection: what can we learn from them, and why asking the right question before measurements matters? *Environmental Pollution*, 231: 1256–1264.

Eskandarloo, H., Kierulf, A. and Abbaspourrad, A. (2017), Light-harvesting synthetic nano- and micromotors: a review. *Nanoscale*, 9(34): 12218–12230.

Farrell, P. and Nelson, K. (2013), Trophic level transfer of microplastic: Mytilus edulis (L.) to Carcinus maenas (L.). *Environmental Pollution*, 177: 1–3.

Fries, E., Dekiff, J.H., Willmeyer, J., Nuelle, M.-T., Ebert, M. and Remy, D. (2013), Identification of polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and scanning electron microscopy. *Environmental Science: Processes & Impacts*,15(10): 1949–1956.

Fuller, S. and Gautam, A. (2016), A Procedure for Measuring Microplastics using Pressurized Fluid Extraction. *Environmental Science & Technology*, 50(11): 5774–5780.

Gaspar, T.R., Chi, R.J., Parrow, M.W. and Ringwood, A.H. (2018), Cellular Bioreactivity of Micro- and Nano-Plastic Particles in Oysters. *Frontiers in Marine Science*, 5: 345.

Ghosal, S., Chen, M., Wagner, J., Wang, Z.-M. and Wall, S. (2018), Molecular identification of polymers and anthropogenic particles extracted from oceanic water and fish stomach - A Raman micro-spectroscopy study. *Environmental Pollution*, 233: 1113–1124.

Giacomucci, L., Raddadi, N., Soccio, M., Lotti, N. and Fava, F. (2020), Biodegradation of polyvinyl chloride plastic films by enriched anaerobic marine consortia. *Marine Environmental Research*, 158, 104949.

Gohla, J., Bračun, S., Gretschel, G., Koblmüller, S., Maximilian, W. and Pacher, C. (2020), Potassium Carbonate (K2CO3) {\textendash} A cheap, non-toxic and high-density floating solution for microplastic isolation from beach sediments. *BioRxiv*, Cold Spring Harbor Laboratory. https://doi.org/10.1101/2020.11.17.386417

Goss, H., Jaskiel, J. and Rotjan, R. (2018), Thalassia testudinum as a potential vector for incorporating microplastics into benthic marine food webs. *Marine Pollution Bulletin*, 135: 1085–1089.

Goswami, P., Vinithkumar, N.V. and Dharani, G. (2020), First evidence of microplastics bioaccumulation by marine organisms in the Port Blair Bay, Andaman Islands. *Marine Pollution Bulletin*, 155: 111163.

Gowen, A.A., O'Donnell, C.P., Cullen, P.J., Downey, G. and Frias, J.M. (2007), Hyperspectral imaging – an emerging process analytical tool for food quality and safety control. *Trends in Food Science & Technology*, 18(12): 590–598

Gutow, L., Eckerlebe, A., Giménez, L. and Saborowski, R. (2016), Experimental evaluation of seaweeds as a vector for microplastics into marine food webs. *Environmental Science & Technology*, 50(2): 915–923.

Hartmann, N.B., Hüffer, T., Thompson, R.C., Hassellöv, M., Verschoor, A., Daugaard, A.E., Rist, S., et al. (2019), *Are We Speaking the Same Language? Recommendations for a Definition and Categorization Framework for Plastic Debris*. ACS Publications.

Hendrickson, E., Minor, E.C. and Schreiner, K. (2018), Microplastic abundance and composition in Western Lake Superior as determined via microscopy, Pyr-GC/MS, and FTIR. *Environmental Science & Technology*,52(4): 1787–1796.

Hengstmann, E. and Fischer, E.K. (2019), Nile red staining in microplastic analysis – proposal for a reliable and fast identification approach for large microplastics. *Environmental Monitoring and Assessment*, 191(10): 612.

Heo, N.W., Hong, S.H., Han, G.M., Hong, S., Lee, J., Song, Y.K., Jang, M., et al. (2013), Distribution of small plastic debris in cross-section and high strandline on Heungnam beach, South Korea. *Ocean Science Journal*, 48(2): 225–233.

Hidalgo-Ruz, V., Gutow, L., Thompson, R.C. and Thiel, M. (2012), Microplastics in the Marine Environment: A Review of the Methods Used for Identification and Quantification. *Environmental Science & Technology*, 46(6): 3060–3075.

Huppertsberg, S. and Knepper, T.P. (2018), Instrumental analysis of microplastics – benefits and challenges. *Analytical and Bioanalytical Chemistry*, 410(25): 6343–6352.

Imhof, H.K., Schmid, J., Niessner, R., Ivleva, N.P. and Laforsch, C. (2012), A novel, highly efficient method for the separation and quantification of plastic particles in sediments of aquatic environments. *Limnology and Oceanography: Methods*, 10: 524–537.

Ioakeimidis, C., Zeri, C., Kaberi, H., Galatchi, M., Antoniadis, K., Streftaris, N., Galgani, F., et al. (2014), A comparative study of marine litter on the seafloor of coastal areas in the Eastern Mediterranean and Black Seas. *Marine Pollution Bulletin*, 89(1): 296–304.

Ismail, A., N.M.B., Adilah and M.J., Nurulhudha. (2009), Plastic pellets along Kuala Selangor-Sepang coastline. *Applied Biology Journal*, 38 (1): 85–88.

Isobe, A., Kubo, K., Tamura, Y., Kako, S., Nakashima, E. and Fujii, N. (2014), Selective transport of microplastics and mesoplastics by drifting in coastal waters. *Marine Pollution Bulletin*, 89(1): 324–330.

Ivar do Sul, J.A., Costa, M.F., Barletta, M. and Cysneiros, F.J.A. (2013), Pelagic microplastics around an archipelago of the Equatorial Atlantic. *Marine Pollution Bulletin*, 75(1): 305–309.

Jahan, S., Strezov, V., Weldekidan, H., Kumar, R., Kan, T., Sarkodie, S.A., He, J., et al. (2019), Interrelationship of microplastic pollution in sediments and oysters in a seaport environment of the eastern coast of Australia. *Science of the Total Environment*, 695: 133924.

Jurado-Sánchez, B. and Wang, J. (2018), Micromotors for environmental applications: a review. *Environmental Science: Nano*, 5(7): 1530–1544.

Kanhai, L.D.K., Gårdfeldt, K., Lyashevska, O., Hassellöv, M., Thompson, R.C. and O'Connor, I. (2018), Microplastics in sub-surface waters of the Arctic Central Basin. *Marine Pollution Bulletin*, 130: 8–18.

Karakolis, E.G., Nguyen, B., You, J.B., Rochman, C.M. and Sinton, D. (2019), Fluorescent dyes for visualizing microplastic particles and fibers in laboratory-based studies. *Environmental Science & Technology Letters*, 6(6): 334–340.

Karlsson, T.M., Grahn, H., van Bavel, B. and Geladi, P. (2016), Hyperspectral imaging and data analysis for detecting and determining plastic contamination in seawater filtrates. *Journal of Near Infrared Spectroscopy*, 24(2): 141–149.

Kershaw, P., Turra, A. and Galgani, F. (2019), Guidelines for the Monitoring and Assessment of Plastic Litter in the Ocean-GESAMP Reports and Studies No. 99. *GESAMP Reports and Studies*.

Li, J., Yang, D., Li, L., Jabeen, K. and Shi, H. (2015), Microplastics in commercial bivalves from China. *Environmental Pollution*, 207: 190–195.

Li, J., Qu, X., Su, L., Zhang, W., Yang, D., Kolandhasamy, P., Li, D., et al. (2016), Microplastics in mussels along the coastal waters of China. *Environmental Pollution*, 214: 177–184.

Lim, S.J., Wan Aida, W.M., Maskat, M.Y., Mamot, S., Ropien, J. and Mazita Mohd, D. (2014), Isolation and antioxidant capacity of fucoidan from selected Malaysian seaweeds. *Food Hydrocolloids*, 42: 280–288.

Lin, L., Ma, L.-S., Li, H.-X., Pan, Y.-F., Liu, S., Zhang, L., Peng, J.-P., et al. (2020), Low level of microplastic contamination in wild fish from an urban estuary. *Marine Pollution Bulletin*, 160: 111650.

Löder, M.G.J. and Gerdts, G. (2015), Methodology used for the detection and identification of microplastics-A critical appraisal. *Marine Anthropogenic Litter*, pp. 201–227.

Löder, M.G.J., Kuczera, M., Mintenig, S., Lorenz, C. and Gerdts, G. (2015), Focal plane array detector-based micro-Fourier-transform infrared imaging for the analysis of microplastics in environmental samples. *Environmental Chemistry*, 12(5): 563–581.

Lu, Y., Zhang, Y., Deng, Y., Jiang, W., Zhao, Y., Geng, J., Ding, L., et al. (2016), Uptake and accumulation of polystyrene microplastics in zebrafish (*Danio rerio*) and toxic effects in liver. *Environmental Science & Technology*, 50(7): 4054–4060.

Lusher, A.L., Welden, N.A., Sobral, P. and Cole, M. (2017), Sampling, isolating and identifying microplastics ingested by fish and invertebrates. *Analytical Methods*, 9(9): 1346–1360.

Maes, T., Jessop, R., Wellner, N., Haupt, K. and Mayes, A.G. (2017), A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile Red. *Scientific Reports*, 7(1): 44501.

Majewsky, M., Bitter, H., Eiche, E. and Horn, H. (2016), Determination of microplastic polyethylene (PE) and polypropylene (PP) in environmental samples using thermal analysis (TGA-DSC). *Science of the Total Environment*, 568: 507–511.

Mani, T., Frehland, S., Kalberer, A. and Burkhardt-Holm, P. (2019), Using castor oil to separate microplastics from four different environmental matrices. *Analytical Methods*, 11(13): 1788–1794.

Marić, M., Grassino, A.N., Zhu, Z., Barba, F.J., Brnčić, M. and Rimac Brnčić, S. (2018), An overview of the traditional and innovative approaches for pectin extraction from plant food wastes and by-products: Ultrasound-, microwaves-, and enzyme-assisted extraction. *Trends in Food Science and Technology*, 76(January): 28–37.

Martins, J. and Sobral, P. (2011), Plastic marine debris on the Portuguese coastline: A matter of size? *Marine Pollution Bulletin*, 62(12): 2649–2653.

McGaw, I.J. and Curtis, D.L. (2013), A review of gastric processing in decapod crustaceans. *Journal of Comparative Physiology B*, 183(4): 443–465.

Mecozzi, M., Pietroletti, M. and Monakhova, Y.B. (2016), FTIR spectroscopy supported by statistical techniques for the structural characterization of plastic debris in the marine environment: Application to monitoring studies. *Marine Pollution Bulletin*, 106(1): 155–161.

Mohamed Nor, N.H. and Obbard, J.P. (2014), Microplastics in Singapore's coastal mangrove ecosystems. *Marine Pollution Bulletin*, 79(1): 278–283.

Möller, J.N., Löder, M.G.J. and Laforsch, C. (2020), Finding Microplastics in Soils: a Review of Analytical Methods. *Environmental Science & Technology*, 54(4): 2078–2090.

Nuelle, M.-T., Dekiff, J.H., Remy, D. and Fries, E. (2014), A new analytical approach for monitoring microplastics in marine sediments. *Environmental Pollution*, 184: 161–169.

Ohkubo, N., Ito, M., Hano, T., Kono, K. and Mochida, K. (2020), Estimation of the uptake and gut retention of microplastics in juvenile marine fish: mummichogs (*Fundulus heteroclitus*) and red seabreams (*Pagrus major*). *Marine Pollution Bulletin*, 160: 111630.

Ory, N., Chagnon, C., Felix, F., Fernández, C., Ferreira, J.L., Gallardo, C., Garcés Ordóñez, O., et al. (2018a), Low prevalence of microplastic contamination in planktivorous fish species from the southeast Pacific Ocean. *Marine Pollution Bulletin*, 127: 211–216.

Ory, N.C., Gallardo, C., Lenz, M. and Thiel, M. (2018b), Capture, swallowing, and egestion of microplastics by a planktivorous juvenile fish. *Environmental Pollution*, 240: 566–573.

Pearson, K. (1901), Principal components analysis. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 6(2): 559.

Phuong, N.N., Poirier, L., Lagarde, F., Kamari, A. and Zalouk-Vergnoux, A. (2018a), Microplastic abundance and characteristics in French Atlantic coastal sediments using a new extraction method. *Environmental Pollution*, 243(A): 228–237.

Phuong, N.N., Poirier, L., Pham, Q.T., Lagarde, F. and Zalouk-Vergnoux, A. (2018b), Factors influencing the microplastic contamination of bivalves from the French Atlantic coast: location, season and/or mode of life? *Marine Pollution Bulletin*, 129(2): 664–674.

PlasticsEurope. (2019), *Plastics – the Facts 2019*. <https://plasticseurope.org/wp-content/uploads/2021/10/2019-Plastics-the-facts.pdf>.

Prata, J.C., da Costa, J.P., Lopes, I., Duarte, A.C. and Rocha-Santos, T. (2019), Effects of microplastics on microalgae populations: A critical review. *The Science of the Total Environment*, 665: 400–405.

Quinn, B., Murphy, F. and Ewins, C. (2017), Validation of density separation for the rapid recovery of microplastics from sediment. *Analytical Methods*, 9(9): 1491–1498.

Rajakumar, K., Sarasvathy, V., Chelvan, A.T., Chitra, R. and Vijayakumar, C.T. (2009), Natural weathering studies of polypropylene. *Journal of Polymers and the Environment*, 17(3): 191.

Renner, G., Schmid, T.C. and Schram, J. (2017), Characterization and quantification of microplastics by infrared spectroscopy. *Comprehensive Analytical Chemistry*, 75: 67–118.

Renner, G., Schmidt, T.C. and Schram, J. (2018), Analytical methodologies for monitoring micro (nano) plastics: which are fit for purpose? *Current Opinion in Environmental Science & Health*, 1: 55–61.

Ribeiro-Claro, P., Nolasco, M.M. and Araújo, C. (2017), Characterization of microplastics by Raman spectroscopy. *Comprehensive Analytical Chemistry*, 75: 119–151.

Rist, S., Steensgaard, I.M., Guven, O., Nielsen, T.G., Jensen, L.H., Møller, L.F. and Hartmann, N.B. (2019), The fate of microplastics during uptake and depuration phases in a blue mussel exposure system. *Environmental Toxicology and Chemistry*, 38(1): 99–105.

Roch, S. and Brinker, A. (2017), Rapid and efficient method for the detection of microplastic in the gastrointestinal tract of fishes. *Environmental Science & Technology*, 51(8): 4522–4530.

Rochman, C.M., Browne, M.A., Underwood, A.J., van Franeker, J.A., Thompson, R.C. and Amaral-Zettler, L.A. (2016), The ecological impacts of marine debris: unraveling the demonstrated evidence from what is perceived. *Ecology*, 97(2): 302–312.

Rodríguez, C. M., Sierra, I., Pérez, P. A., Fornaro, L. (2018) Identification and quantitation of semi-crystalline microplastics using image analysis and differential scanning calorimetry. *Environmental Science and Pollution Research International*, 25(17): 16767–16775.

Rusch, A., Huettel, M. and Forster, S. (2000), Particulate organic matter in permeable marine sands – dynamics in time and depth. *Estuarine, Coastal and Shelf Science*, 51(4): 399–414.

Santana, M.F.M., Ascer, L.G., Custódio, M.R., Moreira, F.T. and Turra, A. (2016), Microplastic contamination in natural mussel beds from a Brazilian urbanized coastal region: Rapid evaluation through bioassessment. *Marine Pollution Bulletin*, 106(1–2): 183–189.

Santos, J. Dos and Jobling, M. (1992), A model to describe gastric evacuation in cod (Gadus morhua L.) fed natural prey. *ICES Journal of Marine Science*, 49(2): 145–154.

Seng, N., Lai, S., Fong, J., Saleh, M.F., Cheng, C., Cheok, Z.Y. and Todd, P.A. (2020), Early evidence of microplastics on seagrass and macroalgae. *Marine and Freshwater Research*, 71(8): 922–928.

Serranti, S., Palmieri, R., Bonifazi, G. and Cózar, A. (2018), Characterization of microplastic litter from oceans by an innovative approach based on hyperspectral imaging. *Waste Management*, 76: 117–125.

Shan, J., Zhao, J., Zhang, Y., Liu, L., Wu, F. and Wang, X. (2019), Simple and rapid detection of microplastics in seawater using hyperspectral imaging technology. *Analytica Chimica Acta*, 1050: 161–168.

Shaw, D.G. and Day, R.H. (1994), Colour-and form-dependent loss of plastic micro-debris from the North Pacific Ocean. *Marine Pollution Bulletin*, 28(1): 39–43.

Shim, W.J., Hong, S.H. and Eo, S.E. (2017), Identification methods in microplastic analysis: a review. *Analytical Methods*, 9(9): 1384–1391.

Sierra, I., Chialanza, M.R., Faccio, R., Carrizo, D., Fornaro, L. and Pérez-Parada, A. (2020), Identification of microplastics in wastewater samples by means of polarized light optical microscopy. *Environmental Science and Pollution Research*, 27(7): 7409–7419.

Silva, A. de S. e., de Magalhães, W.T., Moreira, L.M., Rocha, M.V.P. and Bastos, A.K.P. (2018a), Microwave-assisted extraction of polysaccharides from Arthrospira (Spirulina) platensis using the concept of green chemistry. *Algal Research*, 35(March): 178–184.

Silva, A. de S. e, de Magalhães, W.T., Moreira, L.M., Rocha, M.V.P. and Bastos, A.K.P. (2018b), Microwave-assisted extraction of polysaccharides from Arthrospira (Spirulina) platensis using the concept of green chemistry. *Algal Research*, 35: 178–184.

Song, Y.K., Hong, S.H., Jang, M., Han, G.M., Rani, M., Lee, J. and Shim, W.J. (2015), A comparison of microscopic and spectroscopic identification methods for analysis of microplastics in environmental samples. *Marine Pollution Bulletin*, 93(1–2): 202–209.

Stanton, T., Johnson, M., Nathanail, P., Gomes, R.L., Needham, T. and Burson, A. (2019), Exploring the efficacy of nile red in microplastic quantification: a costaining approach. *Environmental Science & Technology Letters*, 6(10): 606–611.

Stolte, A., Forster, S., Gerdts, G. and Schubert, H. (2015), Microplastic concentrations in beach sediments along the German Baltic coast. *Marine Pollution Bulletin*, 99(1–2): 216–229.

Sundbæk, K.B., Koch, I.D.W., Villaro, C.G., Rasmussen, N.S., Holdt, S.L. and Hartmann, N.B. (2018), Sorption of fluorescent polystyrene microplastic particles to edible seaweed Fucus vesiculosus. *Journal of Applied Phycology*, 30(5): 2923–2927.

Thompson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., McGonigle, D., et al. (2004), Lost at sea: where is all the plastic? *Science*, 304(5672): 838.

Türker-Kaya, S. and Huck, C.W. (2017), A review of mid-infrared and near-infrared imaging: principles, concepts and applications in plant tissue analysis. *Molecules*, 22(1): 168.

Uurasjärvi, E., Hartikainen, S., Setälä, O., Lehtiniemi, M. and Koistinen, A. (2020), Microplastic concentrations, size distribution, and polymer types in the surface waters of a northern European lake. *Water Environment Research*, 92(1): 149–156.

Van Cauwenberghe, L. and Janssen, C.R. (2014), Microplastics in bivalves cultured for human consumption. *Environmental Pollution*, 193: 65–70.

Van Cauwenberghe, L., Claessens, M., Vandegehuchte, M.B. and Janssen, C.R. (2015), Microplastics are taken up by mussels (Mytilus edulis) and lugworms (Arenicola marina) living in natural habitats. *Environmental Pollution*, 199: 10–17.

von Friesen, L.W., Granberg, M.E., Hassellöv, M., Gabrielsen, G.W. and Magnusson, K. (2019), An efficient and gentle enzymatic digestion protocol for the extraction of microplastics from bivalve tissue. *Marine Pollution Bulletin*, 142: 129–134.

Waite, H.R., Donnelly, M.J. and Walters, L.J. (2018), Quantity and types of microplastics in the organic tissues of the eastern oyster Crassostrea virginica and Atlantic mud crab Panopeus herbstii from a Florida estuary. *Marine Pollution Bulletin*, 129(1): 179–185.

Walkinshaw, C., Lindeque, P.K., Thompson, R., Tolhurst, T. and Cole, M. (2020), Microplastics and seafood: lower trophic organisms at highest risk of contamination. *Ecotoxicology and Environmental Safety*, 190: 110066.

Wang, Z.-M., Wagner, J., Ghosal, S., Bedi, G. and Wall, S. (2017), SEM/EDS and optical microscopy analyses of microplastics in ocean trawl and fish guts. *Science of the Total Environment*, 603: 616–626.

Wang, L., Kaeppler, A., Fischer, D. and Simmchen, J. (2019), Photocatalytic TiO2 Micromotors for Removal of Microplastics and Suspended Matter. *ACS Applied Materials & Interfaces*, 11(36): 32937–32944.

Wang, S., Wang, Y., Liang, Y., Cao, W., Sun, C., Ju, P. and Zheng, L. (2020), The interactions between microplastic polyvinyl chloride and marine diatoms: Physiological, morphological, and growth effects. *Ecotoxicology and Environmental Safety*, 203: 111000.

Winkler, A., Santo, N., Ortenzi, M.A., Bolzoni, E., Bacchetta, R. and Tremolada, P. (2019), Does mechanical stress cause microplastic release from plastic water bottles? *Water Research*, 166: 115082.

Workman Jr, J. and Weyer, L. (2012), *Practical Guide and Spectral Atlas for Interpretive Near-infrared Spectroscopy*. CRC Press, Boca Raton, Florida, pp. 89–96.

Wright, S.L., Thompson, R.C. and Galloway, T.S. (2013), The physical impacts of microplastics on marine organisms: a review. *Environmental Pollution*, 178: 483–492.

Xu, J.-L. and Gowen, A.A. (2019), Investigation of plasticizer aggregation problem in casein based biopolymer using chemical imaging. *Talanta*, 193: 128–138.

Xu, J.-L., Thomas, K. V, Luo, Z. and Gowen, A.A. (2019), FTIR and Raman imaging for microplastics analysis: state of the art, challenges and prospects. *TrAC Trends in Analytical Chemistry*, 119: 115629.

Xu, J.-L., Hassellöv, M., Yu, K. and Gowen, A.A. (2020a), Microplastic characterization by infrared spectroscopy. In: Rocha-Santos, T., Costa, M. and Mouneyrac, C. (Eds.), *Handbook of Microplastics in the Environment*, Springer International Publishing, Cham, pp. 1–33.

Xu, J., Lesniak-Podsiadlo, A. and Gowen, A.A. (2020b), Predictive modelling of the in vitro responses of pre-osteoblastic MC3T3-E1 cells on polymeric surfaces using Fourier transform infrared spectroscopy. *ACS Applied Materials & Interfaces.* doi:10.1021/acsami.0c04261.

Xu, J.-L., Hugelier, S., Zhu, H. and Gowen, A.A. (2021), Deep learning for classification of time series spectral images using combined multi-temporal and spectral features. *Analytica Chimica Acta*, 1143: 9–20.

Zarfl, C. (2019), Promising techniques and open challenges for microplastic identification and quantification in environmental matrices. *Analytical and Bioanalytical Chemistry*, 411: 1–14.

Zhang, C., Chen, X., Wang, J. and Tan, L. (2017), Toxic effects of microplastic on marine microalgae Skeletonema costatum: Interactions between microplastic and algae. *Environmental Pollution*, 220: 1282–1288.

Zhang, S., Yang, X., Gertsen, H., Peters, P., Salánki, T. and Geissen, V. (2018), A simple method for the extraction and identification of light density microplastics from soil. *Science of the Total Environment*, 616–617: 1056–1065.

Zhu, Z., Wang, S., Zhao, F., Wang, S., Liu, F. and Liu, G. (2019), Joint toxicity of microplastics with triclosan to marine microalgae Skeletonema costatum. *Environmental Pollution*, 246: 509–517.

Zhu, C., Kanaya, Y., Nakajima, R., Tsuchiya, M., Nomaki, H., Kitahashi, T. and Fujikura, K. (2020), Characterization of microplastics on filter substrates based on hyperspectral imaging: Laboratory assessments. *Environmental Pollution*: 114296.

5

Estimating Microplastics in Deep Water

Winnie Courtene-Jones[1], Kai Liu[2], and Daoji Li[2]

[1] *International Marine Litter Research Unit, School of Biological and Marine Sciences, University of Plymouth, Drake Circus, Plymouth, Devon, United Kingdom*
[2] *State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai, China*

5.1 Introduction

Over the last seven decades, since the mass production of plastic commenced, the quantities of mismanaged waste entering the environment have continued to increase (Borrelle et al. 2020), in line with global plastic consumption (Geyer et al. 2017; PlasticsEurope 2019). Since the 1950s, the total emissions of buoyant plastics into the marine environment is estimated to have amounted to tens of millions of metric tons (Geyer et al. 2017; Jambeck et al. 2015). The vast majority of plastics entering the marine environment originates from land-based sources and therefore enters the ocean at its surface, where they either sink or float depending on their density. Approximately two-third of the plastics produced annually consist of polymers with a density similar to, or lower than seawater (Geyer et al. 2017) and consequently float at the surface of the ocean where their transport is influenced by ocean currents, waves, and wind (Lebreton et al. 2012; van Sebille et al. 2020).

Extensive monitoring efforts of plastics within surface waters has yielded a reasonable global coverage (reviewed in Burns and Boxall (2018)) and furthered the understanding of quantities of plastics afloat in the ocean (Barrows et al. 2018; Suaria et al. 2020; van Sebille et al. 2015b). Yet empirical studies report up to 100 times less plastic afloat at the ocean surface than is expected (Cozar et al. 2014; Eriksen et al. 2014), with a conspicuous lack of microplastics <1 mm in diameter. Furthermore, while some multidecadal analyses indicate increasing trends in floating plastics as one might expect from increasing emissions into the ocean (Goldstein et al. 2012; Thompson et al. 2004), such trends are noticeably absent from other investigations (Beer et al. 2018; Law et al. 2010). The discrepancies between observational data and the estimated inputs (Geyer et al. 2017; Jambeck et al. 2015) have prompted several scientific papers to pose the question, “where is the missing plastic?” (Cozar et al. 2014; Thompson et al. 2004).

A number of hypotheses were proposed to explain the lower than expected quantities of (micro) plastics in surface waters (summarized in Andrady 2017; Kane and Clare 2019). These include (i) incomplete observations leading to under-reported quantities of plastics present in the oceans, (ii) the degradation of plastics into minute fragments below size detection limits, (iii) stranding of debris on coastlines, (iv) ingestion of microplastics by marine species, or (v) the settlement of plastics to the seafloor. As research focussed on understanding where these “missing plastics” are located has intensified, it has motivated investigation into the fate of microplastics beyond surface waters.

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

While far from sight, the deep sea is of global importance and constitutes the largest habitat on Earth. The deep ocean not only supports some of the highest levels of biodiversity (Ramirez-Llodra et al. 2010; Serpetti et al. 2013; Snelgrove and Smith 2002) but also is a major sink of dissolved greenhouses gas, methane oxidation, nutrient regeneration, and valuable resources such as mineral deposits and energy reserves (Thurber et al. 2014). While localized activities such as trawling and seabed mining, as well as events such as oil spills, have exerted pressures on the deep-ocean environment, the sheer size and inaccessibility of the deep ocean have broadly limited direct anthropogenic impacts.

Easily dispersed pollutants, such as microplastics, have the ability to permeate throughout the ocean. Studies have documented the widespread presence of plastics within the deep sea (Bergmann et al. 2017; Courtene-Jones et al. 2017; Jamieson et al. 2019; Kanhai et al. 2018; Woodall et al. 2014), and it is considered that much of the aforementioned "lost" 99% of ocean plastics may have sunk away from the surface toward the ocean depths (Egger et al. 2020). Recent evidence suggests that microplastics may rapidly reach the seabed and have been present for a number of decades (Courtene-Jones et al. 2019, 2020; Martin et al. 2017). While microplastics research has increased within this realm, the majority of studies have focused on deep-sea sediments, and by comparison, there is a paucity of knowledge regarding microplastics within the deep-water column. Yet such investigation is vital to elucidate the distribution and dynamic behavior of microplastics, which in turn will influence the associated ecological risks.

5.2 Sampling Methods

Based on sampling techniques, the collection of microplastic samples in the subsurface water could be universally ascribed into three protocols: (i) bulk water sampling (Bagaev et al. 2017, 2018; Cordova et al. 2018; Dai et al. 2018; Di Mauro et al. 2017; Ding et al. 2019; Kanhai et al. 2018; Peng et al. 2018; Uurasjärvi et al. 2021), (ii) net sampling (Castillo et al. 2020; Lattin et al. 2004; Lenaker et al. 2019), and (iii) submersible pumps/in situ filtration devices (Choy et al. 2019; Liu et al. 2019; Song et al. 2018; Zobkov et al. 2019). The aforementioned sampling methods could be applied to some aquatic environments, each with their own advantages but have led to difficulty when trying to make regional comparison. For the bulk collection, this sampling technique usually enables fast collection of water samples at specific depth, which greatly contributes to lower volume sampling of microplastics research. Sampling instruments include a plexiglass water sampler (Ding et al. 2019) (Figure 5.1c), a Rosette sampler system (CTD sampler) (Bagaev et al. 2017, 2018; Cordova et al. 2018; Dai et al. 2018; Di Mauro et al. 2017; Kanhai et al. 2018) (Figure 5.1b), and a lander system equipped with Niskin bottles (Peng et al. 2018) (Figure 5.1g). Especially for microplastics sampling in deep-ocean water, a CTD sampler has been applied in some regions of North Atlantic Ocean (Courtene-Jones et al. 2017), Arctic Ocean (Kanhai et al. 2018), Pacific Ocean (Dai et al. 2018), Indian Ocean (Cordova and Hernawan 2018), and Baltic Sea (Bagaev et al. 2017). In addition, suspended microplastics in the water column could also be sampled using vertical or oblique trawls. The collection of microplastics samples was primarily performed using plankton trawls (Baini et al. 2018; Di Mauro et al. 2017; Doyle et al. 2011; Goldstein et al. 2013; Gorokhova 2015; Güven et al. 2017; Lefebvre et al. 2019; Oztekin et al. 2015; Rowley et al. 2020) (Figure 5.1e), multinet trawls (Kooi et al. 2016; Reisser et al. 2015) (Figure 5.1f), and multiple opening and closing nets (Egger et al. 2020). Other sampling instruments to collect microplastics in the water column include submerged pumps (Ng and Obbard 2006; Song et al. 2019; Zobkov et al. 2019) (Figure 5.1d), sediment traps (Ballent et al. 2016; Reineccius et al. 2020), and in situ filtration devices (Choy et al. 2019; Li et al. 2020; Liu et al. 2019; Tekman et al. 2020) (Figure 5.1h). In particular in situ filtration instruments allow large water volumes to be sampled, which could be an

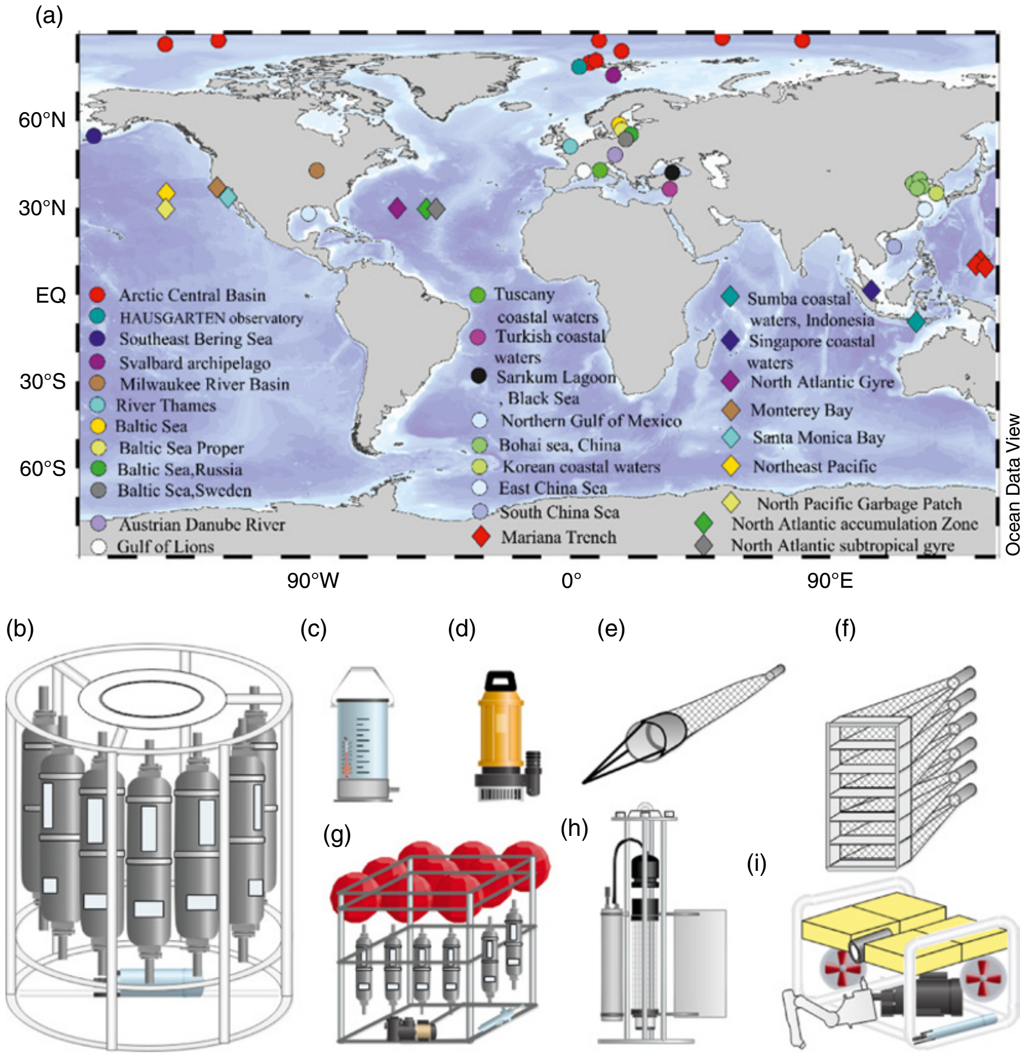


Figure 5.1 Geolocation of sampled water columns for MPs research (a). Sampling device used for collecting MPs in the water column (b: CTD sampler; c: plexiglass water sampler; d: submersible pump; e: plankton net; f: multinet trawls; g: lander system; h: plankton pump; i: remotely operated vehicle (ROV)). *Source:* Liu et al. (2020).

efficient and promising technique for future work, considering the heterogeneous distribution of microplastics. In addition, an underway water intake system was also used to collect subsurface seawaters at a constant and single depth (Lusher et al. 2015; Ryan et al. 2020).

5.3 Spatial Patterns of MPs in Water Columns

5.3.1 Global Mapping of microplastic Research in the Deep Ocean

Despite the water column representing the largest ecosystem on Earth, relatively few studies have examined plastic pollution within this oceanic realm when compared to surface water. It was not until 2013 that the first study documented the presence of microplastics in deep-sea sediment (Van Cauwenberghe et al. 2013), and subsequent research has tended to focus on plastic debris on the ocean floor (Bergmann et al. 2017; Courtene-Jones et al. 2020; Fischer et al. 2015; Kane et al. 2020; Peng et al. 2018; Woodall et al. 2014) rather than within the water column.

Over recent years, this body of research is growing, providing evidence of the pathways by which neustonic microplastics may sink to the ocean interior. There have been some measurements in Santa Monica Bay (Lattin et al. 2004), the Rockall Tough (Courtene-Jones et al. 2017), the Arctic Basin (Kanhai et al. 2018; Tekman et al. 2020), the Gulf of Lions, the Mediterranean Sea (Lefebvre et al. 2019), and the West Pacific and East Indian Oceans (Li et al. 2020) (Figure 5.1a; Table 5.1). The vertical distribution of microplastics have been shown to vary greatly between geographic regions and also within a particular area. For instance, Kanhai et al. (2018) sampled the microplastics at different locations (50–4,369 m depth) in the Arctic Basin using a CTD sampler, and report an abundance of microplastics 0-375 microplastics/m^3. However, an approximate order of higher content (0–1287 n/m^3) was detected around HAUSGARTEN observatory (1–5350 m) also located within the Arctic (Tekman et al. 2020). This difference could possibly result from the sampling and analysis techniques, hydraulic conditions between the locations and the physical–chemical properties of microplastics (Khatmullina and Isachenko 2017). Further research also indicated the depth-dependent profiles of microplastics in the water, where an exponential decrease of microplastics abundance or size with depth has been observed, especially in the pelagic zone (Kooi et al. 2016; Li et al. 2020; Reisser et al. 2015). However, some research has indicated no significant relationship between microplastics abundance and sampling depth, and more abundant plastic microdebris was observed both in upper mixed water and deep water (Kanhai et al. 2018; Uurasjärvi et al. 2021). This vertical profile may be linked to the structure of water masses, and pycnocline (halocline and thermocline) which may hinder the deposition of microplastics into deeper water masses. As such a considerable number of microplastics may be stored within this layer, meriting further evaluation.

5.3.2 Modeling and Transport Simulations

Modelling the transport of microplastics in the subsurface water could be of great importance to decipher the ultimate sink and further assess potential ecological effects of microplastics. Currently, knowledge regarding the transport of microplastics in subsurface waters is limited. In addition to ocean currents (van sebille et al 2020), a number of biological processes, including biofouling (Katija et al. 2017; Kooi et al. 2017) can influence the vertical distribution of plastics. The contribution of these biological parameters to the vertical transport of plastics are not well quantified (discussed further in Section 5.4), and thus adds uncertainty when attempting to model or implement computational transport simulations in the water column. However recently some studies have used three-dimensional (3D) computational models to investigate transport pathways. Tekman et al. (2020) used a 3D backward particle tracking model (Lagrangian particle tracking algorithm) coupled with empirical data, to examine microplastic sources and transport pathways in the Fram Strait. They indicated that due to the localised water dynamics and the sinking velocity of microplastics, particles may recirculate and be transported horizontally via lateral advection over considerable distances. Downward displacement of microplastics due to biofouling processes were modeled by Kooi et al. (2017). The model explored the vertical movement of microplastics in relation to the photoperiod, water density, temperature, salinity and viscosity of the surrounding water. The simulations indicated cyclical behaviour of microplastics, where biofouling caused them to settle, whereupon the removal of biofouling due to grazing for example, caused the particles to rise again. This behaviour was also found to be influenced by differences between the density of the seawater and the plastic particle, suggesting that the microplastics size and density are important factors in addition to fouling processes.

Table 5.1 Summary of published studies quantifying microplastic pollution in subsurface waters.

Location	Water depth (m)	Method of sample collection	Filter aperture (μm) (lowest limit)	Microplastic (MP) concentration	Reference
Atlantic Ocean					
Santa Monica Bay, USA	0–30	Multinet system (manta trawl, bongo net, and epibenthic sled)	333	3.92 MP/m^3	Lattin et al. (2004)
Southern California	0–212	Bongo net (vertical trawl)	505	0–0.0248 MP/m^3	Doyle et al. (2011)
North Atlantic Gyre	5, 10, and 20	Multinet trawl	Not stated	Observations confirmed presence in 81% of trawls	Kukulka et al. (2012)
North Atlantic Gyre	0–5	Multinet trawls	150	Median: 1.69 MP/m^3	Reisser et al. (2015)
Atlantic Ocean	3	Vessel underway system	10	13–501 MP/m^3	Enders et al. (2015)
Rockall Tough, North Atlantic Ocean	2227	NISKIN bottles on a CTD sampler	80	66.7–70.8 MP/m^3	Courtene-Jones et al. (2017)
Northern Gulf of Mexico	0–15	Bongo net and oblique tow	335	6.0 ± 1.0 MP/m^3	Di Mauro et al. (2017)
Subtropical North Atlantic	2000–3000	Sediment traps	0.4	18–3039 fibers*/g^1 of flux mass **Only fibers were counted.*	Reineccius et al. (2020)
Atlantic Ocean	5	Vessel underway system	20, 50, and 63	0.5 ± 0.49 fibers/L^1 (mean, SD) *Corrected to account for variable filter aperture size*	Suaria et al. (2020)
Atlantic Ocean	10–270	In situ stand-alone pumps	55	1602 ± 1551 PE/m^3; 180 ± 822 PP/m^3; 180 ± 439 PS/m^3 (mean ± SD) *only PE, PP, and PS particles quantified*	Pabortsava and Lampitt (2020)
Arctic Ocean					
Barents Sea, Norway	6	Vessel underway system	250	0–11.5 MP/m^3 (av. 2.68 ± 2.95 SD)	Lusher et al. (2015)
Arctic Ocean	1001 –4369	NISKIN bottles on a CTD sampler	1.2	0–104 MP/m^3	Kanhai et al. (2018)
Arctic Ocean	1–5350	Pump system	32	0–1287 MP/m^3	Tekman et al. (2020)

(Continued)

Table 5.1 (Continued)

Location	Water depth (m)	Method of sample collection	Filter aperture (μm) (lowest limit)	Microplastic (MP) concentration	Reference
Pacific Ocean					
Mariana Trench, Pacific Ocean	2500–11000	CTD sampler	0.2–1.2	2.06–13.51 MP/L[1]	Peng et al. (2018)
Bohai Sea, Northwest Pacific Ocean	0–30	CTD sampler	5	0.2–23 MP/L[1] (av. 4.4 ± 5.0 SD)	Dai et al. (2018)
Monterey Bay, Pacific Ocean	5–1000	In situ filtration attached to ROV	100	2.9–15 MP/L[1]	Choy et al. (2019)
North Pacific Gyre	0–2000	Multiple opening and closing net with an environmental sensing system	500	0.0004–0.352 MP/m^3	Egger et al. (2020)
South Korea coastal waters	3–58	Pump	20	10–2200 MP/m^3 (av. 412 ± 391.6)	Song et al. (2018)
Korean coastal waters	3–58	Submersible pump	20	180 ± 106 to 4064 ± 1075 MP/m^3	Song et al. (2018)
China Sea	4	In situ filtration device	60	0.13 to 5 MP/m^3, (av. 1.02 ± 1.19 SD. MP/m^3)	Liu et al. (2019)
South China Sea	10–40	NISKIN bottles on a CTD sampler	0.45	0.2–11.2 MP/L[1]	Ding et al. (2019)
West Pacific Ocean	2–200	In situ pump	60	1.20 ± 0.57 MP/m^3	Li et al. (2020)
	200–500			0.88 ± 0.45 MP/m^3	
	1000			0.84 ± 0.52 MP/m^3	
	2000–4000			0.43 ± 0.22 MP/m^3	
Indian Ocean					
Sumba, eastern Indonesia	5–300	Rosette water sampler	0.45	44 ± 24.59 MP/m^3	Cordova and Hernawan (2018)
East Indian Ocean	2–200	In situ pump	60	1.37 ± 0.58 MP/m^3	Li et al. (2020)
	500			1.27 ± 0.38 MP/m^3	
	1000			1.28 ± 0.58 MP/m^3	

Southern Ocean					
Southern Ocean	5	Vessel underway system	20, 50, and 63	2.03 ± 4.66 fibers/L[1] (mean, SD) *Corrected to account for variable filter aperture size*	Suaria et al. (2020)
Mediterranean Sea					
Turkish coastal water. Mediterranean Sea	0–55	WP2 zooplankton sampling net Manta trawl	200 335	16 339–520 213 MP/km^2	Guven et al. (2017)
Tuscany coastal waters, Mediterranean Sea	0– 100	Plankton net – vertical trawl	200	0.16 ± 0.47 MP/m^3	Baini et al. (2018)
Gulf of Lions, Mediterranean Sea	0– 100	Plankton net – vertical trawl	200	0.23 ± 0.20 MP/m^3	Lefebvre et al. (2019)
Baltic sea					
Baltic Sea, Sweden	0–100	Plankton net – vertical trawl	90	10^2–10^4 MP/m^3	Gorokhova (2015)
Baltic Sea	0.5–217.5	NISKIN bottles on a CTD sampler	174	0–2.6 fibers*/L[1] **Only fibers were counted*	Bagaev et al. (2017)
Baltic Sea	1–217	NISKIN bottle	174	0.092 ± 0123 to 0.933 ± 0.844 MP/L[1] (av. 0.400 ± 0.576/L[1])	Bagaev et al. (2018)
Baltic Sea	0–106	In situ filtration: “PLEX” custom built system.	174	11.1–79.1 MP/m^3 (av. 32.2 ± 50.4)	Zobkov et al. (2019)
Baltic Sea	Vertical tows ranging between 75 and 10 m	WP2 trawl net	100	0.92 ± 0.61 MP/m^3	Uurasjarvi et al. (2020)
Baltic Sea	14–98	Jussi sampler	50	0.44 ± 0.52 MP/m^3	Uurasjarvi et al. (2020)

5.4 The Export of Microplastics from the Surface Water to the Deep Sea

To date, there have been thousands of polymers synthesized, varying in their chemical composition and density (Andrady 2011). Understanding the processes involved in vertical transport can be challenging, since the physical characteristics (e.g., density, size, shape) of microplastics vary widely. Further, the export of microplastics from surface waters can be modified by interactions with biotic and abiotic factors. As such, microplastics should be thought of as dynamic, rather than having fixed parameters.

Factors influencing the export of microplastics:

i) **Intrinsic properties** of the microplastic, such as its size, shape/surface area (fragment, pellet, film, and fiber), and the density of the polymeric material (Ballent et al. 2013; Kowalski et al. 2016). These properties are modified by the addition of additives incorporated into the plastic during manufacture or adsorbed from the environment (Turner and Filella 2020).
ii) **Biotic factors** include the mass of biofilm on the surface of the microplastic (Rummel et al. 2017), the entrainment with natural marine particles, e.g., marine snow (Long et al. 2015; Porter et al. 2018; Summers et al. 2018), and incorporation into fecal pellets following consumption and subsequent egestion (Cole et al. 2016; Coppock et al. 2019).
iii) **Abiotic factors** such as oceanographic processes, for example turbulent mixing and the seawater density profile.

There are a lack of studies, and in particular field-based assessments, considering the sedimentation of microplastics, which limits detailed investigation of transport processes. The majority of studies, which have been conducted, have considered the effect of each of the aforementioned transport mechanisms separately. However, in reality, these processes do not act in isolation, and the fate, settling behavior, and residence times of microplastics in the water column will be influenced by complex interactions between the numerous factors (i–iii) listed above. This is emphasized through observational studies, which have documented the absence of clear vertical distribution patterns of polymer types within deep water (Peng et al. 2018; Tekman et al. 2020). Broadly, the processes discussed below (Sections 5.4.1–5.4.5) can act on an ocean-wide scale, potentially leading to the modification of microplastic sinking rates of up to hundreds of meters per day (Enders et al. 2015; Kooi et al. 2017) and thus having the potential to accelerate the removal of microplastics from the sea surface. Numerous studies have now documented both positively and negatively buoyant polymers within the deep-sea ecosystem (Bergmann et al. 2017; Choy et al. 2019; Courtene-Jones et al. 2017, 2020; Tekman et al. 2020), indicating that export processes play an important, yet not fully understood, role in the redistribution of plastics through the ocean interior.

5.4.1 Intrinsic Properties of the Plastic Particle

The physical properties of microplastic particles, such as their density, size, and geometric shape, define their behavior in the ocean. Virgin resins of plastics range in density from ~0.8 to 1.4 g/cm^3 (Andrady 2011) and can be modified considerably depending on the manufacturing processes and chemical additives. Most often the sinking of plastics has been linked to the inherent density of a particle, with those plastics with a density close to or less than seawater, such as polyethylene, polypropylene, and polystyrene, displaying a positive buoyancy; while those with densities greater than the ambient water, such as polyester, PVC, and polyamide, having a negative buoyancy and sinking. This is however an over-simplified approach, and in reality, there are complex interactions between ocean processes, biological interactions, and other physical properties of the plastic particles which influence their fate in the marine environment.

The geometric shape of a microplastic is a critical morphological parameter, which can broadly be divided into regular and irregular. The shape will largely depend on their origin and the fragmentation process (Ter Halle et al. 2016). Theoretical calculations of sinking velocities assume a smooth geometry, while natural sediment particles and microplastics are highly variable in their shape which is further influenced by aging and weathering processes to yield irregularly shaped particles (Waldschlager and Schuttrumpf 2019). Studies have found that theoretical sinking of an object can substantially deviate from experimental data (Chubarenko and Stepanova 2017; Khatmullina and Isachenko 2017; Kowalski et al. 2016). Shape can influence particle sedimentation rates due to its influence over the surface area to volume ratio (Filella 2015; Ryan 2015). For example, items with the same volume but with different shapes have different surface area to volume ratios, with spheres having the lowest ratios and thin rectangles, such as films or fibers, having the highest. This not only provides a greater exterior for biofilms to colonize and in turn increase the density of the particle but can also influence the drag forces and settling behavior of a particle (Chubarenko et al. 2016). Experiments using three different shaped particles made of polycaprolactone (PCL) indicated that angular cylinders oscillated and rotated during settlings (Khatmullina and Isachenko 2017), and other studies show that fibers have a lower buoyant rise velocity compared to fragments of the same size (Kooi et al. 2016; Kukulka et al. 2012). This indicates that wind-driven mixing might redistribute small microplastics and fibers out of the surface layer and deeper in the oceans.

Particle size influences settling, with microplastics behaving distinctively different from meso/macroplastics (Chubarenko et al. 2016). Small plastic particles loose buoyancy faster than larger items and thus sink more rapidly (Fazey and Ryan 2016) and have lower buoyant terminal velocities than larger plastics (Kooi et al. 2016; Kukulka et al. 2012). As such, small microplastics have an increased propensity to sink out of surface waters, suggesting size-specific sedimentation, which has been reported in both observational and modeling studies (Kooi et al. 2017; Reisser et al. 2015; Song et al. 2018). Small plastic pieces behave like colloidal particles and primarily exist as suspended particles in the water column (Filella 2015). Processes such as fragmentation, flocculation, and aggregation (discussed below) modify the size of microplastics and in turn further affect their behavior and residence times within the water column.

The influence of additives on the behaviour of marine microplastics has received notably less attention. The majority of manufactured plastic products contain a variety of mineral or organic-based additives, which have a range of functions including as stabilizers, fillers, flame retardants, and plasticizers. Some of the compounds used have high densities, which can modify the overall properties of the plastic sufficiently to facilitate sinking. For example, the use of barium as a filler modifies the density of polyolefins (polyethylene and polypropylene) to greatly exceed that of seawater. Barium-containing polyolefins are common in consumer products yet rarely found in beached litter (Turner and Filella 2020), which the authors attribute to the permanent deposition of these items to the seafloor. While factors such as the surface polarity of the plastic, its crystallinity, and functional groups included during manufacture may influence the potential for additives to leach from or accumulate environmental pollutants on its surface (Ma et al. 2020), further research is required to ascertain how this affects the behavior and fate of marine microplastics.

5.4.2 Biofilm

Biofilms are assemblages of microbial cells enclosed in an extracellular polymeric substance matrix (Donlan 2002). Biofilms have been shown to rapidly form on the surface of plastic particles when they are in aquatic systems (Lobelle and Cunliffe 2011). Indeed, the first organic films can form in a matter of hours after initial contact between a surface with ambient water (Loeb and Neihof 1975; Rummel et al. 2017). From a hydrodynamic perspective, biofilm formation on plastic debris may have substantial implications (Chen et al. 2019; Rummel et al. 2017), as the fouling organisms themselves may lead to an increase in particle mass and thus a reduction in its buoyancy (Kaiser et al. 2017; Lagarde et al. 2016; Ryan 2015). While the buoyancy of an item is generally related to its volume, the capacity for biofouling is related to the surface area. Laboratory experiments using different sized biofouled plastic particles (5–50 mm) demonstrated that smaller plastics sank faster than larger particles (Fazey and Ryan 2016). Indeed the rate of colonization and sinking is directly proportionate to the particle diameter (Chubarenko et al. 2016).

Once in the marine environment, plastics undergo weathering processes, which can alter their surface characteristics from smooth to rough with numerous cracks and pits (Ter Halle et al. 2016). This increases the surface area of a particle and its biofilm carrying capacity. Further, the presence of biofilm facilitates the accumulation of metals from the aquatic environment (Johansen et al. 2018; Richard et al. 2019), causing further modifications to particle mass. Studies have shown that microorganisms attach more rapidly to hydrophobic, nonpolar surfaces (such as plastics) than to hydrophilic surfaces (such as glass and stainless steel), and specific communities can differ between the material types (Oberbeckmann et al. 2016; Ogonowski et al. 2018; Pinto et al. 2019; Zettler et al. 2013).

The growth of biofilm-forming organisms largely depends on light, temperature, and the productivity of the ambient water (Kaiser et al. 2017; Oberbeckmann et al. 2016). Therefore, the role of biofilm in the export of microplastics might be more marked at certain geographic locations than other, for example this process may be less important in the oligotrophic ocean gyres (Hale et al. 2020). As biofouled microplastics sink below the photic zone and into unfavorable conditions, or are grazed upon by marine species, particles may become defouled. This causes the microplastic to regain buoyancy and rise/resurface, at which point biofilm may form once again, leading to submerging—resurfacing cycles (Kooi et al. 2017). Kooi et al. (2017) modeled the dynamics of biofouling and predicted that larger particles (1–10 mm in diameter) remain in surface waters for longer due to them having a greater settling onset period, and when they do begin to settle, they oscillate within the water column at a faster rate than smaller particles. By contrast, plastics < 10μm in diameter settle slowly but do not resurface and thus could be distributed within the water column. Over time, this causes a size selective vertical export of smaller microplastics, suggesting they are "lost" to mid-depths of the ocean, which corroborates the early observations of Cozar et al. (2014).

A further consideration is that the presence of nutrient-rich biofilm on the surface of microplastics could cause them to be preferentially ingested by organisms mistaking them for food items (Vroom et al. 2017). If microplastics are able to transit through the digestive systems of these organisms, they can be repackaged in fecal pellets, which could also facilitate their downward flux (see Section 5.4.3).

5.4.3 Fecal Pellets

Consumption of microplastics by a myriad of species is well evidenced (see Courtene-Jones et al (2022)). In some cases, microplastics can transit through the digestive systems of an organism and become egested within the fecal material. Naturally, the fecal matter will gradually sink to the seafloor, and it plays an important role in the ocean's biological carbon pump (Turner 2015). Several studies have now investigated the potential for fecal pellets to transport microplastics. Cole et al. (2016) tested the sinking rate of polystyrene bead–containing copepod fecal pellets. The authors report an average settling velocity of 38.3 ± 2.6 m/day, which was significantly slower than compared to a natural fecal pellet (2.25-fold reduction) but faster than the microplastic in its free state.

A recent study found this was also the case for polystyrene nanoparticles contained within the fecal pellets of Antarctic krill (Bergami et al. 2020). However, not all microplastic polymers display this trend. Further investigation considering different shapes and polymers (low-density polyethylene fragments, nylon fibers and fragments, and polyethylene terephthalate fibers) revealed that fecal pellets contaminated with high-density polymers (nylon and PET) sank at a faster rate than uncontaminated pellets (Coppock et al. 2019), while feces containing low-density polyethylene sank significantly more slowly than controls. The aforementioned studies also found that fecal pellets containing plastics had a greater likelihood of fragmenting in the water column during settling. Fecal pellets provide a food source to pelagic corophagic species, who may feed upon this plastic-contaminated matter. As these species intercept the sinking pellets, they could offer a process which keeps the microplastics in suspension within the water column, repackaging the microplastics several times before the particles reach the seafloor, and altering the timescale of removal to the seafloor.

5.4.4 Marine Aggregates

Aggregation of particles is a natural and well-documented process in the marine environment (Alldredge and Gotschalk 1988; Shanks and Trent 1979). Aggregation depends largely on the probability of particle collision and the efficiency with which two colliding particles stick together (Alldredge and McGillivary 1990; Engel 2000). The presence of cellular organisms, such as bacteria and phytoplankton, contained within biofilms can encourage particle adhesion through exuded exopolymeric substances (EPS) (Flemming and Wingender 2010; Michels et al. 2018). EPS consists largely of long-chained polysaccharides that can link to form gels, mucilage, and slime aggregates, which promote the adhesion with other marine particles or suspended microplastics and the formation of heteroaggregates (Long et al. 2015; Summers et al. 2018) which form particles with greater sizes and densities than in their free state. Aggregate formation strongly depends on the stickiness (or coagulation efficiency) of the particles involved (Michels et al. 2018), and EPS may play an important role in mediating coagulation (Summers et al. 2018).

Microplastics have been identified in natural marine aggregates (Zhao et al. 2018), and laboratory experiments have demonstrated that plastic particles readily attach and incorporate into existing aggregates (Long et al. 2015; Möhlenkamp et al.; Porter et al. 2018). Opposing surface charges on microplastics and natural organic compounds and minerals facilitate their interactions in the aquatic environment (Oriekhova and Stoll, 2018). The flocculation of microplastics and particulate matter can modify the resultant flocs such that they are prone to gravity-driven settling in the water column. Indeed, the sinking rate of flocs could reach hundreds of meters per day compared with the settling rate of < 4 mm/day of microplastics in the free state (Long et al. 2015). Experimental work by Porter et al. (2018) demonstrated that for polyamide fragments the sinking rate increased by 916 m/day, when incorporated into marine snow, than compared to their free state. A less conclusive effect was noted for small agglomerates containing nanoplastics (Summers et al. 2018). While the authors reported altered sinking velocities, this was not significant as the values recorded were still within the broad range of measurements documented for marine snow sedimentation.

Katija et al. (2017) investigated the potential of the mucus housings produced by pelagic giant larvaceans to trap microplastics and act as a transport pathway. Giant larvaceans construct mucus structures to trap particulate food, which are discarded after use and sink to the seafloor. Larvacean "sinkers" were found to contain substantial numbers of microplastics (Choy et al. 2019; Katija et al. 2017), which could have been incorporated during filter feeding or become entrained from the water column; regardless of the specific mechanisms, this process may alter the fate and residence time of microplastics within the deep water column.

When considering that each marine floc may contain multiple microplastic particles (Kvale et al. 2020), microplastic-contaminated marine aggregates constitute a vertical pathway for microplastics through the water column transporting even low-density microplastics (such as PE and PP) out of the surface layers (Long et al. 2015; Porter et al. 2018; Zhao et al. 2017). The relative importance of this transport mechanism may vary geographically. Many temperate and subpolar regions can experience cyanobacterial blooms or spring phytoplankton blooms. During the bloom, EPS is produced in abundance, which is attributed to the rapid sedimentation of aggregates once the bloom terminates (Engel, 2000; Passow et al. 2001) and can export microplastics from surface waters in the process.

5.4.5 Environmental Factors

The majority of plastics enter the marine environment from land-based sources (Borrelle et al. 2020; Jambeck et al. 2015) introduced at the ocean surface. The main oceanographic processes involved in the surface transport of microplastics, such as wind and ocean currents, are relatively well understood (Onink et al. 2019; van Sebille et al. 2015a, 2020). Reconciling the vertical distribution of microplastics and the oceanic factors associated are more complex, as the vertical flow of the ocean is governed by several processes acting at different spatial and temporal scales (van Sebille et al. 2020). Wind-induced turbulence, breaking waves, bubble injection, and Langmuir circulations can mix microplastics down to several hundreds of meters (Enders et al. 2015; Kukulka et al. 2012; Poulain et al. 2019). Often the microplastic particles will ascend back to the surface after waves and turbulence decay, yet for small microplastics, their rise velocity may not be sufficient for them to resurface (Kooi et al. 2017).

As particles descend through the water column, they will encounter different water masses which vary in salinity, temperature and density. It is hypothesized that microplastics will sink until they reach a water mass with the same density as that of the plastic polymer. It is possible that isopycnal layers, and in particular the pycnocline, could create a density "boundary" limiting the further vertical export and so maintaining the microplastics in suspension. Such a phenomenon is most easily observed in locations with strong stratification, for example in the Baltic Sea. The Baltic Sea undergoes pronounced seasonal stratification, where marked differences in salinity and density exist between the bottom and surface waters. The differing water properties coupled with the warming of surface waters during summer prevents the water column mixing (Leppäranta and Myrberg 2009), and microplastics were shown to accumulate between the halocline and thermocline (Uurasjarvi et al. 2020; Zobkov et al. 2019).

Where a stratified water column interacts with pronounced seafloor topography, internal tides often develop in response to surface tides. Internal tides can modify transport processes often acting to resuspend and transport sediments within rugose areas such as canyons and around seamounts (Inman et al. 1976; Lee et al. 2009; Zhao et al. 2012). For example, numerical modeling indicated that internal tides can resuspend and move microplastic particles within the Nazaré Canyon, Northeast Atlantic Ocean (Ballent et al. 2013). Such processes likely occur in other canyons, which are prevalent globally (Harris and Whiteway 2011), and can act to keep microplastics within suspension in deep water. Canyons are conduits for gravity-driven avalanches of sediment called turbidity currents, which transfer sediment and organic particles from shallow to deep water (Canals et al. 2013; Puig et al. 2014). Turbidity currents are important for the flow of sediment and other hydrodynamically light material into the deep sea and might be significant agents for dispersing microplastics (Ballent et al. 2013; Kane et al. 2020; Pierdomenico et al. 2020; Pohl et al. 2020). A further transport route is within deep-water cascading events, which can carry plastics to the ocean interior (Sanchez-Vidal et al. 2015; Tubau et al. 2015).

5.5 Knowledge gaps and conclusion

In this chapter, sampling techniques, occurrence, and transport mechanisms of floating microplastics sinking cross the water column had been summarized and demonstrated, and given the many deficiencies in this area, more efforts should be made on the following aspects:

i) **Comparable dataset yielded by validated sampling techniques.** So far, the knowledge for microplastics in water columns is quite limited, and though a variety of sampling methods were adopted, few researchers have ever tried to determine their efficiency capturing these suspended microplastics. For instance, limited bulk sampling would often lead to highly variable results, compared with large-volume filtration methodology. Former techniques could be efficient to obtain fibrous microplastics using a finer pore size filter membrane, but fragmented microplastics could be underestimated since the uneven distribution. However, latter sampling methods usually required extended time duration, which may be difficult to balance during a field sampling campaign.

ii) **More field-based data by international collaborations.** Field-based microplastic data in the water column is of great value to estimate the global plastic budget and understand their residence time in the ocean. Therefore, more cruises are urgently needed (especially in the open ocean), and there is no doubt that international collaborations would greatly facilitate this process. In addition, some collections from former cruises could be utilized unless they were not carefully preserved (free from airborne contamination).

iii) **Deciphering the sinking mechanisms.** To facilitate further tracking, it could be critical to understand why floating plastic debris and microplastics would sink to deeper layers of water columns. Although some studies reported biofouling on plastics which could greatly contribute to their vertical displacement, not all observations in the field could be explained by this hypothesis. In fact, this process could be a combination of fragmentation, gravitation, hydraulic conditions, and biofouling, and thus work to decipher the importance of these mechanisms would be beneficial.

iv) **Track the transport of oceanic microplastics and simulate their movement by thermohaline circulation.** In the end, to assess the potential interactions and effects on deep water ecosystems, a lifecycle of oceanic microplastics should be mapped with modeling approaches. First of all, their transport through water masses should be estimated, and their exchange within the pycnocline should be further studied.

References

Alldredge, A. L., Gotschalk, C. 1988. In situ settling behavior of marine snow. *Limnology and Oceanography*, 33: 339–351.

Alldredge, A. L., Mcgillivary, P. 1990. The attachment probabilities of marine snow and their implications for particle coagulation in the ocean. *Deep Sea Research*, 38: 431–443.

Andrady, A. L. 2011. Microplastics in the marine environment. *Marine Pollution Bulletin*, 62: 1596–605. doi:10.1016/j.marpolbul.2011.05.030

Andrady, A. L. 2017. The plastic in microplastics: a review. *Marine Pollution Bulletin*, 119: 12–22. doi:10.1016/j.marpolbul.2017.01.082

Ballent, A., Pando, S., Purser, A. et al. 2013. Modelled transport of benthic marine microplastic pollution in the Nazaré Canyon. *Biogeosciences*, 10: 7957–7970. doi:10.5194/bg-10-7957-2013

Barrows, A. P. W., Cathey, S. E., Petersen, C. W. 2018. Marine environment microfiber contamination: Global patterns and the diversity of microparticle origins. *Environmental Pollution*, 237: 275–284. doi:10.1016/j.envpol.2018.02.062

Beer, S., Garm, A., Huwer, B. et al. 2018. No increase in marine microplastic concentration over the last three decades—a case study from the Baltic Sea. *Science of the Total Environment*, 621: 1272–1279. doi:10.1016/j.scitotenv.2017.10.101

Bergami, E., Manno, C., Cappello, S. et al. 2020. Nanoplastics affect moulting and faecal pellet sinking in Antarctic krill (Euphausia superba) juveniles. *Environment International*, 143: 105999. doi:10.1016/j.envint.2020.105999

Bergmann, M., Wirzberger, V., Krumpen, T. et al. 2017. High quantities of microplastic in Arctic deep-sea sediments from the HAUSGARTEN observatory. *Environmental Science & Technology*, 51: 11000–11010. doi:10.1021/acs.est.7b03331

Borrelle, S. B., Ringma, J., Law, K. L. et al. 2020. Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. *Science*, 369: 1515–1518. doi:10.1126/science.aba3656

Burns, E. E., Boxall, A. B. A. 2018. Microplastics in the aquatic environment: evidence for or against adverse impacts and major knowledge gaps. *Environmental Toxicology and Chemistry*, 37: 2776–2796. doi:10.1002/etc.4268

Canals, M., Company, J. B., Martín, D. et al. 2013. Integrated study of Mediterranean deep canyons: novel results and future challenges. *Progress in Oceanography*, 118: 1–27. doi:10.1016/j.pocean.2013.09.004

Chen, X., Xiong, X., Jiang, X. et al. 2019. Sinking of floating plastic debris caused by biofilm development in a freshwater lake. *Chemosphere*, 222: 856–864. doi:10.1016/j.chemosphere.2019.02.015

Choy, C. A., Robison, B. H., Gagne, T. O. et al. 2019. The vertical distribution and biological transport of marine microplastics across the epipelagic and mesopelagic water column. *Scientific Reports*, 9: 7843. doi:10.1038/s41598-019-44117-2

Chubarenko, I., Bagaev, A., Zobkov, M. et al. 2016. On some physical and dynamical properties of microplastic particles in marine environment. *Marine Pollution Bulletin*, 108: 105–112. doi:10.1016/j.marpolbul.2016.04.048

Chubarenko, I., Stepanova, N. 2017. Microplastics in sea coastal zone: lessons learned from the Baltic amber. *Environmental Pollution*, 224: 243–254. doi:10.1016/j.envpol.2017.01.085

Cole, M., Lindeque, P. K., Fileman, E. et al. 2016. Microplastics alter the properties and sinking rates of zooplankton faecal pellets. *Environmental Science & Technology*, 50: 3239–3246. doi:10.1021/acs.est.5b05905

Coppock, R. L., Galloway, T. S., Cole, M. et al. 2019. Microplastics alter feeding selectivity and faecal density in the copepod, *Calanus helgolandicus*. *Science of the Total Environment*, 687: 780–789. doi:10.1016/j.scitotenv.2019.06.009

Courtene-Jones, W., Clark, N. J., Fischer, A. C., Smith, N. S., Thompson, R. C. 2022. Ingestion of microplastics by Marine Animals, In: Andrady A. (eds.) *Plastics in the Ocean*. Wiley, 349–366.

Courtene-Jones, W., Quinn, B., Ewins, C. et al. 2019. Consistent microplastic ingestion by deep-sea invertebrates over the last four decades (1976-2015): a study from the North East Atlantic. *Environmental Pollution*, 244: 503–512. doi:10.1016/j.envpol.2018.10.090

Courtene-Jones, W., Quinn, B., Ewins, C. et al. 2020. Microplastic accumulation in deep-sea sediments from the Rockall Trough. *Marine Pollution Bulletin*, 154: 111092. doi:10.1016/j.marpolbul.2020.111092

Courtene-Jones, W., Quinn, B., Gary, S. F. et al. 2017. Microplastic pollution identified in deep-sea water and ingested by benthic invertebrates in the Rockall Trough, North Atlantic Ocean. *Environmental Pollution*, 231: 271–280. doi:10.1016/j.envpol.2017.08.026

Cozar, A., Echevarria, F., Gonzalez-Gordillo, J. I. et al. 2014. Plastic debris in the open ocean. *Proceedings of the National Academy of Sciences of the United States of America*, 111: 10239–10244. doi:10.1073/pnas.1314705111

Donlan, R. M. 2002. Biofilms: Microbial Life on Surfaces. *Emerging Infectious Diseases*, 8: 881–890.

Egger, M., Sulu-Gambari, F., Lebreton, L. 2020. First evidence of plastic fallout from the North Pacific Garbage Patch. *Scientific Reports*, 10: 7495. doi:10.1038/s41598-020-64465-8

Enders, K., Lenz, R., Stedmon, C. A. et al. 2015. Abundance, size and polymer composition of marine microplastics ≥10μm in the Atlantic Ocean and their modelled vertical distribution. *Marine Pollution Bulletin*, 100: 70–81. doi:10.1016/j.marpolbul.2015.09.027

Engel, A. 2000. The role of transparent exopolymer particles (TEP) in the increase in apparent particle stickiness during the decline of a diatom bloom. *Journal of Plankton Research*, 22: 485–497.

Eriksen, M., Lebreton, L. C., Carson, H. S. et al. 2014. Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. *PLoS One*, 9: e111913. doi:10.1371/journal.pone.0111913

Fazey, F. M., Ryan, P. G. 2016. Biofouling on buoyant marine plastics: an experimental study into the effect of size on surface longevity. *Environmental Pollution*, 210: 354–360. doi:10.1016/j.envpol.2016.01.026

Filella, M. 2015. Questions of size and numbers in environmental research on microplastics: methodological and conceptual aspects. *Environmental Chemistry*, 12. doi:10.1071/en15012

Flemming, H. C., Wingender, J. 2010. The biofilm matrix. *Nature Reviews Microbiology*, 8: 623–633. doi:10.1038/nrmicro2415

Gage, J. D., Tyler, A. P. 1991. *Deep-Sea Biology: A Natural History of Organisms at the Deep-Sea Floor*. Cambridge University Press, 957–986.

Geyer, R., Jambeck, J. R., Law, K. L. 2017. Production, use, and fate of all plastics ever made. *Science Advances*, 3: e1700782. doi:10.1126/sciadv.1700782

Goldstein, M. C., Rosenberg, M., Cheng, L. 2012. Increased oceanic microplastic debris enhances oviposition in an endemic pelagic insect. *Biology Letters*, 8: 817–820. doi:10.1098/rsbl.2012.0298

Hale, R. C., Seeley, M. E., La Guardia, M. J. et al. 2020. A global perspective on microplastics. *Journal of Geophysical Research: Oceans*, 125: e2018JC014719. doi:10.1029/2018jc014719

Harris, P. T., Whiteway, T. 2011. Global distribution of large submarine canyons: geomorphic differences between active and passive continental margins. *Marine Geology*, 285: 69–86. doi:10.1016/j.margeo.2011.05.008

Inman, D. L., Nordstrom, C. E., Flick, R. E. 1976. Currents in submarine canyons: an air-sea-land interaction. *Annual Review of Fluid Mechanics*, 8: 275–310. doi:10.1146/annurev.fl.08.010176.001423

Jambeck, J. R., Geyer, R., Wilcox, C. et al. 2015. Plastic waste inputs from land into the ocean. *Science*, 347: 768–771. doi:10.1126/science.1260352

Jamieson, A. J., Brooks, L. S. R., Reid, W. D. K. et al. 2019. Microplastics and synthetic particles ingested by deep-sea amphipods in six of the deepest marine ecosystems on Earth. *Royal Society Open Science*, 6: 180667. doi:10.1098/rsos.180667

Johansen, M. P., Prentice, E., Cresswell, T. et al. 2018. Initial data on adsorption of Cs and Sr to the surfaces of microplastics with biofilm. *Journal of Environmental Radioactivity*, 190–191: 130–133. doi:10.1016/j.jenvrad.2018.05.001

Kaiser, D., Kowalski, N., Waniek, J. J. 2017. Effects of biofouling on the sinking behavior of microplastics. *Environmental Research Letters*, 12. doi:10.1088/1748-9326/aa8e8b

Kane, I. A., Clare, M. A. 2019. Dispersion, accumulation, and the ultimate fate of microplastics in deep-marine environments: a review and future directions. *Frontiers in Earth Science*, 7. doi:10.3389/feart.2019.00080

Kane, I. A., Clare, M. A., Miramontes, E. et al. 2020. Seafloor microplastic hotspots controlled by deep-sea circulation. *Science.* doi:10.1126/science.aba5899

Kanhai, D. K., Gardfeldt, K., Lyashevska, O. et al. 2018. Microplastics in sub-surface waters of the Arctic Central Basin. *Marine Pollution Bulletin*, 130: 8–18. doi:10.1016/j.marpolbul.2018.03.011

Katija, K., Choy, C. A., Sherlock, R. E. et al. 2017. From the surface to the seafloor: how giant larvaceans transport microplastics into the deep sea. *Science Advances*, 3: e1700715. doi:10.1126/sciadv.1700715

Khatmullina, L., Isachenko, I. 2017. Settling velocity of microplastic particles of regular shapes. *Marine Pollution Bulletin*, 114: 871–880. doi:10.1016/j.marpolbul.2016.11.024

Kooi, M., Nes, E. H. V., Scheffer, M. et al. 2017. Ups and downs in the ocean: effects of biofouling on vertical transport of microplastics. *Environmental Science & Technology*, 51: 7963–7971. doi:10.1021/acs.est.6b04702

Kooi, M., Reisser, J., Slat, B. et al. 2016. The effect of particle properties on the depth profile of buoyant plastics in the ocean. *Scientific Reports*, 6: 33882. doi:10.1038/srep33882

Kowalski, N., Reichardt, A. M., Waniek, J. J. 2016. Sinking rates of microplastics and potential implications of their alteration by physical, biological, and chemical factors. *Marine Pollution Bulletin*, 109: 310–319. doi:10.1016/j.marpolbul.2016.05.064

Kukulka, T., Proskurowski, G., Morét-Ferguson, S. et al. 2012. The effect of wind mixing on the vertical distribution of buoyant plastic debris. *Geophysical Research Letters*, 39. doi:10.1029/2012gl051116

Kvale, K. F., Prowe, F. A. E., Oschlies, A. 2020. A critical examination of the role of marine snow and zooplankton fecal pellets in removing ocean surface microplastic. *Frontiers in Marine Science*, 6: 808. doi:10.3389/fmars.2019.00808

Lagarde, F., Olivier, O., Zanella, M. et al. 2016. Microplastic interactions with freshwater microalgae: hetero-aggregation and changes in plastic density appear strongly dependent on polymer type. *Environmental Pollution*, 215: 331–339. doi:10.1016/j.envpol.2016.05.006

Law, K. L., Moret-Ferguson, S., Maximenko, N. A. et al. 2010. Plastic accumulation in the North Atlantic subtropical gyre. *Science*, 329: 1185–1188. doi:10.1126/science.1192321

Lebreton, L. C., Greer, S. D., Borrero, J. C. 2012. Numerical modelling of floating debris in the world's oceans. *Marine Pollution Bulletin*, 64: 653–61. doi:10.1016/j.marpolbul.2011.10.027

Lee, I. H., Lien, R.-C., Liu, J. T. et al. 2009. Turbulent mixing and internal tides in Gaoping (Kaoping) Submarine Canyon, *Taiwan. Journal of Marine Systems*, 76: 383–396. doi:10.1016/j.jmarsys.2007.08.005

Leppäranta and Myrberg (2009) Circulation. Physical Oceanography of the Baltic Sea. Berlin, Germany, Springer: 131–187.

Lobelle, D., Cunliffe, M. 2011. Early microbial biofilm formation on marine plastic debris. *Marine Pollution Bulletin*, 62: 197–200. doi:10.1016/j.marpolbul.2010.10.013

Loeb, G. I., Neihof, R. A. 1975. Marine Conditioning Films. Applied Chemistry at Protein Interfaces, 319–335.

Long, M., Moriceau, B., Gallinari, M., et al. 2015. Interactions between microplastics and phytoplankton aggregates: impact on their respective fates. *Marine Chemistry*, 175: 39–46. doi:10.1016/j.marchem.2015.04.003

Ma, H., Pu, S., Liu, S. et al. 2020. Microplastics in aquatic environments: toxicity to trigger ecological consequences. *Environmental Pollution*, 261: 114089. doi:10.1016/j.envpol.2020.114089

Martin, J., Lusher, A., Thompson, R. C. et al. 2017. The deposition and accumulation of microplastics in marine sediments and bottom water from the Irish continental shelf. *Scientific Reports*, 7: 10772. doi:10.1038/s41598-017-11079-2

Michels, J., Stippkugel, A., Lenz, M. et al. 2018. Rapid aggregation of biofilm-covered microplastics with marine biogenic particles. *Proceedings of the Royal Society B: Biological Sciences*, 285: 20181203. doi:10.1098/rspb.2018.1203

Möhlenkamp, P., Purser, A., Thomsen, L. 2018. Plastic microbeads from cosmetic products: an experimental study of their hydrodynamic behaviour, vertical transport and resuspension in phytoplankton and sediment aggregates. *Elementa Science of the Anthropocene*. doi:10.1525/journal.elementa.317

Oberbeckmann, S., Osborn, A. M., Duhaime, M. B. 2016. Microbes on a bottle: substrate, season and geography influence community composition of microbes colonizing marine plastic debris. *PLoS One*, 11: e0159289. doi:10.1371/journal.pone.0159289

Ogonowski, M., Motiei, A., Ininbergs, K. et al. 2018. Evidence for selective bacterial community structuring on microplastics. *Environmental Microbiology*, 20: 2796–2808. doi:10.1111/1462-2920.14120

Onink, V., Wichmann, D., Delandmeter, P. et al. 2019. The role of Ekman currents, geostrophy, and Stokes drift in the accumulation of floating microplastic. *Journal of Geophysical Research: Oceans*, 124: 1474–1490. doi:10.1029/2018JC014547

Oriekhova, O., Stoll, S. 2018. Heteroaggregation of nanoplastic particles in the presence of inorganic colloids and natural organic matter. *Environmental Science: Nano*, 5: 792–799. doi:10.1039/c7en01119a

Passow, U., Shipe, R. F., Murray, A. et al. 2001. The origin of transparent exopolymer particles (TEP) and their role in the sedimentation of particulate matter. *Continental Shelf Research*, 21: 327–346.

Peng, X., Chen, M., Chen, S. et al. 2018. Microplastics contaminate the deepest part of the world's ocean. *Geochemical Perspectives Letters*, 1–5. doi:10.7185/geochemlet.1829

Pierdomenico, M., Casalbore, D., Chiocci, F. L. 2020. The key role of canyons in funnelling litter to the deep sea: a study of the Gioia Canyon (Southern Tyrrhenian Sea). *Anthropocene*, 30. doi:10.1016/j.ancene.2020.100237

Pinto, M., Langer, T. M., Huffer, T. et al. 2019. The composition of bacterial communities associated with plastic biofilms differs between different polymers and stages of biofilm succession. *PLoS One*, 14: e0217165. doi:10.1371/journal.pone.0217165

PlasticsEurope 2019. *Plastics-the facts 2019*. https://plasticseurope.org/wp-content/uploads/2021/10/2019-Plastics-the-facts.pdf

Pohl, F., Eggenhuisen, J. T., Kane, I. A. et al. 2020. Transport and burial of microplastics in deep-marine sediments by turbidity currents. *Environmental Science & Technology*, 54: 4180–4189. doi:10.1021/acs.est.9b07527

Porter, A., Lyons, B. P., Galloway, T. S. et al. 2018. Role of marine snows in microplastic fate and bioavailability. *Environmental Science & Technology*, 52: 7111–7119. doi:10.1021/acs.est.8b01000

Poulain, M., Mercier, M. J., Brach, L. et al. 2019. Small microplastics as a main contributor to plastic mass balance in the North Atlantic subtropical gyre. *Environmental Science & Technology*, 53: 1157–1164. doi:10.1021/acs.est.8b05458

Puig, P., Palanques, A., Martin, J. 2014. Contemporary sediment-transport processes in submarine canyons. *Annual Review of Marine Science*, 6: 53–77. doi:10.1146/annurev-marine-010213-135037

Ramirez-Llodra, E., Brandt, A., Danovaro, R. et al. 2010. Deep, diverse and definitely different: unique attributes of the world's largest ecosystem. *Biogeosciences*, 7: 2851–2899. doi:10.5194/bg-7-2851-2010

Reisser, J., Slat, B., Noble, K. et al. 2015. The vertical distribution of buoyant plastics at sea: an observational study in the North Atlantic Gyre. *Biogeosciences*, 12: 1249–1256. doi:10.5194/bg-12-1249-2015

Richard, H., Carpenter, E. J., Komada, T. et al. 2019. Biofilm facilitates metal accumulation onto microplastics in estuarine waters. *Science of the Total Environment*, 683: 600–608. doi:10.1016/j.scitotenv.2019.04.331

Rummel, C. D., Jahnke, A., Gorokhova, E. et al. 2017. Impacts of biofilm formation on the fate and potential effects of microplastic in the aquatic environment. *Environmental Science & Technology Letters*, 4: 258–267. doi:10.1021/acs.estlett.7b00164

Ryan, P. G. 2015. Does size and buoyancy affect the long-distance transport of floating debris? *Environmental Research Letters*, 10. doi:10.1088/1748-9326/10/8/084019

Sanchez-Vidal, A., Llorca, M., Farré, M. et al. 2015. Delivery of unprecedented amounts of perfluoroalkyl substances towards the deep-sea. *Science of the Total Environment*, 526: 41–48. doi:10.1016/j.scitotenv.2015.04.080

Serpetti, N., Gontikaki, E., Narayanaswamy, B. E. et al. 2013. Macrofaunal community inside and outside of the Darwin Mounds Special Area of Conservation, NE Atlantic. *Biogeosciences*, 10: 3705–3714. doi:10.5194/bg-10-3705-2013

Shanks, A. L., Trent, J. D. 1979. Marine snow: sinking rates and potential role in vertical flux. *Deep Sea Research*, 27, 137–143.

Snelgrove, P. V. R., Smith, C. R. 2002. A riot of species in an environmental calm: the paradox of the species-rich deep-sea floor. *Oceanography and Marine Biology: An Annual Review*, 40: 311–342.

Song, Y. K., Hong, S. H., Eo, S. et al. 2018. Horizontal and Vertical distribution of microplastics in Korean coastal waters. *Environmental Science & Technology*, 52: 12188–12197. doi:10.1021/acs.est.8b04032

Suaria, G., Achtypi, A., Perold, V. et al. 2020. Microfibers in oceanic surface waters: a global characterization. *Science Advances*, 6. doi:10.1126/sciadv.aay8493

Summers, S., Henry, T., Gutierrez, T. 2018. Agglomeration of nano- and microplastic particles in seawater by autochthonous and de novo-produced sources of exopolymeric substances. *Marine Pollution Bulletin*, 130: 258–267. doi:10.1016/j.marpolbul.2018.03.039

Tekman, M. B., Wekerle, C., Lorenz, C. et al. 2020. Tying up loose ends of microplastic pollution in the arctic: distribution from the sea surface through the water column to deep-sea sediments at the HAUSGARTEN observatory. *Environmental Science & Technology*, 54: 4079–4090. doi:10.1021/acs.est.9b06981

Ter Halle, A., Ladirat, L., Gendre, X. et al. 2016. Understanding the fragmentation pattern of marine plastic debris. *Environmental Science & Technology*, 50: 5668–5675. doi:10.1021/acs.est.6b00594

Thompson, R. C., Olsen, Y., Mitchell, R. P. et al. 2004. Lost at sea: where is all the plastic. *Science*, 304: 838.

Thurber, A. R., Sweetman, A. K., Narayanaswamy, B. E. et al. 2014. Ecosystem function and services provided by the deep sea. *Biogeosciences*, 11: 3941–3963. doi:10.5194/bg-11-3941-2014

Tubau, X., Canals, M., Lastras, G. et al. 2015. Marine litter on the floor of deep submarine canyons of the northwestern Mediterranean Sea: the role of hydrodynamic processes. *Progress in Oceanography*, 134: 379–403. doi:10.1016/j.pocean.2015.03.013

Turner, A., Filella, M. 2020. The influence of additives on the fate of plastics in the marine environment, exemplified with barium sulphate. *Marine Pollution Bulletin*, 158: 111352. doi:10.1016/j.marpolbul.2020.111352

Turner, J. T. 2015. Zooplankton fecal pellets, marine snow, phytodetritus and the ocean's biological pump. *Progress in Oceanography*, 130: 205–248. doi:10.1016/j.pocean.2014.08.005

Uurasjarvi, E., Paakkonen, M., Setala, O. et al. 2020. Microplastics accumulate to thin layers in the stratified Baltic Sea. *Environmental Pollution*, 268: 115700. doi:10.1016/j.envpol.2020.115700

Van Sebille, E., Aliani, S., Law, K. L. et al. 2020. The physical oceanography of the transport of floating marine debris. *Environmental Research Letters*, 15. doi:10.1088/1748-9326/ab6d7d

Van Sebille, E., Scussolini, P., Durgadoo, J. V. et al. 2015a. Ocean currents generate large footprints in marine palaeoclimate proxies. *Nature Communications*, 6: 6521. doi:10.1038/ncomms7521

Van Sebille, E., Wilcox, C., Lebreton, L. et al. 2015b. A global inventory of small floating plastic debris. *Environmental Research Letters*, 10. doi:10.1088/1748-9326/10/12/124006

Vroom, R. J. E., Koelmans, A. A., Besseling, E. et al. 2017. Aging of microplastics promotes their ingestion by marine zooplankton. *Environmental Pollution*, 231: 987–996. doi:10.1016/j.envpol.2017.08.088

Waldschlager, K., Schuttrumpf, H. 2019. Effects of particle properties on the settling and rise velocities of microplastics in freshwater under laboratory conditions. *Environmental Science & Technology*, 53: 1958–1966. doi:10.1021/acs.est.8b06794

Woodall, L. C., Sanchez-Vidal, A., Canals, M. et al. 2014. The deep sea is a major sink for microplastic debris. *Royal Society Open Science*, 1: 140317. doi:10.1098/rsos.140317

Zettler, E. R., Mincer, T. J., Amaral-Zettler, L. A. 2013. Life in the “plastisphere”: microbial communities on plastic marine debris. *Environmental Science & Technology*, 47: 7137–7146. doi:10.1021/es401288x

Zhao, S., Danley, M., Ward, J. E. et al. 2017. An approach for extraction, characterization and quantitation of microplastic in natural marine snow using Raman microscopy. *Analytical Methods*, 9: 1470–1478. doi:10.1039/c6ay02302a

Zhao, S., Ward, J. E., Danley, M. et al. 2018. Field-based evidence for microplastic in marine aggregates and mussels: implications for trophic transfer. *Environmental Science & Technology*, 52: 11038–11048. doi:10.1021/acs.est.8b03467

Zhao, Z., Alford, M. H., Lien, R. C. et al. 2012. Internal tides and mixing in a submarine canyon with time-varying stratification. *Journal of Physical Oceanography*, 42: 2121–2142. doi:10.1175/jpo-d-12-045.1

Zobkov, M. B., Esiukova, E. E., Zyubin, A. Y. et al. 2019. Microplastic content variation in water column: the observations employing a novel sampling tool in stratified Baltic Sea. *Marine Pollution Bulletin*, 138: 193–205. doi:10.1016/j.marpolbul.2018.11.047

6

Marine Litter, Plastic, and Microplastics on the Seafloor

Francois Galgani[1], Angiolillo Michela[2,3], Olivia Gérigny[1], Thomas Maes[4], Eric Tambutté[5], and Peter T. Harris[4]

[1] *Institut Français de Recherche pour l'Exploitation de la MER (IFREMER), Centre Méditerranée, La Seyne-sur-Mer, France*
[2] *Istituto Superiore per la Protezione e Ricerca Ambientale (ISPRA), Via Vitaliano Brancati, Roma, Italy*
[3] *Stazione Zoologica Anton Dohrn (SZN), Villa Comunale, Napoli, Italy*
[4] *Grid Arendal, Teaterplassen 3, Arendal, Norway*
[5] *Centre Scientifique de Monaco, Avenue Saint Martin, Monaco, Principality of Monaco*

6.1 Introduction

Recent assessments of floating large debris and microparticles (Eriksen et al. 2014; Van Sebille et al. 2015) have shown that quantities located on the surface are limited and that the presence of sinks should be considered. With a surface area of 361 220 420 km^2, of which 300 875 000 km^2 is deep sea (worldatlas.com), the seafloor constitutes an important component of the marine environment and is known for its important role, supplying abundant resources, and ecosystem services (Canals et al. 2020). It is also the ultimate sink for all marine litter (Woodall et al. 2014).

The geomorphology of the global ocean floor includes the continental shelf, continental slope, the abyssal environments that include abyssal plains and mid-ocean spreading ridges, and the hadal zone found below a depth of 6000 m (Harris et al. 2014). The greatest depths occur in ocean trenches on subducting ocean margins, with the deepest location being at approximately 11 000 m in the Mariana Trench in the Western Pacific. The presence of plastic items (Peng et al. 2018) and ingested microplastics in amphipod populations in deep ocean trenches (Jamieson et al. 2019) illustrates that microplastics contaminants occur in the very deepest, most remote places of the oceans.

Given that approximately half of the plastics produced is heavier than seawater (Geyer et al. 2017), the seafloor, from intertidal to abyssal and hadal depths, is an important long-term sink for marine macro and microplastics (Figure 6.1; Galgani et al. 1996; Harris 2020; Kane et al. 2020; Pham et al. 2014; Sanchez-Vidal et al. 2018). Accumulation in the deep sea is of particular concern, since most polymers are highly persistent in the marine environment and only degrade slowly as a result of photolysis (Andrady 2011) and physical wear and tear, which are processes that occur only over geologic timescales. Degradation is also likely to be decreased at depth where oxygen concentrations are low in addition to the absence of light (Ioakeimidis et al. 2016). Estimates for the longevity of plastics are variable, but are believed to be in the range of hundreds of years depending on the physical and chemical properties of the polymer and the size of the item.

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

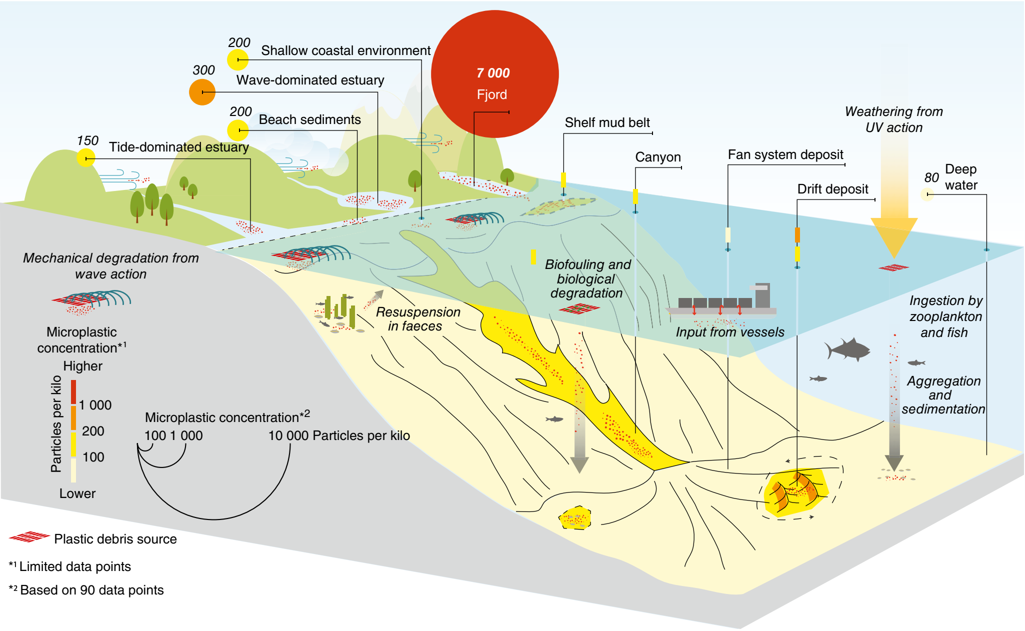


Figure 6.1 Natural processes affecting the distribution and fate of microplastics (after UNEP, 2021).

The first evidence of the presence of plastics on the seabed dates back to 1971 (Heezen and Hollister 1971) and then 1976 when Holmström (1975) was trying to understand why plastic polyethylene bags were found on the bottom of the Baltic Sea. Although many fishermen or divers were aware of the presence of waste on the seabed, it was not until 1987 a first summary assessment and comparison of the quantity of waste was done between several sites in a coastal bay of Turkey in the Mediterranean Sea (Bingel et al. 1987). In the 1990s, several fish stock assessment surveys with a bottom trawl monitored waste presence/absence based on a limited number of categories, in particular plastics, glass, metals, etc. (Galgani et al. 1995; Galil et al. 1995). It quickly became clear that seafloor litter was causing an impact on the seabed (Laist 1997), fishing gear was omnipresent (Hess et al. 1999; June 1990; Laist 1997; Link et al. 2019; Macfadyen et al. 2009), and coastal canyons acted as litter traps (Galgani et al. 1996). The first large-scale studies and assessment of seafloor litter in European seas, integrating data from different surveys and areas, date from the end of the 1990s (Galgani et al. 2000). A recent study using the same approach looked at trends over a 25-year period (Maes et al. 2018), surprisingly no trends were actually found, possibly because the surveys did not distinguish between long-term depositional and transitory (or erosional) environments (Harris 2020). The desire to integrate litter monitoring into the European Marine Strategy Framework Directive (MSFD 2008/56/EC) and the consideration of an indicator relating to seafloor litter has undoubtedly been a powerful driving force for research and monitoring in Europe.

More recently, attention has shifted toward microplastics in seafloor sediments, which are considered to be the ultimate sink for all marine litter (Van Cauwenberghe et al. 2013; Woodall et al. 2014). Seafloor sediments are the topic of many studies addressing the various types of sediments in different marine environments and habitats including bays, mangroves, fjords, harbors, shelves, slopes, canyons, and deep sea sediments in the bathyal, abyssal, and hadal zones (Harris 2020).

Collecting substantial information on the quantities and ubiquitous distribution of litter on the seabed, in particular for those parts that are inaccessible by conventional methods, has become critical. Together with data on harm to marine organisms, especially entanglement in lost fishing gear, ingestion by benthic species, and colonization of the deep sea, this information will greatly improve our knowledge, enabling more precise assessments of distribution, trends, and impacts, while also supporting dedicated reduction measures for seafloor litter.

6.2 Methods Used to Monitor Seafloor Litter

Some seafloor areas can be difficult to monitor due to differences in the seabed, e.g. structures and types, which can be sandy, muddy, or rocky (GESAMP 2019). A range of different approaches may be used to cost effectively monitor seafloor areas, e.g. using simple litter quantification protocols based on existing fish stock surveys. Some of the most common approaches use bottom trawls, visual surveys via SCUBA divers, and/or video imagery via remotely operated vehicles (ROVs; Figure 6.2). For shallow waters, the most common method used to estimate marine litter densities, alongside assessments of benthic species, encompasses diving activities that are sometimes coupled with compliance surveys relating to, e.g. pipelines, marine-protected areas, oil platforms, inventories of biodiversity, since their methods are similar (Galgani et al. 2013).

In the past, benthic trawling techniques were recommended to monitor litter, often piggybacking on fish stock assessment programs taking place regularly across many regions (Goldberg 1995). Fish stock assessment surveys have been designed to evaluate fish stocks and have been used in many surveys for marine litter; however, the approach has some critical drawbacks. Because the seafloor topography may affect the accumulation of litter on the seafloor and impose sampling restrictions in rocky areas, trawling is limited to shelf areas made of soft bottoms, between 10 and

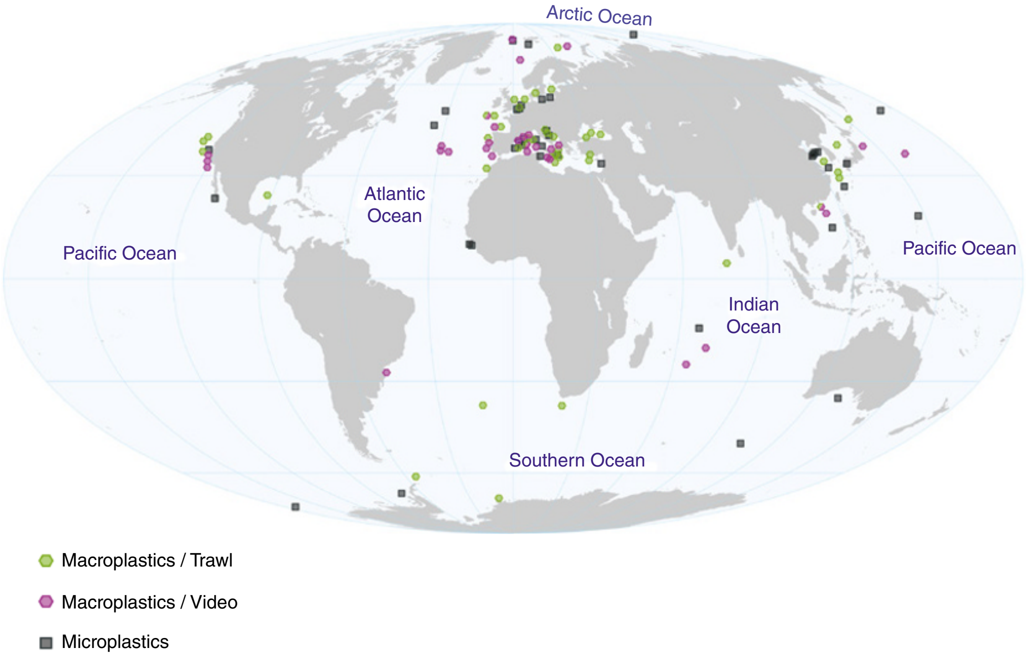


Figure 6.2 An overview of experiments on seafloor litter and sediment microplastics performed during the past decade (2010–2020).

a few hundred meters depth. Moreover, most trawling nets, except for beam trawls, are designed to roll over the seafloor while collecting epibenthos, leaving the upper sediments and items buried within the sediment more or less undisturbed. In addition, the significant differences between the catchability of the different trawling nets and their configurations, the diversity of gear types, vessel speed, mesh size, cod ends, and fishing methods used among countries and regions, programs, observers, and studies seriously limit cross-comparison of seafloor macrolitter numbers based on data obtained opportunistically via fisheries surveys.

Standardization on a local or national scale might be possible, e.g. the long-term MEDITS program in the Mediterranean Sea, due to the promotion of one unique type of trawling (Spedicato et al. 2019). Such a situation is, however, difficult to achieve across larger regions since standardized monitoring protocols of bottom trawl surveys differ between marine areas due to different substrate types and targeted fish stocks. Moreover, seafloor litter monitoring is mostly a secondary objective in fisheries surveys; therefore, the interpretation, interest, and attention given by observers differ from survey to survey and year to year, making temporal and spatial trend analysis very difficult. Due to the high variability in the observed seafloor litter concentrations, resulting from the many issues described earlier, the power of seafloor litter monitoring programs is rather low, so only reductions in the range of 40–60% can be measured with certainty (Maes et al. 2015).

Recent studies, based on model-based predictions of seafloor litter densities (review in Canals et al. 2020), might be useful to identify litter hot spots and accumulation zones. Such approaches must still be validated with field data. Last but not least, the degradation of seafloor habitats resulting from destructive trawling does not warrant obtaining marine seafloor litter data from the field solely; nonetheless, this balance certainly deserves future consideration.

Thanks to technological advances and the increasing accessibility of innovative instruments, imaging techniques using submersibles, ROVs, underwater autonomous vehicles (AUVs), and towed cameras, have allowed researchers to estimate litter distribution, while abundance and at the same time detect litter occurrence and impacts, describing litter interactions with marine organisms through direct visual observations (Angiolillo 2019). Video imagery has been increasingly used, addressing the demand for new indicators of harm within the MSFD (Galgani et al. 2013). These techniques are also well adapted to the study of submarine canyons and other areas inaccessible by trawling, such as steep slopes, rocky bottoms, and ultradeep areas such as the oceanic trenches (Bergmann and Klages 2012; Chiba et al. 2018; Galgani and Lecornu 2004; Hiroshi et al. 2011; Ioakeimidis et al. 2015; Tekman et al. 2017). When using video imagery, the area inspected during transects is measured by multiplying the transect length by the field of vision or width of the camera (using laser pointer scale or calculated altitude), and items are counted and results expressed in densities (per km^2) or alternatively in the absence of lasers, in numbers of items per line kilometer. Recently, artificial intelligence has been proposed for the successful visual detection of litter in underwater environments (Fulton et al. 2019). This automatic detection approach appears to support and facilitate future real-time surveys and analysis. In some specific cases, AUVs can also be used successfully in combination with acoustic tools to detect lost/derelict fishing traps (Clark et al. 2012).

The disadvantages of these image-based approaches include the minimum area and size of litter that can be identified. Depending on the resolution offered by imaging tools, the burying or coverage of litter by sediments and organisms, the possible mixing of items together with sediments or natural debris in accumulation areas, and the fine identification of items can be difficult (Canals et al. 2020).

On the other hand, image-based systems are noninvasive, in that they do not harm benthic organisms and may be operated at all depths and in all landscapes, possibly georeferencing individual items and enabling local and small-scale observations. Moreover, these systems allowed researchers to assess litter interaction with marine organisms. In addition, upscaling monitoring to the global scale is not possible with methods such as trawling, as they cannot be used everywhere.

Regarding the seafloor, the main categories of litter are considered by material type, but individual subcategories can be related to specific sources or uses such as fishing gear. When using imagery, litter objects may simply be quantified by size (Mordecai et al. 2011), because the item itself, its weight, or use cannot be determined (Buhl-Mortensen and Buhl-Mortensen 2017).

Citizen science can also play a useful role in monitoring seafloor litter. Assessments are generally limited to scuba divers in shallow waters during regular observations or cleaning operations (Galgani et al. 2013). Many underwater cleanups organized by clubs or Non Governmental Organizations (NGOs) can be a valuable source of information and part of regular surveys. For example, the AWARE Project's 'Dive Against Debris' program has been shown to be an efficient network for shallow water litter monitoring using scuba divers worldwide (Consoli et al. 2020; Morales-Caselles et al. 2021). Other practical initiatives dedicated to the "Fishing For Litter" (FFL) philosophy, involving the fishing industry, have been shown to provide valuable information on seafloor litter, which may be useful to support regular assessments and monitoring.

Specific tools and important means are needed for microplastics sampling in the deep sea. Furthermore, the methodological challenges involved in analyzing sediments and microplastic polymer types can be rather costly and require dedicated laboratory equipment. Generally, sediment samples and replicates are collected from surface and near-surface sediment scrapes obtained from a bulk sample collected by a grab or core sampler operated by divers, ROVs, or from the vessel. Sediment cores can be sliced into depositional sections to record the vertical distribution and accumulation of microplastics over time (Kukkola et al. 2020). In order to do so, the sediments need to be relatively undisturbed by physical or biological (bioturbation) processes (Brandon et al. 2019).

Generally, authors choose to express microplastics abundance in sediments as items per gram or kilogram sediment dry weight to eliminate the variability of volume calculation. Such reporting units provide information on the occurrence of microplastics and some information on their abundance, but are not useful for modeling the fate of plastics in the environment, which requires measurements of mass per unit area per unit time (Harris 2020).

A common issue with microplastics numbers arises from the fact that data sets are further complicated by the wide variety of methodological approaches applied by different researchers to extract, identify, quantify, and characterize microplastics with methodological inconsistencies related to differences in size limits, extraction technique, and variations in sampling techniques (GESAMP 2016). Counting the numbers of particles is problematic where laboratory procedures could cause fragmentation of plastic particles; such procedures include that the sediment sample is sieved, dried, rehydrated, centrifuged, stirred vigorously, and/or disaggregated by mortar and pestle. Finally, environmental levels of microplastics may be difficult to compare due to the lack of QA/QC and consistency between extraction protocols. Procedural contamination by airborne particles (GESAMP 2016) and the blind spots of each method mean that no technique is perfect (Primpke et al. 2017). The visual identification of microplastics alone has become inappropriate for studies on particles below a few hundred micrometers in size. New approaches for the analysis of microplastics in environmental samples, based on selective fluorescent staining using Nile Red, followed by density-based extraction and filtration, have been used for rapid screening approaches (Bakir et al. 2020; Maes et al. 2017a). In the Western world, more often costly analytical methods have been applied, such as Fourier transform infrared spectroscopy and Raman spectroscopy, and introduced globally to determine particle composition.

6.3 Sources

Despite the patchiness in terms of coverage of the deep seafloor by fish stock surveys, a large number of records exist thanks to studies covering extensive geographic areas or considerable water depths (Canals et al. 2020; Galgani et al. 2000; Harris 2020; Keller et al. 2010; Maes et al. 2018; Pasquini et al. 2016; Pham et al. 2014; Pierdomenico et al. 2019; Ramirez-Llodra et al. 2013; Woodall et al. 2015). These data show that benthic litter is not homogeneously distributed. The variability of litter composition and abundance in deep sea environments is strongly influenced by both natural and anthropogenic factors linked to sources, transport, and depositional mechanisms. Variations in the distribution of litter may relate to differences in inputs; bottom structures, including slopes, the sedimentation rate, and the presence of special features like canyons; and local hydrographic situations. Flow dynamics are also controlled by meteorological conditions, as well as by water column stratification and vertical and horizontal transport (Canals et al. 2020).

Sources of litter arriving on the seabed can be distinguished as either land or sea based, the former including wind, riverine inputs, discharge from urban and industrialized areas, and coastal touristic activities, the latter mainly represented by commercial shipping and recreational boating, fishing activities, aquaculture, and offshore installations (Angiolillo et al. 2015; GESAMP 2021; Lopez-Lopez et al. 2017; Loulad et al. 2019). In 2018, about 348 million metric tons (MT) of plastic waste was generated in the world (PlasticsEurope 2019), with amounts entering the ocean every year evaluated for 2010 in the range of 4.8–12.7 million MT (Jambeck et al. 2015), of which between 1.15 and 2.41 million tons from rivers alone (Lebreton et al. 2017).

There is growing evidence that the atmospheric transport of microplastics is an important mode of transport and delivery to remote environments, including the deep sea (Zhang et al. 2020b). Unfortunately, there are very little data available, and further research is needed to assess the overall significance of wind-borne microplastics.

In general, the magnitude of land-based litter input, the largest source of seafloor litter, is largely dependent on the anthropization of the surrounding coastal area and watersheds (Mordecai et al. 2011b), while its transport to the deep sea is mostly controlled by oceanographic processes and the physiography of the marine area in which the item finds itself in Pham et al. (2014). Interestingly, a study in the Bay of Biscay showed that the most important driver for benthic litter distribution was human population, as litter density increased linearly with this variable. Similarly, the number of ports in neighboring areas had a positive effect on litter densities on the seafloor, while fishing effort had a nonlinear effect on benthic litter density, a finding that could be explained by litter upheaval during fishing operations (Lopez-Lopez et al. 2017).

Regions characterized by heavily industrialized and populated coastal areas (e.g. the Mediterranean Sea) have some of the highest densities of seafloor litter pollution worldwide (Galgani et al. 1995; Pierdomenico et al. 2020), with some accumulation points where enormous amounts of litter have been recorded (Angiolillo et al. 2021; Peng et al. 2020; Pierdomenico et al. 2019). High densities of microplastics, in particular fibers, have also been recorded in Mediterranean seabed sediments (Kane et al. 2020; Sanchez-Vidal et al. 2018; Woodall et al. 2014). For microplastics, the greatest concentration reported in the review by Harris (2020) was in sediments adjacent to a sewage ocean outfall in Byfjorden, Bergen, Norway, where Haave et al. (2019) reported 200 000 particles per kg dry weight.

Maritime sources can be important along major shipping routes and on rocky habitats, where fishing-related debris may accumulate (Danovaro et al. 2020; Ramirez-Llodra et al. 2013), or when shipping can be the major source like on remote islands (Mifsud et al. 2013).

Large vessels with many crew members may carry supplies for several months and daily generate solid waste that may end up as marine litter, most often disposed accidentally through bad handling, unfavorable weather conditions, inadequate handling, and lack of reception facilities in ports (GESAMP 2016). The shipping industry can also be a source of microplastics (accidental spills of industrial resin pellets, paint particles, gray waters, etc.) and industrial fishing vessels, such as supply or catch transport vessels, may deliberately or accidentally release litter items such as gloves, fish boxes, storage drums, and personal waste into the marine environment (Richardson et al. 2018, 2019). Some marine litter items are exclusive to shipping sources, such as large ropes, injection gun cartridges, oil drums, and clinkers, which are residues from coal burning steamships that are largely found along historic shipping routes. In the Mediterranean Sea, data collected through trawling indicate that clinkers are a very common type of litter, representing up to 28% of total litter by weight (García-Rivera et al. 2018). In addition, container losses from ships, in the range of thousands every year, quickly sink to the seafloor and represent an important source of debris close to shipping lanes (Galafassi et al. 2019; GESAMP 2019).

Much lower litter abundances are often recorded along the continental margin, especially on soft bottoms (Galgani et al. 1995; Peng et al. 2020), but a prevalence of maritime-related litter can be found in fishing grounds. When artisanal fishing is locally developed, or when trawling is forbidden, fishing nets are found close to the coast within a distance of a few nautical miles (Strafella et al. 2015). The depositional mechanisms for litter of maritime origin mostly include the settling of lost or discarded material (Ramirez-Llodra et al. 2013) and the entanglement of fishing-related debris in rocky outcrops (Angiolillo et al. 2015). It is clear that the surrounding local activities determine the plastic footprint found on the seafloor. An emerging type of plastic is single-use plastic items, e.g. food packaging that often represents the largest fraction of litter and contributes the most to seafloor litter on the continental shelf and upper slope (Fortibuoni et al. 2019), while in some areas, aquaculture represents a key activity-producing marine litter. Some authors also indicated that illegal dumping (construction and electronic goods) is, together with single-use plastics, a major source of litter in coastal areas and bays (GESAMP 2021).

Once on the seabed, litter is subject to a variety of human activities, such as dredging or bottom trawling. These activities may remobilize litter items, contributing to their further degradation and fragmentation. Bottom trawling, for instance, can remobilize light litter, which can again be reburied in sediments or recarried in sediment density flows, e.g. deep water sediment transport (Canals et al. 2020).

Dumping sites, including warfare material, ammunition, toxic substances, wrecks, and other related material, although often not counted as marine litter, are important types of anthropogenic material that need to considered for monitoring seafloor debris and its impacts.

6.4 Oceanographic Conditions on the Seafloor

In estuaries, large rivers are responsible for significant inputs of waste to the oceans, some of it will sink rapidly to the seabed or get transported offshore due to high flow rates and strong currents (Lebreton et al. 2017). Alternatively, small rivers and estuaries also transport litter; weak currents facilitate deposition on shores and banks (Galgani et al. 2000). In addition, litter may accumulate upstream of estuarine salinity fronts and eventually be transported to the sea when river flow velocity increases (Acha et al. 2003).

A lower litter concentration may be found along the continental margin (Peng et al. 2020; Pierdomenico et al. 2020), due to the main transport processes for benthic litter, which are mostly driven by sedimentary gravity flows and oceanic currents, delivering high energy in specific cases, e.g. canyons (Pierdomenico et al. 2019; Tubau et al. 2015). Confirmation that litter is transported downslope into canyons and deep sea fan and drift deposits via hyperpycnal turbidity flows awaits evidence of litter incorporated into turbidite beds sampled in sediment cores (Harris 2020).

Numerical models can be used to predict the fate of litter in the sea, but we are far from having a full understanding of all the parameters involved and require multidisciplinary approaches to build realistic simulations. Most model setups focus on surface and subsurface circulation, and only a few studies have investigated the fate of marine litter, taking into account loss by degradation, fragmentation, sinking, ingestion, and biofouling.

In the Mediterranean, sinking processes have been computed in a statistical way, taking into account the age of particles by a three-dimensional current field (Liubartseva et al. 2018), while neglecting particle buoyancy changes, subsurface transport, and seafloor resuspension. Using different settling rate coefficients, the mathematical consideration of the sinking particles is the same for both microplastics and macroplastics. In a modeled study where all the existing processes were included, the water column, plastic density, biofilm thickness, and biofilm density had the biggest effect on transport, followed by turbulent dispersion (Jalón-Rojas et al. 2019).

Land-sourced litter can be a major fraction of total litter in coastal waters and may come from distant inland sources through riverine and aeolian transport, the latter being a possible important source of microplastics in remote parts of the oceans. Extreme events such as heavy rainfall, floods, sewage overflow, coastal storms, hurricanes, and tsunamis can carry large amounts of debris onto beaches and in coastal waters within only a few hours or days. Part of this debris spreads seawards and settles on the seafloor (Canals et al. 2020; Galgani et al. 2000, 2015). Floating litter, in particular, eventually reaches the seabed in shallow coastal zones, due to fouling together with passive sinking, but it may already have been transported for considerable distances before sinking through ocean currents (Galgani et al. 2000; Pierdomenico et al. 2019).

Annual variations in litter transport, such as seasonal changes in the flow rate of deep currents, sediment transport, and ocean circulation patterns, cause considerable spatial variability of litter abundance, with accumulation areas in bays and canyons, often near large cities, rather than in the open sea. In the deep sea, hydrodynamic conditions and current regimes differ locally due to the geomorphology, topography, and habitat heterogeneity of the seabed, influencing litter distribution. It is important to note that the timescales over which this transport arises depend on the frequency of the currents transiting these oceanic systems. Litter and microplastic transport is also controlled by other transport processes, such as internal tides, advection, and vertical settling (Pohl et al. 2020). Even the smallest, most buoyant microplastic will eventually sink to the seabed as a consequence of flocculation, biofouling, or ingestion and excretion via fecal pellets. It has been shown that velocities of particles differ significantly as a result of variations in densities, sizes, and shapes, leading to inconsistencies in assessments of depth-integrated buoyant plastic concentrations (Kooi et al. 2017). Polymers with densities above 1.15 g/cm^3, e.g. polyamide (fishing nets), polyvinyl chlorides, polyesters, polyethylene terephthalate (PET bottles), and rayon (Harris 2020), are commonly found on the seafloor and in deep sea sediments, while the presence of polyethylene and polypropylene is more widely spread. Floating plastic debris at sea undergoes fouling that may result in a loss of buoyancy and form a possible transfer mechanism toward the seafloor by increasing the density of the debris. The presence of large amounts of microplastics in the water column has been demonstrated recently. In deeper waters, the density of the water is often higher because of lower temperature and/or higher salinities, limiting the sinking of particles, keeping them motionless under certain conditions, and capturing them within high-density layers. Debris may also undergo rapid defouling because of grazing or the decay of organisms, making it resurface, after which the cycle of events repeats itself (Ye and Andrady 1991).

It is clear that marine litter and microplastics share some important attributes of natural sediments and organic material when arriving in the marine environment (Harris 2020).

Their physical transport and dispersal into coastal environments often follow similar pathways, with the more coarse-grained and dense items or particles deposited close to source. In high-energy, coastal and shelf environments, macroplastic items break down into smaller microplastics via fracturing during bedload transport. Finer, less dense particles may remain in suspension.

For microplastics, common transport schemes have been proposed in line with pathways for Particulate Organic Carbion (POC) matter and sediment particles (Enders et al. 2019; Harris 2020). The delivery of microplastic particles and other litter to the deep sea is not likely to commonly occur via turbidity flows down submarine canyons. Such flows are rare with the modern earth's high sea level where the coastal sediment source is far removed from the shelf edge where submarine canyons commence.

Only about 3% of shelf-incising canyons are geomorphologically linked to a contemporary fluvial system (Harris and Whiteway 2011). Thus, most canyon systems may not currently function as conduits for microplastics from the coast to the deep ocean floor.

The distribution of microplastic particles is heterogeneous in all environments. It is evident that some coastal environments contain higher concentrations of microplastic particles than others because they are closer to highly populated, industrial or touristic areas, and more exposed to plastic pollution. However, the occurrence of locally high numbers of litter and microplastic particles in remote, deep sea environments, far removed from any clear anthropogenic point source, can only be explained by natural processes. Microplastics are dispersed widely over the ocean but appear to be spatially concentrated in specific deep sea environments, particularly in canyons, deep ocean trenches, sediment drift deposits, and beneath surface water areas of high productivity that export POC to the seafloor. The latter POC export mechanism is suggested by Bergmann et al. (2017) and Tekman et al. (2017) who reported a correlation with POC at Arctic Ocean Hausgarten observatory stations, possibly as a result of the flocculation of algae-incorporating microplastic during their descent through the water column to the seabed. In this way, plankton blooms may act as local vacuum-cleaners for microplastic particles, removing them from the water column.

Although distance from the coast is an important factor in explaining microplastics distributions in coastal areas (Alomar et al. 2020), the abundance of litter and microplastics on the deep seafloor does not decrease with distance from terrestrial input sources (Chiba et al. 2018; Harris 2020; Peng et al. 2020). It appears that microplastics are concentrated by bottom currents that transport particles into local depositional environments, whereas microplastics are depleted in other sites where bottom currents erode the seabed. Interestingly, converging currents were also shown to mix particles with sediments and benthic organisms (Harris 2020).

6.5 Accumulation Areas of Litter at the Seafloor

Submarine canyons with heads close to the coast, or other submarine structures (i.e. seamounts, steep and vertical walls, channels, etc.), funneling large masses of dense water, can act as primary vectors of litter transport from the coast to the deep sea (Danovaro et al. 2020; Galgani et al. 1996; Tubau et al. 2015), where litters accumulates.

Gravity-driven avalanches, known as turbidity currents, form the primary process for delivering terrestrial sediment and organic carbon to the deep sea through submarine canyons. However, the ability of turbidity currents to transport and bury plastics has never been shown to occur. Downflowing bottom currents can be intense in submarine canyons (Canals et al. 2006) and result from abrupt topographic changes that produce upslope and/or downslope currents driven by geostrophic pressure gradients (Pierdomenico et al. 2020). The strongest effects on circulation are produced by narrow canyons and large amounts of litter can be funneled through them by multiple processes (Alomar et al. 2020), showing that the magnitude of this pollution may be greater than expected. This funneling phenomenon has been documented as creating litter "hot spots" (i.e. large accumulations of litter) formed by mixtures of land and marine sourced and natural debris items in canyons, showing how efficient this transport can be and that the magnitude of this pollution may be greater than previously thought (Canals et al. 2020; Galgani et al. 1996; Mordecai et al. 2011a; Pham et al. 2014; Pierdomenico et al. 2019, 2020; Ramirez-Llodra et al. 2013; Tubau et al. 2015; Watters et al. 2010; Wei et al. 2012). Flume studies reveal that turbidities such as those deposited in canyons may contain microplastics (Pohl et al. 2020). As another possible explanation, a boundary current flowing along (parallel to) the continental shelf encountering head of a submarine canyon must slow down because of the mass conservation, allowing more time for particles to settle, then resulting in a higher concentration of particles arriving on the canyon seabed compared with the seabed under the faster flowing current. Large debris objects may further tumble down the steep slope, unless entangling like ALDFG (abandoned, lost or otherwise discarded fishing gear) in rocks, stones, or reefs (Pham et al. 2014; Schlining et al. 2013), further concentrating litter in the canyon thalweg.

Gravity flows may be increased by hyperpycnal flows generated during flash-flood events (Galgani et al. 2000; Pierdomenico et al. 2019), also resulting in the burial of land-based litter beneath the seafloor. In some canyons, specifically, the widespread occurrence of partially buried terrestrial vegetal debris, including large tree trunks and other large-sized items, testifies the occurrence of hyperpycnal flows (Pierdomenico et al. 2020). In some coastal canyons, a strong role of direct riverine inputs has been shown, as suggested by the occurrence of sandy seafloors intermingled with vegetal material, most often light items (Pierdomenico et al. 2020).

The majority of the observed debris seems to be concentrated within the thalwegs of the canyons and is often composed of plastic, e.g. PET bottles, indicating a predominantly land-based origin for litter in the canyons, as opposed to the prevalence of fishing-related debris observed along the continental margin.

Deposition in canyons may be favored by higher sedimentation rates near the bottom, which depend on the water flow, the type of litter, the size of the items, and complex seafloor morphologies (i.e. canyons' flanks; Schlining et al. 2013; Tubau et al. 2015). This includes the settling of lost or discarded material and the entanglement of fishing-related debris on rocky outcrops (Angiolillo et al. 2015, 2021). In addition, interactions with the seafloor morphology, e.g. crevices and cliffs, as well as trapping by vegetal debris and wrecks (Galgani et al. 1996; Pierdomenico et al. 2019; Schlining et al. 2013), can promote litter deposition.

6.6 Importance of ALDFG

ALDFG is one of the major components of sea-based marine litter and seafloor litter (FAO 2016; GESAMP 2021). Global fish production peaked at 171 million tons in 2016, with 53% coming from capture fisheries and 47% from aquaculture (FAO 2018). A large variety of technologies and very different gear types are being used, including different nets and trawls (seine, purse seines, trawl nets, lift nets, gillnets, and entangling nets), ropes, lines, dredges, bottom gear, and traps.

While some fishing gear components are made of nondegradable polymer materials such as metal or ceramic (sinkers, beam materials, anchors, pots, and traps), more often, they are made of woven polymer fibers (polyamide/nylon, high-density polyethylene, PET). Ropes and lines are mainly composed of polymer fibers such as polypropylene, polyethylene, and polyamide materials (GESAMP 2021).

Marine aquaculture is practiced using net and floating systems for grow-out of fish stocks and ropes that hang from a floating system and bottom-cage systems for shellfishes. A significant portion of gear utilized for aquaculture in marine systems is composed of plastic (FAO 2016), but currently, there is no global estimate of the amount of plastic waste generated by the aquaculture sector or systematic monitoring of plastic waste generated by aquaculture operations anywhere in the world (GESAMP 2021). Gear loss is ubiquitous around the world but varies by geography, fisheries, and type. The causes of ALDFG vary across fisheries, including the gear's operational context, gear handling and manipulation, the intensity of the fishing pressure, type of aquatic habitat, fishermen's skills, and environmental conditions (bottom structure, tides, currents, swells, and heavy winds). Lost fishing gear can float long distances via winds and ocean currents before either sinking or beaching (Macfadyen et al. 2009) and is often entrapped in rocky bottoms, reefs, and animal forests (Galgani et al. 2018; Pham et al. 2014). Eriksen et al. (2014) estimate 233 400 tons of larger plastic items plus 35 540 tons of microplastics are floating on the surface of the world ocean; they reported that 70.4% of large items (by weight) found floating at sea were related to the fishing industry (mainly buoys and floats; 54%).

High concentrations of ALDFG from commercial and/or recreational fisheries have mainly been found in areas where intensive fishing occurs (Galgani et al. 2000; GESAMP 2021). These areas can be predicted by assessments of fishing efforts, providing relevant information on where ALDFG losses may occur, depending on the gear type (Kroodsma et al. 2018). However, no information is available on artisanal and recreational fishing effort, because these types of fisheries are not subjected to any monitoring system. It is not mandatory to carry any location system or to have fishing logbooks to track their catches (Enrichetti et al. 2019). In future, data on small fisheries (artisanal and recreational) should be collected in appropriate databases to assess this effort and the resulting source of impact and to obtain data to define mitigation measures (Angiolillo and Fortibuoni, 2020; Bo et al. 2019).

The composition of the fishing litter on the seabed is influenced by local fishing activities, e.g. the seafloor litter composition within Maltese circalittoral waters revealed that about 83% of the total litter was composed of items related to Fishing Aggregating Devices (FADs) used in the main fishing activities in this area (Sinopoli et al. 2020). This was also observed in studies looking at ALDFG from the recreational sector; e.g. in Puget Sound, the recreational contribution to ALDFG Dungeness crab pots ranges from 70 to 85% of the total amount of pots lost, while recent studies from Norway estimate that over 14 000 recreational lobster pots are lost each year in Norwegian waters (GESAMP 2021). High densities of mussel nets (4.3 items/100 m^2) have been documented in the northern and central Adriatic Sea (Melli et al. 2017; Pasquini et al. 2016; Strafella et al. 2015), suggesting the mismanagement of mussel culture waste in the area.

Seamounts are particularly exposed to human fishing activities. Recently, significant amounts of lost fishing gear were reported on the summit and slopes of seamounts (Pham et al. 2013), suggesting a fishery-related origin of lost or dumped materials.

The importance of ALDFG input has not been assessed in detail until recently. Richardson et al. (2019) estimated that 5.7% of all fishing nets, 8.6% of all traps, and 29% of all lines were lost to the world's oceans for the year 2017, representing together with litter from fishing vessels a large input of litter. Previous studies have identified ALDFG as the most abundant type of litter (60–90%) in rocky environments (Melli et al. 2017), possibly reaching 100% in some fishing grounds (Pham et al. 2014). It has been shown (Richardson et al. 2018) that there is an overall increasing trend in gear losses with time. While gillnets and trammel nets have the highest proportion of net loss, there was a greater proportion and number of units of gear lost per vessel when nets touched the bottom.

6.7 Nature and Distribution of Seafloor Litter

The nature, presence, and abundance of anthropogenic debris on the seafloor (Figure 6.3) are much less widely investigated compared to sea surface litter. Studies typically focus on beaches, coastal environments, and continental shelves, while almost half of the planet's surface is the deep sea. Litter has been recorded on almost all kind of seafloors, but the highest concentrations have been observed

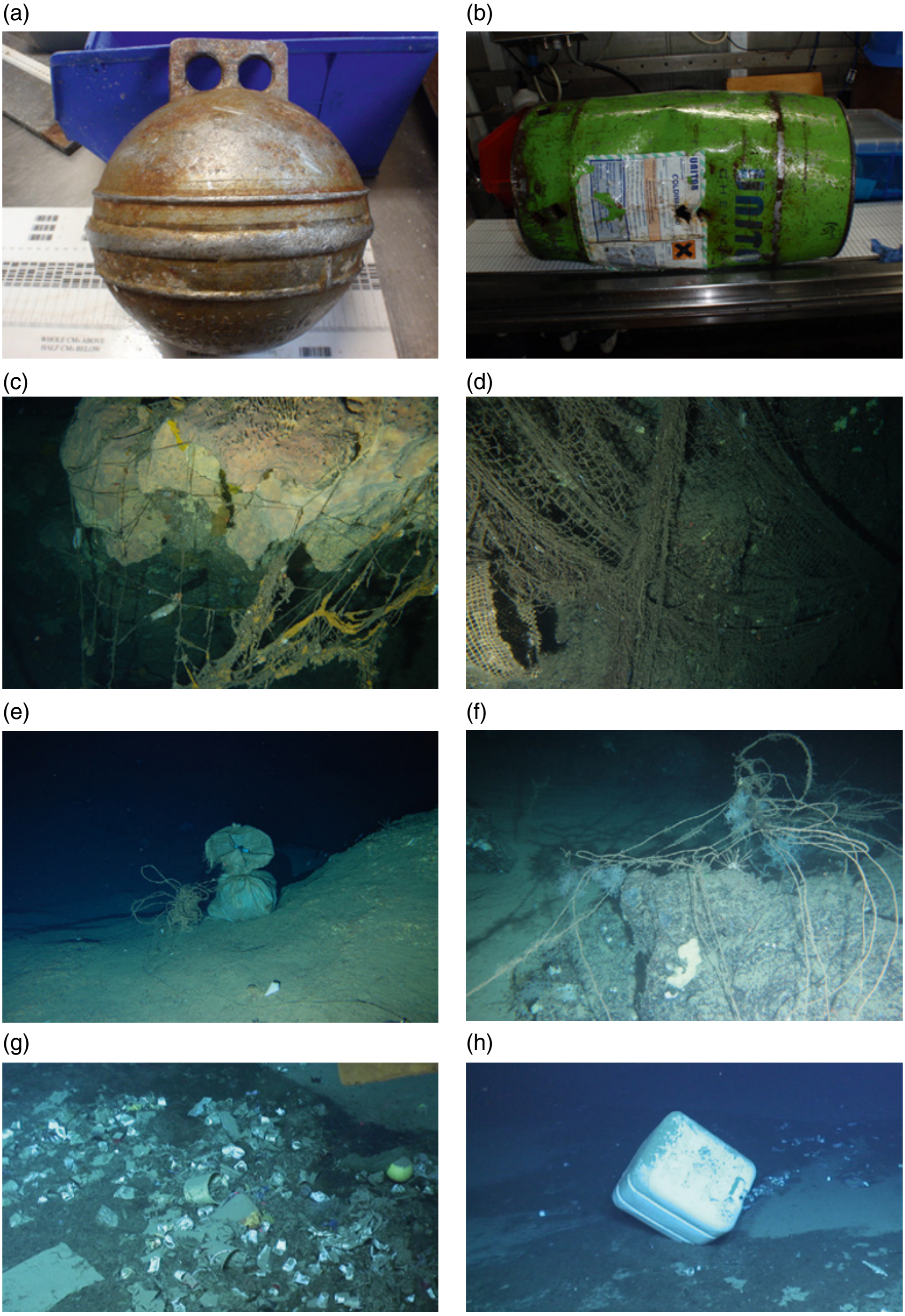


Figure 6.3 (a) Fishing buoy (Celtic Sea, 2015, 113 m). (b) Barrel collected after trawling (Greater North Sea, 2014, 57 m). (c, d) Fishing nets entrapped in the rocky outcrops, observed by ROV (Ligurian Sea and Tyrrhenian Sea/Red Coral Cruise, 2012, 125 and 130 m, respectively). (e) A lost fishery-related line and lest (Southern Tyrrhenian Sea/Red Coral Cruise, 2012, 135 m). (f) *Leiopathes glaberrima* entangled by fishing lines (North West Mediterranean Sea, Red Coral Sardinia, 2013, 250 m). (g) Marine litter accumulation area. (h) Big plastic box observed by ROV (French Mediterranean canyon, Cruise Ramoge, 2018, 2200 m).

in canyons and trenches (Angiolillo et al. 2021; Galgani et al. 1996; Mordecai et al. 2011a; Pierdomenico et al. 2019, 2020; Schlining et al. 2013; Tubau et al. 2015; Van Den Beld et al. 2016), due to their physical characteristics (Cau et al. 2018; Chiba et al. 2018; Consoli et al. 2020; Schlining et al. 2013; Van Den Beld et al. 2016). Monitoring litter abundance and composition (Alvito et al. 2018; Angiolillo et al. 2015; Cau et al. 2018) makes it possible to assess human impacts on deep sea environments (Chiba et al. 2018; Mordecai et al. 2011b); determine the temporal trends or environmental status (Alomar et al. 2016; Gerigny et al. 2019); focus on specific litter types, items (Sinopoli et al. 2020), or specific sources (Richardson et al. 2019); and evaluate the effectiveness of measures (Maes et al. 2018). Some seafloor litter surveys even covered the deepest areas, like the Mariana Trench, where a plastic bag was found (Chiba et al. 2018).

The abundance of plastic litter on the seafloor shows strong spatial variations, with mean densities ranging from 0 to more than 7700 items/km^2 (Table 6.1). Sites in the Mediterranean show the greatest densities of seafloor litter, a result of the highly populated coastline, high volumes of maritime traffic (30%), the presence of large rivers (Nile, Po), and intensive tourism activities around this closed basin (UNEP 2015).

The highest densities of litter are found in coastal areas, on strandflats, in closed bays, including lagoons with coral reefs, fjords, and at the heads and upper slopes of marine canyons. These litter items may eventually become trapped at the bottom of the canyons or in areas of low circulation where sediments accumulate (Buhl-Mortensen and Buhl-Mortensen 2017; Galgani et al. 1996; Pham et al. 2014; Pierdomenico et al. 2019; Schlining et al. 2013). Although most seafloor litter data are collected on continental shelves, the highest densities of total debris as well as plastic debris have been found at depths of 400 m in the Barents Sea (Grøsvik et al. 2018), at depths of 800–1100 and 1400–1700 m in the Bay of Biscay (NE Atlantic; Van Den Beld et al. 2016), and within depth ranges of 1000–2000 m in the Western Pacific (Chiba et al. 2018). Besides canyons, the presence of deep, converging currents, leading to high sedimentation rates, were presented as an explanation for these accumulations in the abyss (Fischer et al. 2015; Galgani and Lecornu 2004; Peng et al. 2020; Tekman et al. 2017; Woodall et al. 2015).

Based on the available scientific data from comparable quantitative surveys, the average values of seafloor litter range from 40 to 1000 items/km^2. Arctic regions can also receive substantial amounts of litter (5351–8082 items/km^2; Tekman et al. 2017), probably because of deep sea and converging currents (Galgani and Lecornu 2004; Tekman et al. 2017). However, the amounts are far lower in the Antarctic region, the only region with a survey where no items were found (Barnes et al. 2010).

A region where surveys have reported no items were found (Barnes et al. 2010). This points to the broader issue of confirmation bias in marine litter research because negative results are rarely reported and most studies target environments that are known to be polluted.

On the abyssal plain, seafloor litter densities may reach high levels (Galgani and Lecornu 2004); this litter originates from populated areas and regions where maritime activities occur (Galgani et al. 2000; Morales-Caselles et al. 2021).

Some extreme mean values were found in Sardinia (17 700/km^2; Cau et al. 2017), Malta (Consoli et al. 2020), California (3500 items/km^2, one tow at 36 000 items/km^2; Watters et al. 2010), and the South China Sea (36 818 and 51 929 items/km^2 in two canyons; Peng et al. 2020). The maximum concentration was observed in a canyon adjacent to the Messina Strait, Italy (1.3 million items/km^2). These extreme findings, three of five surveys with the highest concentrations (Pierdomenico et al. 2019), confirm how the Mediterranean Sea is greatly affected by plastic waste. Overall, all reports of marine litter in the deep sea indicate that plastic is the most common material, dominated by single-use items (Harris 2020; Mecho et al. 2020). Other common litter materials found in the deep sea are metal (Cau et al. 2018; Gerigny et al. 2019; Ramirez-Llodra et al. 2013; Schlining

Table 6.1 A review of data published since 2010 on seafloor litter, as collected by trawling.

Location	Habitat	Bottom	Date	Method (mesh in the codend)	Sampling	Depth (m)	Density, items/km^2, unless specified (min–max)	% Plastics	% Metals	% Fishing-related debris	References
Polar regions											
Antarctica	Slopes and bathyal	Sand	2008	Agassiz trawl (10)	37 tows	472–3213	0	0	—	—	Barnes et al. (2010)
Northern Antarctic Peninsula and Scotia Arc	Slopes and bathyal	Sand	2006	Agassiz trawl (10)	32 tows	200–1500	2 pieces only	1 plastic	1 piece	—	Barnes et al. (2009)
Barents Sea	Shelves	Soft	2010–2016	Beam trawl (30)	1860 hauls	10–400	0.77	86 (by number)	—	—	Grøsvik et al. (2018)
Pacific Ocean											
Western Pacific (East China Sea, West Japan)	Margin, canyon	Soft	2014–2019	Bottom trawl (60)	63 surveys	67–830 (most 100–200)	2926.1 (53 kg/km^2)	35–83	—	21–26	Kuroda et al. (2020)
East China Sea and Yellow Sea	Shelves	Soft bottom	2019	Bottom trawl (20)	43 hauls	9–19	375.44 (9.64 kg/km^2)	95	—	>50	Zhang et al. (2020b)
Southern China	Shelves	Sand	2009–2010	Bottom trawl	4 hauls	0–10	693 (147–5000)	47	ND	23.5	Zhou et al. (2011)
US West Coast	Shelves	Sand	2007–2008	Bottom trawl (30)	13 000 cells/606 sites, stratified random sampling	55–183	30	23	ND	5.1	Keller et al. (2010)
US West Coast	Slopes					183–550	59	ND	ND	ND	Keller et al. (2010)
US West Coast	Slopes/ bathyal					550–1280	129	ND	ND	ND	Keller et al. (2010)
Atlantic Ocean											
Europe/Atlantic and Mediterranean	Mixed (sea bed, slopes/ abyssal)	Various types	Compilation, 1999-2011	Trawl surveys and ROV/ Imagery	35 sites/588 videos, 7 platforms	60–5552	Shelves: 222, Seamounts: 550, Canyons: 870, Slopes 315, Ridges 390	40	8	38	Pham et al. (2014)

Southeastern North Sea	Shelves	Soft bottoms	2014–2016	beam trawl (10)	122 hauls	<40	96–33 675	95	—	76	Gutow et al. (2018)
U.K. waters, Western North Sea	Shelves	Sand	1992– 2012	IBTS protocol (20)	44 surveys, 74–441 stations/year, 0.06–0.15 km^2/stations	0–200	115 (0–14 550)	72–82	5	ND	Maes et al. (2018)
Celtic Sea	Shelves	Soft bottoms	2010–2014	OSPAR protocol (20)	170/year	0–200	57% of tows with litter	84	—	51	Moriarty et al. (2016)
North Sea/ Belgium	Shelf	Sand	2010	Beam trawl (10)	3 tows/site, 5 sites (41 ha/sample)	10–30	3125 (max 11 227)	95.7	ND	ND	Van Cauwenberghe et al. (2013)
Baltic Sea	Shelf	Soft bottom	2012–2017	Bottom trawl (20)	2377 hauls/53 cruises	10–50	21–25 (2–8 kg)	64–80	—	—	Urban-Malinga et al. (2018); Zablotski and Kraak (2019)
Baltic-North Sea	Shelf	Soft bottom	2015–2015	IBTS protocol (20)	175 hauls	19–70	16.8 (North sea), 5.07 (Baltic Sea)	83 (North sea), 56 (Baltic Sea)	—	>50	Kammann et al. (2018)
Spain (Bay of Biscay)	—	—	2006–2010	IBTS protocol (20)	136 hauls	70–500	74	52	—	—	Lopez-Lopez et al. (2017)
Portugal	Shelves	Soft bottoms Canyon heads	2013	Bottom trawl	2117 km surveys (56 km^2)	90–350	36	76	—	39	Neves et al. (2015)
Morocco	Shelves	Soft bottoms	2012–2015	Bottom trawl	62 stations	50–500	69)	73	—	—	Loulad et al. (2019)
Gulf of Mexico	Mississippi seabed, slopes/abyssal	various types of bottom	2000–2003	Otter trawl (38)	40 hauls, 30 min tows/3 knots for every 1 km in depth	250–3650	140 (0–6500)	44	5.5	27.6	Wei et al. (2012)

(*Continued*)

Table 6.1 (Continued)

Location	Habitat	Bottom	Date	Method (mesh in the codend)	Sampling	Depth (m)	Density, items/km^2, unless specified (min–max)	% Plastics	% Metals	% Fishing-related debris	References
U.K. South Atlantic Islands	Coastal, microplastics	Various	2016–2018	Mini Agassiz trawl (150), camera system/ diving	2498 seabed images	100–900 (trawl)	10/km^2	<27 (fishing grounds)	—	—	Barnes et al. (2018)
South Africa	Shelves	Soft bottoms	2019	—	235 hauls	30–850	3.4 items/km^2	88	—	22	Ryan et al. (2020)
Indian Ocean											
India	Shelves	Soft bottoms	2016–2017	Commercial	5 sites, monthly	10–40	10.95 ± 3.05 kg/km^2 (2.1–55 kg/km^2)	100	—	high magnitude	Kaladharan et al. (2020)
Mediterranean Sea											
Spain/ Mediterranean Sea	Shelves	Soft bottoms	2011–2018	MEDITS protocol (20°)	1323 hauls	10–800	9.8 kg/km^2	29	—	—	García Rivera et al. (2018)
Adriatic	Shelves	Soft bottoms	2014	EU MSFD protocol (20)	67 stations	0–100	913 ± 80	80	—	ND	Pasquini et al. (2016)
Adriatic	Shelves	Soft bottoms	2014	EU MSFD protocol (20)	121 hauls	10–110	0–2145	86.3	—	Limited	Fortibuoni et al. (2019)
North West Pacific Kuril Kamchatka	Abyssal plain, trench	Soft	2012	Agassiz trawl	12 hauls	4870–5770	—	—	—	<60	Fisher et al. (2015)
Mediterranean (NW and Ionian)	Fishing grounds	Sand	2009	Iron-framed trawl (10)	4 sites, 6 × 1.5 ha samples/ site	40–80	Tyrrhenian Sea: 5960, Ionian Sea: 2510, Spain: 4424, Catalunya: 7003	76	<2	8	Sanchez et al. (2013)

Mediterranean Sea	Bathyal/ abyssal	Sand	2007–2010	Agassiz trawl (12)	292 tows, Otter/ Agassiz trawl, 12 mm mesh/ codend	900–3000	0.02–3264.6 kg/ km^2 (including clinkers)	ND	ND	ND	Ramirez-Llodra et al. (2013)
North-East Adriatic Sea	Shelves and canyons	Soft bottom	2011–2016	Beam trawl	67 stations	10–260	85 ± 26 kg/km^2	34	28	50% of plastic is from fishing/ aquaculture	Strafella et al. (2015)
Central Mediterranean Sea	Shelves and canyons	Soft bottom	2015–2019	Bottom trawl (20)	600 sites	10–800	79.6	60	—	12	Garofalo et al. (2020)
Western part of the Turkish Black Sea	Shelf	Sand	2007–2008	Bottom trawl (22)	14 tows	Shelf	128–1320	91.4	2.1	<2	Topçu and Öztürk. (2010)
Turkey/ Levantine Basin	Bottom/ bathyal	Sand	2012	Bottom trawl (24)	32 hauls (2.7–8.2 ha/ sample)	200–800	290 (3264.6 kg/ km^2)	81.1	2.2	ND	Guven et al. (2013)
Turkey/North Eastern Basin	Shelf	Sand	2010–2012	Bottom trawl (24)	132 hauls (commercial, 2.5 knots)	20–180	72 (1–585 kg)/h	73	10	7	Eryaşar et al. (2014)
Malta	Shelves	Sand	2005	Bottom trawl (20)	44 sites (0.042–0.103 km^2/tow)	49–697	97	47	13	ND	Mifsud et al. (2013)
Mediterranean Sea, Sardinia	Shelves, fishing grounds	Soft bottoms	2013, 2014, 2015	MEDITS protocol (20)	302 hauls (18.4 km^2)	10–800	58.6 ± 5.7	59	17	—	Alvito et al. (2018)
Mediterranean and Black sea	Shelves, fishing Grounds	Soft bottoms	2014	Bottom trawl (50)	94 hauls, 713 km covered	<200	24–1211	45–95	—	2–14	Iokemidis et al. (2014)
Turkey/Antalya Bay	Shelves	Soft bottoms	2014–2015	Demersal trawl	68 hauls	10–300	13.3–651.1	71	8	ND	Olguner et al. (2018)

et al. 2013), textile/ropes (Alvito et al. 2018; Gerigny et al. 2019; Lopez-Lopez et al. 2017; Schlining et al. 2013), glass (Alvito et al. 2018; Cau et al. 2018; Debrot et al. 2014; Gerigny et al. 2019), and rubber (Alvito et al. 2018).

A wide range of percentages of litter originating from fisheries found around the world was reported in Table 6.1, starting at less than 10% in open areas like the Gulf of Cadiz (Mecho et al. 2020), the West Coast of the United States (Keller et al. 2010; Watters et al. 2010) in central California, and some Mediterranean sites (Sanchez-Vidal et al. 2018) to more than 50% at fishing grounds such as the Barents and Norwegian Seas (Buhl-Mortensen and Buhl-Mortensen 2017), the East China and Yellow Seas (Zhang et al. 2020b), the Southern California (Watters et al. 2010), the southeastern North Sea (Gutow et al. 2018), around the Azores islands (Rodriguez and Pham 2017), the Celtic Sea (Moriarty et al. 2016), fishing grounds in the Mediterranean Sea (Angiolillo et al. 2021; Cau et al. 2017; Consoli et al. 2020; Enrichetti et al. 2020), banks and mounts offshore Portugal where fishing occurs (Oliveira et al. 2015; Vieira et al. 2015), Condor Mount (Pham et al. 2013), and finally, although less common, more than 80% on the Abyssal Plain in the South-West Indian Ocean and even up to 100% around the Azores (Pham et al. 2014).

Morales-Caselles et al. (2021) performed a comparison between studies and ranked the various categories of litter. Typically, the near-shore seafloor exhibits a more diverse range of categories and items. The near-shore area presents, in percentage of total items, mainly plastic bags (12.1%), wrappers (11.8%), plastics bottles (85%), and fishing-related items (8.5%). The deep seafloor presents less diverse and heavier items such as glass bottles (22.6%), bags (18.5%), cans (10.2%), and fishing-related items (6.5%). Food containers were ranked fifth in both near-shore and deep sea environments. Synthetic ropes were listed as most common only on the deep seafloor, ranked sixth with 6% of the total number of items. Litter items on the near-shore seafloor vary depending on socioeconomic regions, with the majority of fishing-related items found in Western countries, East Europe, and Central Asia (nets and sinkers). Plastic bottles are ranked first in Southeast Asia and sub-Saharan Africa. Wrappers, food containers, and plastic bags are ranked first in East Asia, the Pacific, North Africa, the Middle East, Latin America, and the Caribbean. It is obvious that single-use plastic and fishing-related items predominate significantly everywhere. Not surprisingly, these are also the types of litter policy makers are focusing on for future legislation and measure development.

6.8 Microplastics

In the same way as for large debris, there is growing concern about the implications of the amounts and diversity of microparticles in sediments. Most microparticles are tiny plastic fragments known as microplastics, although other types of microparticles exist, such as fine fly ash particles emitted with combustion gases, rubber from car tyre wear and tear as well as glass and metal particles, all of which constantly enter the marine environment (Hidalgo-Ruz et al. 2012). Some microplastics float on the sea surface because they are less dense than seawater. Other more dense particles will sink. However, the buoyancy and specific gravity of plastics may change during their time at sea due to weathering and biofouling, which results in their dispersal across the sea surface, within the deeper water column, on the seabed, beaches, and within the sea ice (Bergmann et al. 2017, 2019; Harris 2020). There is a lack of understanding of the concentrations, cycling, and fate of plastic litter in subsurface waters. Recent findings suggest that one of the largest and currently underappreciated reservoirs of marine microplastics may be contained within the water column (Pabortsava and Lampitt 2020) and animal communities of the deep sea (Jamieson et al. 2019). The difference in mass estimates between microplastic particles suspended in the water column versus large floating surface debris is vast. Estimates vary from 7000 to 35 000 tons (Cózar et al. 2014) to 233 400 tons (Eriksen et al. 2014) at the surface of the world oceans, compared to 49.3–89.6 million tonnes suspended in the upper 200 m of the ocean as extrapolated from data of Pabortsava and Lampitt (2020) study (i.e. the amount suspended in the upper 200 m is ~200 times greater than the amount floating on the surface). Several studies have suggested that deep sea sediments are sinks for microplastics (Barrett et al. 2020; Woodall et al. 2014). Barrett et al. (2020) estimate that 14 million tonnes of microplastic reside on the ocean floor. If this figure is correct, there is between 3.5 and 6.5 more microplastic currently suspended in the ocean water column than has arrived at its final resting place on the deep ocean floor.

The abundance and global distribution of microplastics in seafloor sediments has received increasing scientific attention. Microplastics have been found in sediments everywhere (Table 6.2). Data extracted from a review of 80 papers on microplastics in marine sediments (Harris 2020) found higher median concentrations of microplastics in fjords (7000 particles/kg dry sediment), followed by 300 particles/kg in estuarine environments, 200 particles/kg in shallow coastal environments, 50 particles/kg on continental shelves, and 80 particles/kg for deep sea environments, with fibers as the dominant microplastics type. It is important to note one sample may contain a large number of very small particles (fibers) and a lower mass of plastic than a sample containing fewer, larger particles. Hence, the reporting unit of gram of plastic per kilogram is preferable to particles per kilogram when computing a mass balance budget. Overall, counts of microplastics in the sediments are highly variable, with heterogeneity between sediment cores from the same location sometimes greater than the variation across sampling sites (Barrett et al. 2020). These authors suggested that although microplastics were numerous, sediments account for only a minuscule proportion of the ocean's "missing plastic."

Concentrations of microplastics in sediments range from zero in some samples collected in the polar regions (Kanhai et al. 2019) to 13 600 items/kg found in the Southern Ocean, south Australia (Barrett et al. 2020). Interestingly, some observations of the deep Arctic seafloor revealed densities of plastic debris of up to 6595 items/kg, comparable to those observed in populated areas (Ramírez-Álvarez et al. 2020) and even higher than quantities reported by many other studies, including of marine canyons (see Table 6.2). These densities were related to atmospheric transport and deposition, a notable pathway for microplastics to remote areas (Bergmann et al. 2019). Recently, microplastics were even found in snow and stream water samples on Mt. Everest (Napper et al. 2020) (Table 6.3).

On the contrary and in comparison, the levels found in the Mediterranean sediments were not as high, remaining at levels of 100–900 items/kg in the North West basin (Alomar et al. 2016; Angiolillo et al. 2021; Sánchez et al. 2013), 71 items/kg (maximum at 3640 items/kg) in the Tyrrhenian Sea (Kane et al. 2020), 0–90 items/kg in the Adriatic Sea, 141 and 461 items/kg in Tunisia (Abidli et al. 2018), and a maximum of 2433 microplastics/kg in the East Mediterranean basin. The North West Pacific does not seem so affected, with most concentrations under 500 items/kg (Chen et al. 2020; Sagawa et al. 2018; Zhang et al. 2019, 2020a, 2020b; Zheng et al. 2019; Zhu et al. 2018), one at 700 items/kg (Peng et al. 2020), and a maximum value at 1674 items/kg sediment (Sui et al. 2020).

In contrast to macroplastics, microplastic concentrations are mostly unassociated with local sources of contamination and no clear trends between sediment grain size and microplastic deposition in sediments was found (Llorca et al. 2020). Several studies highlighted the importance of fibers, with most reporting over 50% of microplastics as fibers, often reaching 70–90% of the total. Microplastics in deep sea sediments contain some orders of magnitude with more microplastics compared to contaminated sea surface waters, supporting the hypothesis of them being a repository of microplastics (Llorca et al. 2020). In laboratory flume studies, Pohl et al. (2020) showed that microplastic fragments become relatively concentrated within the base of turbidity currents, where fibers are preferentially removed from suspension and buried in the deposits as they are trapped between settling sand grains. The presence of fibers may also be related to contamination during sampling or

Table 6.2 A review of data published since 2010 on seafloor litter, as collected by imagery (remotely operated vehicles or diving in shallow waters).

Location	Habitat	Bottom	Date	Sampling	Depth (m)	Density (min–max)	% Plastics	% Metals	% Fishing-related debris	References
Polar regions										
Fram Strait, 79°N	Abyssal plain	Sand	2002–2014	One transect/year, 5 samples (1427–2747 m^2)	2500	5351–8082 items/km^2	47	7	—	Tekman et al. (2017)
Barents Sea	Fjords, valleys, shelves, slopes, abyssal	Soft	2008–2017	23 cruises, 1778 transects (700 × 3 m^2), 3 735 900 m^2 samples	100–1500	230 items/km^2 (174 kg/km^2)	6	—	> 50	Buhl-Mortensen and Buhl-Mortensen (2017)
Norwegian Sea		Soft				646 items/km^2 (601 kg/km^2)	6.5	—		Buhl-Mortensen and Buhl-Mortensen (2017)
Pacific Ocean										
Western Pacific	Margin to hadal	All types	2004–2014	188 dives analyzed	100–10 899	11–342 items/km^2	33	26	—	Chiba et al. (2018)
Northern South China Sea	Canyons		2018	7 dives (33.8 km)	1729–3378	< 500 items/km^2 (36 818 and 51 929 items/km^2 in 2 canyons)	>50	—	—	Peng et al. (2019)
Japan, offshore water	Trenches	Various	From JAMSTEC databank	3 dives (15 h52 min) analyzed on 4861 available	299–400, 1086–1147, 1682–1753	15.9 debris/h	42.8	16.6	12.7	Miyake et al. (2011)
Central California	Canyons and shelves	Various	2007	112 ROV transects, 26.6 km	90–382	3500 items/km^2 (0–38 000)[a]	95	3.5	94	Watters et al. (2010)
Southern California	Canyons and shelves	Various	2002	321 ROV transects, 121.6 km	18–570	2000 items/100 m (0–30 000) [a]	41	38	58.5	Watters et al. (2010)
Monterey Canyon, California	From margin, slopes (0–40°) to abyssal	Various	1989–2011	50 m^2 grid cells, 2429 km^2 in total	25–3971	632 items/km^2	33	23	—	Schlining et al. (2013)

Atlantic Ocean										
Azores, Portugal	Condor seamount	Rocky	2010–2011	45 dives	185–256	1439 items/km^2	No plastic	—	89 (73% fishing lines)	Pham et al. (2013)
Azores, Portugal	Condor seamount	Rocky	2010–2011	3 dives, distance × average width	292–1070	397 items/km^2	No plastic	—	90	Pham et al. (2013)
Portugal	Mount	50% rocky, 50% Soft	2011	3 dives 8800 m	93–553	1.67 ± 1.44) items/100 m	5% plastic bags	—	87	Oliveira et al. (2015)
Atlantic, Azores	Margin/slopes	Various	2009–2011	56 dives, 36 transects, 45.2 km	40–525	2.6 items/km	67	5	64	Rodrigues and Pham (2017)
Atlantic/Gulf of Cadiz	Bathyal/	Slopes/canyon/bottom	2014	17 dives, 0.11 km^2/total	220–1000	692–2440 items/km^2	33	34	6	Mecho et al. (2020)
Portugal	4 Canyons	Various	2007	16 ROV dives, 60 km	850–4574	1100 (417–6600) items/km$^{2\,a}$	68	ND	10	Mordecai et al. (2011)
SW Indian Ocean	Abyssal plain	—	2011–2013	5	—	377 items/km^2 (59–1223)	25	25	25	Woodall al. (2014)
Atlantic/Bay of Biscay	Canyons	—	2009–2010	29 canyons	470–1500	1.66/km (0–8.6)	42	—	16	Van Den Beld et al. (2016)
U.K. South Atlantic Islands	Coastal, microplastics	Various	2016–2018	2498 seabed images	100–900 (trawl)	10/km^2	<27% (fishing grounds)	—	—	Barnes et al. (2018)
Indian Ocean										
SW Indian Ocean	Abyssal plain	—	2011–2013	5	900–1000	708 items/km^2 (75–1739)	<10	—	84	Woodall et al. (2014)
Mediterranean Sea										
South Tyrrhenian	Margin and canyon head	Various	2012–2016	21 dives, 11 979 m survey	17–541	563 items/km	86	—	—	Pierdomenico et al. (2020)

(*Continued*)

Table 6.2 (Continued)

Location	Habitat	Bottom	Date	Sampling	Depth (m)	Density (min–max)	% Plastics	% Metals	% Fishing-related debris	References
North Ionian Sea/Messina Strait	Canyon	Various	2016	7 dives, 6420 m survey	243–581	1200/km (max at 20 000)	78 (52% of total as SUPs)	—	0.9	Pierdomenico et al. (2019)
North West Mediterranean Sea	Canyons/ slopes and abyssal plain	Various	2018	7 dives, 41, 480 km survey (102 km^2)	340–2200	563 items/km^2 (14/km)	56	ND	52 (largely polymers)	Angiolillo et al. (2021)
Malta, Mediterranean Sea	Margin edge	Rocky	2013	1 dive, 2 km	250–400	463 items/km^2	—	—	97 (FAD area)	Consoli et al. (2020)
Sardinia	Slopes	Various	2013	17 sites, 29 ROV dives (15 canyons)	100–480	17 500	10	6	78	Cau et al. (2017)
NW Mediterranean Sea	canyons (head and slopes)	All types (45% hard bottom)	2015	5 sites, 27 838 m^2	0–445	5232 items/km^2	—	1.5	85	Giusti et al. (2019)
French Mediterranean	Slopes	Rocky bottoms	2009	17 canyons, 101 dives, 159.3 km surveys	80–700	3.01/km survey (0–12)	12 (0–100)	27.1	38.6 (0–100)	Fabri et al. (2014)
Malta	Shelves	Soft bottoms/ fishing ground	2013	4000 m^2	250–450	46 300 items/km^2	3	—	96 (fishing ground)	Consoli et al. (2020)

Table 6.3 A review of data published since 2010 on sediment microplastics.

Location	Bottom type	Date	Method	Sampling	Depth (m)	Density (min–max)	%fibers	References
Polar regions								
Antarctic, Ross Sea	Shelves	2015	Van Veen grab, 0.18 m^2, visual sorting (<5 mm)	31 sites	25–140	5–1705 plastic debris per m^2	42.8% fibers	Munari et al. (2017)
Antarctic, Ryder Bay	Bay	2016	Diving or box coring	20 sites	10–2125	0–5/10 mL sediments	42% fibers	Reed et al. (2018)
Arctic, Fram Strait	Abyssal plain	2016	Cores tubes	9 samples	2340–5570	42–6595 items/kg	—	Bergman et al. (2017)
Central Arctic	Abyssal plain	2016	Piston corer/ density separation	11 sites	855–4353	0–200 items/kg	55% (5 on 9)	Kanhai et al. (2019)
Svalbard (South)	Abyssal	2011 (samples from 2001)	Core sediments	2	1000–2000	12.5/50 mL sediments	—	Woodall et al. (2014)
Pacific Ocean								
NW Pacific	Abyssal plain + trench	2012	Corer	12	4870–5770	<100 items/kg	75%	Fisher et al. (2015)
China, Jiaozhou Bay	Bay	2018	PVC cylindrical corer	scuba diving, 5 samples, 32–4431 μm	<10	7–25 items/kg	70.6–90.4%	Zheng et al. (2019)
Polar Ocean, Mediterranean, North Atlantic, Gulf of Guinea	Abyssal plain	2012	core sediment (<1 mm)	4 regions, 1 site/region, 3 replicates each	2750–4880 4840–4840 4790 1180	Southern Ocean: 70 North Atlantic Ocean: 210 Gulf of Guinea: 0 Mediterranean Sea: 70	Extrapolated from densities (Barrett et al. 2020)	Van Cauwenberghe et al. (2013)
Pacific ocean								
North Yellow Sea, China	Open sea	2016	Box corer 30 μm–5 mm	19 sites, 30 μm–5 mm	40	37.1 items/kg	35% fibers	Zhu et al. (2018)

(*Continued*)

Table 6.3 (Continued)

Location	Bottom type	Date	Method	Sampling	Depth (m)	Density (min–max)	%fibers	References
Japan, Hiroshima	Bay		Smith Mac in tyre box coring, 0–11 cm	6 sites, 0–11 cm	< 20	24–253 items/kg	—	Sagawa et al. (2018)
China, Yellow Sea, Sanggou	Bay	2015–2016	Van Veen grab	8 sites, 0-2 cm	7.5 (mean)	1674 ± 526 items/kg	58% from marine culture	Sui et al. (2020)
China, Yellow Sea, Shishili	Bay	2017	Steel box sample, 0–5 cm, density separation,	28 sites, 35 μm–4.985 mm	4–24	499.76 ± 370.07	—	Zhang et al. (2019)
China, marginal seas	Shelves	2016	Stainless steel box sampler	75 sites	12–78	171.8 items/kg (Bohai Sea, Northern Yellow Sea and Southern Yellow Sea) 23.6 items/kg (North Yellow Sea) 72 items/kg (South Yellow Sea)	93.88%	Zhao et al. (2018)
Western Pacific	Abyssal plain	2018	Stainless steel box corer, 0–5 cm, density separation	15 sites	4601–5732	240 items/kg	52% fibers	Zhang et al. (2020)
East China Sea and Yellow Sea	Shelves	2017	Stainless steel box corer, 0–5 cm, density separation	25 sediment samples	10–115	150 items/kg	77% fibers	Zhang et al. (2019)
China, South China Seas	Shelves, canyon, though	2018	Push core sampler	24 samples	24–3400	224 pieces/kg dry weight	—	Chen et al. (2020)
Western Mexico, Todos Santos Bay	Bay	2016	Van Veen grab, 0.1 m^2, 0–5 cm	19 samples	10–400	4720 (850–24 940) items/m^2	10–91%	Ramirez Alvarez et al. (2020)
California	—	2009	corer	1 core	577	Sedimentation rate: 30 items/100 cm^2/year	67.5%	Brandon et al. (2019)

Southern Ocean								
Great Australian Bight	Abyssal plain	2017	Mini core sediment	6 sites, 16 samples	1655–3062	13 600 items/kg	10% fibers	Barrett et al. (2020)
Polar Ocean	Abyssal plain	2012	Core sediment	3	2750–4880	70 items/kg	Extrapolated from densities (Barrett et al. 2020)	Van Cauwenberghe et al. (2013)
Indian Ocean								
SW Indian Ocean	Abyssal plain	—	Core sediment	7	1400–2200	1.3/50 mL sediment	—	Woodall et al. (2014)
Baltic Sea								
Southern Baltic	Shelf	2015–2016	core sediment	8 cruises, 53 samples	3–215	863 ± 1371 items/kg dry weight (103–10 179)	74.5	Chubarenko et al. (2020)
Atlantic Ocean								
North Atlantic	Abyssal plain	2012	Core sediment	3	4840	210 items/kg	Extrapolated from densities (Barrett et al., 2020)	Van Cauwenberghe et al. 2013)
Southern North Sea/Channel	Shelves	2013–2014	Van Veen grab	29 sites	<40	0–3146 particles/kg	47	Maes et al. (2017b)
Southern North Sea (coastal)	Abyssal plain	—	core sediment	—	—	2.8–1188.8 items/kg	—	Lorenz et al. (2019)
Belgium	Shelves and coast	—	Van Veen grab, 0.1 m^2	5 sites (harbors and coastal)	<30	0.84–7.21 mg/kg (38 μm–1 mm)	59% fibers	Claessens et al. (2011)
Southeastern Baltic Sea	Coastal sediments	2015	Transect, rectangular hand-operated dredge	7 samples	3–30	34 ± 10661 items/kg	4–46%	Zobkov and Esiukova (2017)
Gulf of Guinea	Abyssal plain	2012	Core sediment	1 (3 replicates)	4790	0	Extrapolated from density (Barrett et al., 2020)	Van Cauwenberghe et al. (2013)

(*Continued*)

Table 6.3 (Continued)

Location	Bottom type	Date	Method	Sampling	Depth (m)	Density (min–max)	%fibers	References
Mediterranean Sea								
NW Mediterranean Sea	Canyons/ slopes and abyssal plain	2018	Core sediment (MSFD protocol)	7 dives, 11 samples	446–2034	449 items/kg (212–1.040)	—	Angiolillo et al. (2021)
NW Mediterranean Sea	—	—	Core sediment	29 sites	42–3500	390–410 items/kg	—	Sanchez-Vidal et al. (2018)
Central Adriatic	Shelves	2015	140 km transect, Van Veen grab/ 0.1 m, 1.5 mm	16 stations/4 replicates	7–142	2.5–87 items/m^2	69% fibers	Mistri et al. (2017)
Tyrrhenian Sea, Sardinia/Corsica	Slope, bathyal, and abyssal	2008	Box corer, 0–5 mm	16 sediments	100–1400	71 items/kg (max 3640)	70–100%	Kane et al. (2020)
Croatia	Coast	2015	Core sampling/ diving, sieving/ NaCl separation	10 sites, 3 replicates	3–15	0–90 items/kg	90% fibers	Blašković et al. (2017)
Tunisia	Lagoons, coastal sediments	2017	Core sediment, 0–3 cm	5 sites, 0.1–5 mm	<20	141–461 items/kg	67% fibers	Abidli et al. (2018)
Balearic Islands	Coastal sediments	2013	Core tubes, 0–3–5 mm	3 sites	<20	100–900 items/kg	20–80%	Alomar et al. (2016)
Spain/ Mediterranean Sea	Shelves	—	Bulk sediments, density separation (1.2 μm–5 mm)	10 stations	<200	113.2 ± 88.9 microplastics/ kg dry weight	82% fibers	Filgueiras et al. (2019)
Lebanon	Coast	2018	Steel ring, $ZnCl_2$ separation 1–5 mm	3 stations	Coastal (500 m offshore)	2433 microplastics/kg dry weight	Limited number of fibers	Kazour et al. (2019)
Mediterranean Sea	Abyssal plain	2012	Core sediment	2	1180	70	Extrapolated (Barrett et al. 2020)	Van Cauwenberghe et al. (2013)

analysis, requiring special attention to avoid interference in assessments and comparisons (Brandon et al. 2019; Willis et al. 2017).

Litter on the seafloor may be difficult to monitor, already the case near-shore, and even more so in remote areas, which is a constraint for regional and global assessments. The seafloor represents an ultimate sink for all materials lost and discarded, with variable concentrations found ranging from 0 to 20 000 items/km (Peng et al. 2020; Pierdomenico et al. 2019). The interpretation of quantities found is further complicated because the degradation and aging of plastics at depth is unknown and the accumulation of debris varies per location. Measuring how much litter is on the seafloor is, therefore, challenging due our limited knowledge of this environment (Canals et al. 2020). In 2014, a rough estimation of the number of seafloor litter items was given, based on evaluations in open oceans, resulting from large-scale studies using both trawls and ROV surveys (Galgani et al. 2014).

The estimated number of litter items in the three main oceans (Pacific, Atlantic, and Indian) and the Mediterranean Sea, which all together cover a surface area of 385 000 000 km^2 (worldatlas.com), adds up to 71.5–116 billion macroplastic items on the seafloor.

For microplastics, the scaling up of empirical data to a global approximation indicates that there could be as much as 14.4 million tons of microplastics in the top 9 cm of sediment throughout the world's oceans (Barrett et al. 2020). This means that the ocean seafloor contains between 282 and 450 times the standing stock of plastic at the surface, compared to surface estimates of 30 000 tons of microplastics (Eriksen et al. 2014). It is clear that many hot spots have yet to be discovered since our actual coverage is highly limited in terms of available data, and we know very little about deep sea currents and probable deep convergence zones.

6.9 Impacts

One of the main impacts of marine litter on the seafloor is entanglement by marine fauna. It involves benthic and demersal organisms (Angiolillo and Fortibuoni 2020) and has been described on seamounts, canyons, and various areas around the globe (Angiolillo et al. 2015; Oliveira et al. 2015; Rodriguez and Pham 2017; Woodall et al. 2015). In a recent review, worldwide, 418 reef-associated species from across eight taxa were reported to be entangled, leading to major implications for conservation (De Carvalho-Souza et al. 2018), highlighting cnidarians as the main taxa affected by entanglement on the seafloor.

On the seafloor, and in particular the deep sea, some taxa of cnidarians, because of their arborescent morphology and sessile characteristic, are able to create habitats, forming forests or reefs that attract large amounts of associated fauna, enhancing biodiversity (Davies et al. 2007; Roberts et al. 2006; Rossi et al. 2017b). Often, these species are slow growing and long living, exposed to anthropogenic impacts, such as fishing activities, and, therefore, recognized as being Vulnerable Marine Ecosystems (VMEs). Several VMEs, such as cold water coral reefs, hydrothermal vents, canyon heads, and seamounts, can be found on the seafloor and in the deep sea (Danovaro et al. 2020; Van Den Beld et al. 2016). These VMEs support a greater abundance and diversity of vulnerable sessile organisms and pelagic and demersal fish (D'Onghia et al. 2010) and are recognized as important fishing grounds for commercial and recreational fishing (Mecho et al. 2020). Consequently, a large amount of lost fishing gear is recorded entangled on the arborescent coral species, and other seafloor litter is observed in these habitats (Pham et al. 2014; Tubau et al. 2015). The Mediterranean Sea, e.g. contains more than 500 submarine canyons widespread along the continental margin and over 242 recorded seamounts and seamount-like structures (Danovaro et al. 2020; Maurizio and Rovere 2015). Although largely unsurveyed and understudied (Bo et al. 2014, 2019), the impact of marine litter is widely recognized (Battisti et al. 2019).

Other benthic organisms, such as crabs, cephalopods, echinoids, fishes, and many small invertebrates, can get caught in litter items (e.g. derelict pots) on the seafloor, with lethal consequences (Angiolillo and Fortibuoni 2020; Ayaz et al. 2010). This form of entanglement is called ghost fishing. The factors that influence the probability of an vagile organism being entangled in or strangled by litter include the size and structure of the litter item, water turbidity, water depth, and the behavioral traits of the animals itself (Kühn et al. 2015).

Although entanglement has been documented for many different types of litter, most records involve fishing gear, especially ALDFG, with a frequency of incidence that varies by region, type, and quantity of marine litter. ALDFG can have many different impacts on the environment, including the continued catch of target species, the catching of nontarget species, the entanglement of organisms, and the physical impact of the gear on the benthic environment (Gregory 2009).

In some cases, ALDFG may represent almost 100% of total debris, especially in fishing grounds (Consoli et al. 2018b; Pham et al. 2014) with monofilament fishing lines being the most abundant and dangerous kind of litter, representing the largest part of entanglement records (Consoli et al. 2018a). The physical contact of the fishing gear with sessile fauna may cause visible damage. The long-term effect of lines and ropes may eventually lead to abrasion, ruptures, open wounds, and epibiosis. At a seamount, offshore Portugal, up to 31% of litter was found to cause direct impacts on sessile organisms, either entangling fauna (27.6% – lines, ropes, and nets) or covering portions of the rocky reef (3.5% – nets). Coiled-up fishing lines were the primary source of entanglement, mainly for complex or branching fauna such as sponges and corals. The extensive use of specific types of fishing gear in certain areas, such as FADs, leads to a representation of nearly 100% of the total seafloor litter items observed (Malta; Sinopoli et al. 2020), a major source of disturbance for benthic communities (D'Alessandro et al. 2020).

Another form of litter impact is the coverage (Angiolillo and Fortibuoni 2020). It is mainly linked to fishing gear (in particular nets) but also to other litter such as plastic sheets and bags. Coverage can induce stress in sessile organisms determining suffocation by depriving them of light and oxygen. When wide portions of sediment are cover by marine litter, the recolonization of large organisms and the gas exchange may be impeded (Kühn et al. 2015).

Marine litter may also provide new habitats, locally favoring diversity, or colonization, although its impact and consequences on endemic species assemblages are currently unknown. Indeed, this type of interaction between benthic fauna and litter is rarely quantified in the literature and is generally regarded as a neutral or even positive relationship. The introduction of hard materials increases habitat heterogeneity at a small scale (Bergmann and Klages 2012), providing suitable substrates for some species on soft and hard bottoms (Angiolillo et al. 2015; Mordecai et al. 2011b; Schlining et al. 2013; Watters et al. 2010).

Litter has been found to be colonized by a variety of marine taxa, most of which include Actinians, Serpulids, Hydroids (Mordecai et al. 2011b; Van Den Beld et al. 2016; Wei et al. 2012), Brachiopods (Ramirez-Llodra et al. 2013), Tunicates, and Bryozoans (Cau et al. 2017). The percentage of coverage is highly variable, determined by different parameters, e.g. diversity of items, depth at which they occur, the type of habitats, and environmental factors. However, substrates can often be colonized to such an extent that old litter items may be completely covered by organisms, such as for any other artificial substrate, for instance shipwrecks (Cau et al. 2017; Van Den Beld et al. 2016).

Also hard substrates, such as clinker debris and ammunition, can be colonized by sessile organisms (Mecho et al. 2020; Neves et al. 2015). Nets stretched across soft bottoms can provide fixation points for unusual concentrations of filter feeders, such as *Leptometra* sp., apparently because this creates an advantageous position to gather food from the bottom currents (Oliveira et al. 2015).

Litter items may also provide protective structures for mobile fauna, in particular for fish (Bergmann and Klages 2012; Watters et al. 2010), crustaceans, and cephalopods. Other organisms, such as starfish, crabs, and echinoids, are also commonly observed around fishing nets scavenging on other settlers or on litter-entangled animals (Angiolillo et al. 2015). Some organisms can use litter items as a substitute for burrows to hide, for instance cephalopods are commonly observed in ceramics on muddy bottoms (Ayma et al. 2016).

The rate of colonization, measured as the percent of litter items colonized by species, is a good indicator for this type of interaction. This percentage is variable, dependent on the region, type of substrate, depth, and composition of the ecosystem the litter item resides in. In the Bay of Biscay, 13.6% of the observed litter items were colonized. Similar values were reported in the deep Western Pacific (17%, Chiba et al. 2018), whereas higher percentages of colonization were recorded in the Mediterranean Sea: 37% of the items were colonized in Sicily (Consoli et al. 2018a), 65% of the observed items (with epibionts covering almost 100% of the available surface) in Sardinia (Cau et al. 2017), 67% of the items reported in the Arctic (Bergmann and Klages 2012), and 80% of litter reported in the northwestern Mediterranean Sea (Angiolillo et al. 2015).

In addition to the colonization of seafloor litter by macrofauna, small invertebrates may take advantage of the presence of plastic on the seafloor. Although there is no extensive catalog of species that settle, recent work using electron microscopy demonstrated a large variety of unicellular (radiolarians, foraminifera) and small invertebrates (Bachiopods, encrusting worms) colonizing the various types of litter in the deep sea (Figure 6.4). This opens a new field of research; more knowledge is needed to better understand how litter favors certain species in hostile and remote environments, in particular in areas where hard substrates are largely absent.

Seafloor litter is not only harmful to the environment but also contributes to socioeconomic impacts. For some species, unwanted bycatches by ghost fishing, depending on the species and location, may reach a significant share of stock losses (GESAMP 2021). Losses of stocks resulting from ALDFG were shown to reach up to 1–3% for the European hake *Merluccius merluccius* in the Mediterranean, 5% for the Cod *Gadus morhua,* and more than 20% for halibut (*Hippoglossus* sp.) in Norway. Seafloor litter may generate considerable gear-retrieval costs and maritime accidents (GESAMP 2021). Serious problems have been caused by containers and large fishing gear lost or abandoned on the seafloor. Fishermen also have to clean nets and catches and sometimes need to remove dangerous items (e.g. paints, chemicals, ammunition) collected from the seafloor, which might affect the quality of catches and the safety of fishermen.

Microparticles, especially microplastics and microfibers, have been found in seawater, sediments, and biota, polluting marine habitats around the world (Barrows et al. 2018; see Table 6.2). Their widespread distribution and accumulation raises concerns regarding their interaction with and potential effects on marine biota, including zooplankton. Several cases of plastic ingestion, in particular by benthic fishes, are known to occur near the seafloor, with potential ingestion of hazardous chemicals (Anastasopoulou and Fortibuoni 2019; Deudero and Alomar 2015). However, suspension and deposit feeders may also accidentally or selectively ingest microplastics from the seafloor. Microplastics ingestion by coral polyps gives detrimental consequences for the colonies (Hall et al. 2015). A recent study reported increased mortality in oysters who were chronically exposed to environmental loads of microplastics in the lab (Maes et al. 2020). Therefore, taking into account the precautionary principle, plastics and microplastics represent a significant environmental threat to the marine environment. Furthermore, the impact of microparticles on seafloor species and related community effects forms a new area of future scientific interest.

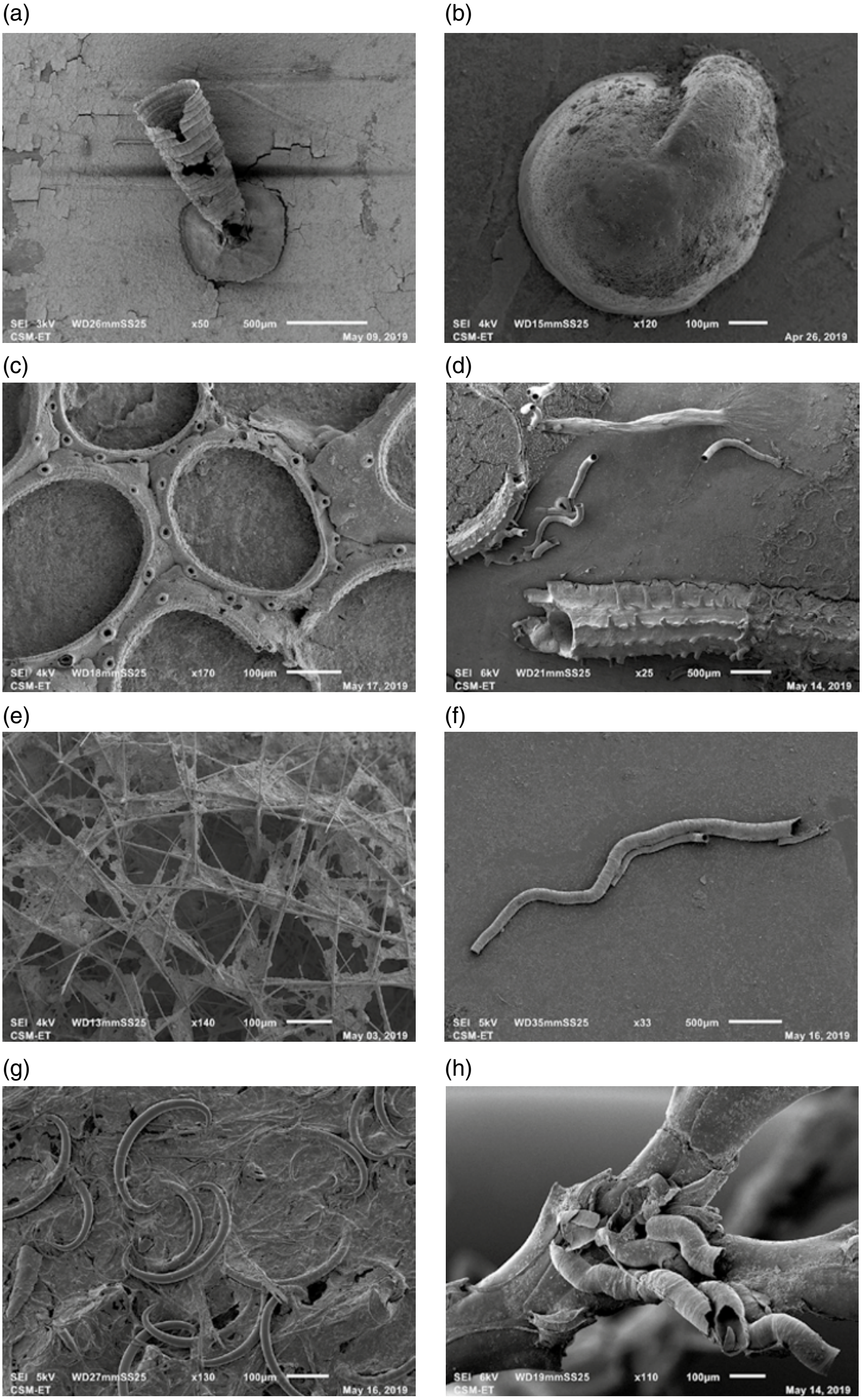


Figure 6.4 Diversity of organisms settled on various litter types collected in the Deep North West Mediterranean Sea. (Cruise Ramoge/IFREMER, 2018, Credit E. tambutté, CSM). Electron microscopy of organisms settled on plastic bottles (a: Chitinous envelope of a scyphozoan polyp, 1440 m; b: Foraminifera, 1440 m; c: Bryozoa, 700 m; d: Bryozoa and microscleres from sponges, 410 m), on rubber (e: Spicules of a sponge, 700 m), on glass (f: Bryozoa, 1050 m), and on PolyChloroVinyls (g: Chelae of sponge/microscleres, 410 m; h: Bryozoa on bryozoa, 410 m).

6.10 Trends and Monitoring

Because litter on the seafloor is usually not retrieved, monitoring it will tend to reflect accumulation processes. Interpreting trends is also difficult because the consequences of aging of plastics at depth are unknown and their accumulation on the seafloor certainly began before scientific investigations started in the 1990s. Timescales of observation should, therefore, be adapted, requiring multiannual frequencies for deep seafloor surveys. General strategies for the investigation of seafloor litter are similar to those used to assess the abundance and composition of benthic species. This enables an opportunistic evaluation to be achieved through widespread biodiversity sampling by diving, trawling, and video/photographic surveys. Recently, trends in the amounts of litter have been analyzed and discussed (Galgani et al. 2021; GESAMP 2019).

Details on the amounts of litter and plastic on the floors of all seas are needed to properly evaluate trends, but such an evaluation is impossible since rates of sinking, behavior on the seafloor and degradation and persistence mechanisms are not fully understood. Time-series data on the composition and abundance of microplastics are sparse. As mentioned by Galgani et al. (2021), monitoring programs or assessments also often report on the results of single surveys and cover different spectra of sizes, types, and shapes. Sampling for microplastics also remains a complex task with various sizes considered, different methods of counting and characterization, and a high risk of sample contamination by fibers, also leading to confusion between natural and polymer materials. Moreover, studies from different locations or time periods cannot currently be accurately compared since harmonization and common analytical approaches are not sufficiently considered for greater comparability.

Typically, available evidence on long-term trends suggests various patterns in concentration of seafloor litter, plastic, and microplastics in sediments. However, most of the work based on regular and periodic monitoring surveys has not demonstrated any real trend in these quantities.

Galgani et al. (2021) described while specific oceanographic features such as converging currents have explained increasing amounts above the Arctic Circle (Tekman et al. 2017), most seafloor litter studies have shown constant levels of litter and plastic. No change was measured in Spain between 2007 and 2017 (García-Rivera et al. 2017) or in the North Sea (Maes et al. 2018). A slight increase in seafloor plastics was observed in recent years only in the Baltic (excluding fishing gear; Zablotski and Kraak 2019), while results from observations in France showed mixed trends, including decreasing amounts between 2000 and 2013, then increases since 2013. No trend was identified in Chinese waters for seafloor litter between 2007 and 2014 (Zhou et al. 2011), with a similar result from data collected during regular State monitoring between 2011 and 2018. In contrast, a decrease in total seafloor litter was measured between 2007 and 2017, in both the Alboran Sea (García-Rivera et al. 2017) and the northern Adriatic (Strafella et al. 2015), without significant temporal trends for plastic in the remaining Adriatic.

Only a few studies have described trends in microplastics in sediments (Harris 2020). Brandon et al. (2019) analyzed microplastics in core sediment layers from California over a span of 175 years, suggesting an increase in the amounts of microplastics, proportional to plastic production worldwide. Two core samples collected from the Derwent estuary in Tasmania, Australia, showed that the MP abundance decreases with depth down-core in both cores (Willis et al. 2017). These authors reported finding fibers in core layers from periods before the 1950s, when polymers did not exist. Martin et al. (2020) used radio carbon dating of cores from the Irish continental shelf to infer sediment accumulation rates and also found MP occurring at depths that should have predated the invention of plastic. Finally, Courtene-Jones et al. (2020) employed the ^{210}Pb method to estimate accumulation rates in deep sea sediment cores and also found plastic particles occurring at depths down-core that predated the invention of plastic. Although contamination is a possible explanation, Courtene-Jones et al. (2020) proposed an alternative hypothesis that very small microplastic particles are transported vertically downward via pore water through the sediment. A similar hypothesis was proposed by Hidalgo-Ruz et al. (2012) to explain the occurrence of microplastic particles in beach sands. Further research is needed to test the hypothesis of pore water transport of microplastics.

The mass of plastic that has entered the oceans is equal to the mass sequestered in different sedimentary environments plus the amounts floating on the ocean surface and suspended in the water column. Barrett et al. (2020) estimate the total mass of microplastics that has accumulated in deep sea sediments is 14 million tonnes, while extrapolation of data from Pabortsava and Lampitt (2020) to the global ocean suggests 49.3–89.6 million tonnes of microplastics is suspended in the upper 200 m of the ocean. The amounts of macro- and micro-plastics that are presently trapped on beaches, in estuaries, deltas, and other coastal and shelf environments are unknown, although the available evidence suggests that shallow water, coastal environments probably, contain the majority of plastic that has entered the ocean (Harris 2020). Given these uncertainties, and until the amounts of plastic recorded in surveys from different sedimentary environments are evaluated systematically and their dynamics are better understood, the identification of possible trends will remain a challenge.

Regarding impacts, epibenthic communities dominated by sessile suspension feeders (e.g. corals, gorgonians), the so-called "marine animal forests," have strong potential for monitoring the temporal and spatial trends of entanglement between marine organisms and marine litter (Galgani et al. 2018). Their increased vulnerability to damage is due to their large morphologies, which easily snagged fishing line, the slow growth rate and longevity (Sheehan et al. 2017), their wide distribution in shallow and deep waters (Rossi et al. 2017a), and their exposure to marine litter, occurring in both fishing areas (Consoli et al. 2018a; Pham et al. 2013) and remote areas after long-distance litter drifting (Pham et al. 2014). Their sessile characteristic allows the precise location of entanglement events to be measured, which is not the case for migrating or mobile organisms. In addition, their immobility reduces the risk of misinterpretation due to possible interaction with active fishing gears. Consoli et al. (2018a) observed a significant positive relationship between the number of litter–fauna interactions and mean litter density, concluding that this indicator could be considered a good tool for monitoring the impact of marine litter on benthic communities. Galgani et al. (2018) noted that regular assessments through opportunistic approaches such as the monitoring of biodiversity in coral reef assemblages by diving or via submersible/ROV operation in deeper areas are possible. Adding marine litter as a routine survey variable in long-term reef monitoring programs of biodiversity (e.g. Reef Check, www.reefcheck.org) is recommended (De Carvalho-Souza et al. 2018) and should be implemented on a regular basis. For the deep sea, organizing databases that compile photographic records of litter on the seafloor (Chiba et al. 2018), such as the Deep-sea Debris Database (Chiba et al. 2018) with records from around the world, or more regionally for data from trawling (DATRAS 2010; ICES/IBTS 2017; Spedicato et al. 2019) will support the implementation of future global monitoring through data collection.

Data collection is also critical to improve knowledge about the fates and impacts of ALDFG, a key and distinct part of the global marine debris issue. Novel approaches to ALDFG data collection, such as engaging citizen snorkelers and scuba divers to collect data about underwater ALDFG, and collaborating with NGOs, marine parks, and wildlife rehabilitation organizations to access data about fishing gear ingestion impacts, are helping to fill previous ALDFG knowledge gaps (Richardson et al. 2019). The Global Ghost Gear Initiative's work (http://globalghostgearportal.net/dp/index.html) to develop a publicly accessible database that allows for standardization of, and comparison between, different ALDFG data sets from around the world has proved to be a powerful tool for informing on trends and supports the further retrieval of lost gear.

Other databases such LITTERBASE (https://litterbase.awi.de/) summarizes results from thousands of scientific studies related to marine litter, including the seafloor. We think that a database intended to host data on microplastics in sediments is still needed; likewise with maintaining a list of species found settled on seafloor litter.

The establishment of international frameworks on monitoring deep sea plastic pollution and a data-sharing protocol is key to delivering support to the effective management of plastic pollution and the conservation of deep sea ecosystems (Maximenko et al. 2019). However, there is no consensus on a standard classification of deep sea plastic pollution, despite some initiatives proposed regionally for regular monitoring such as are in use in the Action Plans of regional seas conventions like OSPAR, NOWPAP, Barcelona (GESAMP 2019), and interregional programs such as MSFD (Galgani et al. 2013). For example, a data management plan for marine litter has been developed at the European level within the existing EMODnet network to collect, homogenize, and provide access to standardized data sets and data products that may be used as a basis for seafloor litter assessment at the pan-European scale (Molina Jack et al. 2019). Harmonization with other national or regional platforms is a long-term perspective (GESAMP 2019), and it also provides a scientific and technical basis for a more global rationalized and integrated observation system.

6.11 Management Measures and Perspectives

Since the seafloor is major sink for marine litter, it is, therefore, an important component of the marine environment to consider in priority for reduction measures. Understanding that management will first prevent littering through the implementation of various and common approaches on land (improving recycling, bans, new plastic materials, improving water treatment, etc.) and at sea (implementation of port reception facilities, best practices, etc.), direct actions on the seafloor are also necessary despite being challenging.

Legal and technical measures to ensure that littering at sea is minimized have been drawn up by international bodies (MARPOL, Basel convention, etc.) and feature in agreements (Honolulu strategy), together with regional actions plans from regional sea conventions and national initiatives (UNEA 2020).

Removal activities are now common operations (GESAMP 2019) and are subdivided into two main categories based on retrieval methods, trawling and diving. The choice between the two methods depends on the water depth and substrate characteristics, with the possible echolocation of lost gear, and lead to different results in terms of amounts and costs. The resulting environmental benefits must exceed the damage caused by operations and must be obtained in a safe and cost-effective way (Williams and Rangel-Buitrago 2019). The implementation of FFL activities not only removes litter from the seafloor but also increases the awareness of the fishery sector of the marine litter issue (Ronchi et al. 2019). Either actively, when fishing operations are dedicated to litter only, or passively during normal fishing operations and without any financial compensation (KIMO 2014), they have been implemented in various regions in the world, including Northern European countries, the Baltic and Mediterranean Seas, and the eastern Pacific (Ronchi et al. 2019).

Trawling activities, however, are not selective, possibly altering habitats and living communities. Diving operations may be more accurate, since dedicated to litter only. However, only a limited amount of materials can be retrieved. The depths, the visibility of distribution, currents, and costs are the main constraints facing such an approach, limiting operations to selected sites of importance, like cleaning harbors, marine-protected areas, and enclosed bays (Consoli et al. 2020).

While the removal of ALDFG has become a common measure implemented in various projects and supported by various action plans on marine litter, new approaches have been proposed to implement automatic or remotely controlled devices that combine accuracy and the sustainability of cleanup interventions, including in deep environments (i.e. http://rozaliaproject.org/about/technology/).

Removal strategies remain curative measures and must be considered less effective than preventing littering and avoiding debris dispersal into the marine environment. For the seafloor, the long-term efficiency of cleanup campaigns is faced with the lack of legal and economic support (Ronchi et al. 2019) and the lack of interest in the materials collected in terms of recyclability.

Understanding that a significant reduction in the number of ALDFG is the first and most important strategy to reduce the impact of marine litter pollution from fishing on the seafloor, different solutions have been proposed, including the tagging of fishing gear and the use of new tools like drifting GPS positioned FADs, the use of biodegradable materials, already tested in oceanic waters (Consoli et al. 2018b; Moreno et al. 2016), the promotion of areas assigned exclusively to a type of gear to exclude important habitats, and citizen programs carried out by volunteers to collect litter in shallow areas (Consoli et al. 2018b). Finally, information aimed at fishermen, including recreative fishermen (GESAMP 2021), and more generally the fishery sector, must be considered a critical step in preventing littering.

6.12 Conclusions and Perspectives

Marine debris is now commonly observed everywhere in the oceans and, in light of available knowledge, the urgency of implementing policies to specifically reduce seafloor litter is largely recognized. Many gaps have been identified from different standpoints, including those of scientists, monitoring agencies, and policy makers.

Better understanding of the transfer of litter to the seafloor, the accurate evaluation of their amounts, the search for accumulation areas/ gyres, mapping and modeling litter sources and distribution, taking advantage of information on maritime traffic, and better linking of the accumulation of debris with deep sea circulation are all critical goals that must be reached to overcome gaps in knowledge. The complexity of sources and pathways involved in the distribution of plastics within the marine environment must be addressed. To this end, understanding the degradation of plastic in the deep sea is also a key point since it will provide better appreciation of the longevity of this kind of pollution.

More specifically, with regard to fishing-related litter, there are many areas that lack scientific knowledge on ALDFG such as the inability to distinguish between wildlife entanglements caused by active gear compared to those caused by ALDFG, and understanding ALDFG macro and microplastic pathways and transport, and the impacts of ALDFG on fish populations and stock losses. Estimates of contributions of ALDFG from recreational fisheries, FADs, ALDFG categories to distinguish the amounts and impacts from hand/pole lines in comparison to longline gear, and from any other specific types of gear are needed as they may represent the largest share of litter in certain fishing grounds. Future research to better understand losses from high-risk gear types, offshore aquaculture, and marine litter events onboard ships is necessary to understand the drivers of pollution and monitoring.

Monitoring must also be reinforced through the development and consistent application of accessible and automated analytical techniques that are necessary to enable the reliable characterization and quantification of plastics, especially microplastics, on a large scale (GESAMP 2019). This will enable the comparability of data and will also take geographic gaps into account. Data on litter and ALDFG from deeper waters that are very limited need reinforced observer coverage and data collection on vessels, including from the fishing fleets, taking advantage of navigation logs that are designed for reporting pollution incidents onboard vessels within MARPOL. An international database is needed for sediment microplastics and listing the species, including microorganisms, settling on deep sea plastics. Building such a database could possibly take advantage of fast sequencing tools to identify any harmful species (pathogens, invasive, toxic species) that are present and where they are located. These tools are required now to better understand the cycling of plastics on the seafloor and their impacts.

Regarding reduction measures, we anticipate the need for specific investigations that integrate risk assessments performed from the environmental and economic standpoints. We think that predicting and cross-mapping litter distribution on the seafloor with the distribution of species and habitats will lead to a better definition of sensitive areas, providing support for targeted measures and addressing the impact on ecosystem services. Regarding vessels, platforms, and other man-made structures, the focus should be on the development and implementation of comprehensive pollution prevention plans, based on advanced understanding of motivations for dumping at sea. More specifically, regarding seafloor litter and microplastics and the assessment and prevention of Illegal dumping, improved management is needed of maritime activities, including offshore oil and gas exploration and extraction and military activities (HELCOM 2013). With targeted measures aimed at abating the incorrect practices of small-scale professional fisheries, and the development of port reception facilities, all these measures together will contribute toward the prevention of littering and add to the prevention measures that must be taken for land-based sources of plastic, which is the largest source of seafloor litter.

Acknowledgments

Part of work was supported by the EU interregs projects CleanATLANTIC, PBMPA, the EU projects JPI/Andromeda and H2020/ EuroQcharm, and the RAMOGE initiative. The authors thank Georgios Flakes and Kristina Thygesen from GRID-Arendal for the preparation of Figures 6.1 and 6.2. PTH and TM gratefully acknowledge financial support from the Norwegian Agency for Development Cooperation, Ministry of Foreign Affairs.

References

Abidli, S., Antunes, J., Ferreira, J., Lahbib, Y., Sobral, P., Trigui El Menif, N., 2018. Microplastics in sediments from the littoral zone of the north Tunisian coast (Mediterranean Sea). *Estuarine, Coastal and Shelf Science*, 205, 1–9.

Acha, E.M., Mianzan, H.W., Iribarne, O., Gagliardini, D.A., Lasta, C., Daleo, P., 2003. The role of the Rio de la Plata bottom salinity front in accumulating debris. *Marine Pollution Bulletin*, 46, 197–202.

Alomar, C., Compa, M., Deudero, S., Guijarro, B., 2020. Spatial and temporal distribution of marine litter on the seafloor of the Balearic Islands (western Mediterranean Sea). *Deep Sea Research Part I: Oceanographic Research Papers*, 155, 103178.

Alomar, C., Estarellas, F., Deudero, S., 2016. Microplastics in the Mediterranean Sea: deposition in coastal shallow sediments, spatial variation and preferential grain size. *Marine Environmental Research*, 115, 1–10.

Alvito, A., Bellodi, A., Cau, A., Moccia, D., Mulas, A., Palmas, F., Pesci, P., Follesa, M.C., 2018. Amount and distribution of benthic marine litter along Sardinian fishing grounds (CW Mediterranean Sea). *Waste Management*, 75, 131–140.

Anastasopoulou, A., Fortibuoni, T., 2019. *Impact of Plastic Pollution on Marine Life in the Mediterranean Sea*. Springer, Berlin, Heidelberg, pp. 1–62.

Andrady, A.L., 2011. Microplastics in the marine environment. *Marine Pollution Bulletin*, 62, 1596–1605.

Angiolillo, M., 2019. Chapter 14 – Debris in deep water, In: Sheppard, C. (Ed.), *World Seas: An Environmental Evaluation* (Second Edition). Academic Press, London pp. 251–268.

Angiolillo, M., di Lorenzo, B., Farcomeni, A., Bo, M., Bavestrello, G., Santangelo, G., Cau, A., Mastascusa, V., Cau, A., Sacco, F., Canese, S., 2015. Distribution and assessment of marine debris in the deep Tyrrhenian Sea (NW Mediterranean Sea, Italy). *Marine Pollution Bulletin*, 92, 149–159.

Angiolillo, M., Fortibuoni, T., 2020. Impacts of marine litter on Mediterranean reef systems: from shallow to deep waters. *Frontiers in Marine Science*, 7, 1–10.

Angiolillo, M., Gerigny, O., Valente, T., Fabri, M.-C., Tambutté, E., Rouanet, E., Claro, F., Tunesi, L., Visso, A., Daniel, B., Galgani, F., 2021. Distribution of seafloor litter and its interaction with benthic organisms in deep waters of the Ligurian Sea (Northwestern Mediterranean). *Science of the Total Environment* 788, 147745. https://doi.org/10.1016/j.scitotenv.2021.147745

Ayaz, A., Ünal, V., Acarli, D., Altınağaç, U., 2010. Fishing gear losses in the Gökova Special Environmental Protection Area (SEPA), eastern Mediterranean, Turkey. *Journal of Applied Ichthyology* 26, 416–419.

Ayma, A., Aguzzi, J., Canals, M., Lastras, G., Bahamon, N., Mecho, A., Company, J.B., 2016. Comparison between ROV video and Agassiz trawl methods for sampling deep water fauna of submarine canyons in the Northwestern Mediterranean Sea with observations on behavioural reactions of target species. *Deep Sea Research Part I: Oceanographic Research Papers*, 114, 149–159.

Bakir, A., Desender, M., Wilkinson, T., Van Hoytema, N., Amos, R., Airahui, S., Graham, J., Maes, T., 2020. Occurrence and abundance of meso and microplastics in sediment, surface waters, and marine biota from the South Pacific region. *Marine Pollution Bulletin*, 160, 111572.

Barnes, D.K.A., Galgani, F., Thompson, R.C., Barlaz, M., 2009. Accumulation and fragmentation of plastic debris in global environments. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364, 1985–1998.

Barnes, D.K.A., Morley, S.A., Bell, J., Brewin, P., Brigden, K., Collins, M., Glass, T., Goodall-Copestake, W.P., Henry, L., Laptikhovsky, V., Piechaud, N., Richardson, A., Rose, P., Sands, C.J., Schofield, A., Shreeve, R., Small, A., Stamford, T., Taylor, B., 2018. Marine plastics threaten giant Atlantic Marine Protected Areas. *Current Biology*, 28, R1137–R1138.

Barnes, D.K.A., Walters, A., Gonçalves, L., 2010. Macroplastics at sea around Antarctica. *Marine Environmental Research*, 70, 250–252.

Barrett, J., Chase, Z., Zhang, J., Holl, M.M.B., Willis, K., Williams, A., Hardesty, B.D., Wilcox, C., 2020. Microplastic pollution in deep-sea sediments from the Great Australian Bight. *Frontiers in Marine Science*, 7, 1–10.

Barrows, A.P.W., Cathey, S.E., Petersen, C.W., 2018. Marine environment microfiber contamination: Global patterns and the diversity of microparticle origins. *Environmental Pollution*, 237, 275–284.

Battisti, C., Kroha, S., Kozhuharova, E., De Michelis, S., Fanelli, G., Poeta, G., Pietrelli, L., Cerfolli, F., 2019. Fishing lines and fish hooks as neglected marine litter: first data on chemical composition, densities, and biological entrapment from a Mediterranean beach. *Environmental Science and Pollution Research*, 26, 1000–1007.

Bergmann, M., Klages, M., 2012. Increase of litter at the Arctic deep-sea observatory HAUSGARTEN. *Marine Pollution Bulletin*, 64, 2734–2741.

Bergmann, M., Mützel, S., Primpke, S., Tekman, M.B., Trachsel, J., Gerdts, G., 2019. White and wonderful? Microplastics prevail in snow from the Alps to the Arctic. *Science Advances*, 5, eaax1157.

Bergmann, M., Wirzberger, V., Krumpen, T., Lorenz, C., Primpke, S., Tekman, M.B., Gerdts, G., 2017. High quantities of microplastic in arctic deep-sea sediments from the HAUSGARTEN observatory. *Environmental Science & Technology*, 51, 11000–11010.

Bingel, F., Avsar, D., Uensal, M., 1987. A note on plastic materials in trawl catches in the northeastern Mediterranean. *Meeresforsch*, 31, 227–233.

Blasković, A., Fastelli, P., ČiSmek, H., Guerranti, C., Renzi, M., 2017. Plastic litter in sediments from the Croatian marine protected area of the natural park of Telaščica bay (Adriatic Sea), *Marine Pollution Bulletin* 114 (1), 583–586.

Bo, M., Bava, S., Canese, S., Angiolillo, M., Cattaneo-Vietti, R., Bavestrello, G., 2014. Fishing impact on deep Mediterranean rocky habitats as revealed by ROV investigation. *Biological Conservation*, 171, 167–176.

Bo, M., Coppari, M., Betti, F., Massa, F., Gay, G., Cattaneo-Vietti, R., Bavestrello, G., 2019. Unveiling the deep biodiversity of the Janua Seamount (Ligurian Sea): first Mediterranean sighting of the rare Atlantic bamboo coral *Chelidonisis aurantiaca* Studer, 1890. *Deep Sea Research Part I: Oceanographic Research Papers*, 156, 103186.

Brandon, J.A., Jones, W., Ohman, M.D., 2019. Multidecadal increase in plastic particles in coastal ocean sediments. *Science Advances* 5, eaax0587.

Buhl-Mortensen, L., Buhl-Mortensen, P., 2017. Marine litter in the Nordic Seas: distribution composition and abundance. *Marine Pollution Bulletin*, 125, 260–270.

Canals, M., Pham, C.K., Bergmann, M., Gutow, L., Hanke, G., Van-Sebille, E., Angiolillo, M., Buhl-Mortensen, L., Cau, A., Ioakeimidis, C., Kammann, U., Lundsten, L., Papatheodorou, G., Purser, A., Sanchez-Vidal, A., Schulz, M., Vinci, M., Chiba, S., Galgani, F., Langenkämper, D., Möller, T., Nattkemper, T., Ruiz, M., Suikkanen, S., Woodall, L., Fakiris, E., Molina-Jack, M.E., Giorgetti, A., 2020. The quest for seafloor macrolitter: a critical review of background knowledge, current methods and future prospects. *Environmental Research Letters*, 1–29.

Canals, M., Puig, P., de Madron, X.D., Heussner, S., Palanques, A., Fabres, J., 2006. Flushing submarine canyons. *Nature*, 444, 354–357.

Cau, A., Alvito, A., Moccia, D., Canese, S., Pusceddu, A., Rita, C., Angiolillo, M., Follesa, M.C., 2017. Submarine canyons along the upper Sardinian slope (Central Western Mediterranean) as repositories for derelict fishing gears. *Marine Pollution Bulletin*, 123, 357–364.

Cau, A., Bellodi, A., Moccia, D., Mulas, A., Pesci, P., Cannas, R., Pusceddu, A., Follesa, M.C., 2018. Dumping to the abyss: single-use marine litter invading bathyal plains of the Sardinian margin (Tyrrhenian Sea). *Marine Pollution Bulletin*, 135, 845–851.

Chen, M., Du, M., Jin, A., Chen, S., Dasgupta, S., Li, J., Xu, H., Ta, K., Peng, X., 2020. Forty-year pollution history of microplastics in the largest marginal sea of the western Pacific. *Geochemical Perspectives Letters* 13, 42–47.

Chiba, S., Saito, H., Fletcher, R., Yogi, T., Kayo, M., Miyagi, S., Ogido, M., Fujikura, K., 2018. Human footprint in the abyss: 30 year records of deep-sea plastic debris. *Marine Policy*, 96, 204–212.

Chubarenko, I., Esiukova, E., Zobkov, M.L., Isachenko, I. (2020). Microplastics distribution in bottom sediments of the Baltic Sea Proper? Abstract of the Micro2020 International Conference, Lanzarote (23–27 November 2020).

Claessens, M., De Meester, S., Landuyt, L., Clerck, K., Janssen, C., 2011. Occurrence and distribution of microplastics in marine sediments along the Belgian coast. *Marine Pollution Bulletin*, 62, 2199–2204.

Clark, R., Pittman, S., Battista, T., Caldow, C., 2012. *Survey and Impact Assessment of Derelict Fish Traps in St. Thomas and St. John, U.S. Virgin Islands*. NOAA National Centers for Coastal Ocean Science, Silver Spring, MD.

Consoli, P., Andaloro, F., Altobelli, C., Battaglia, P., Campagnuolo, S., Canese, S., Castriota, L., Cillari, T., Falautano, M., Pedà, C., Perzia, P., Sinopoli, M., Vivona, P., Scotti, G., Esposito, V., Galgani, F., Romeo, T., 2018a. Marine litter in an EBSA (Ecologically or Biologically Significant Area) of the central Mediterranean Sea: abundance, composition, impact on benthic species and basis for monitoring entanglement. *Environmental Pollution*, 236, 405–415.

Consoli, P., Falautano, M., Sinopoli, M., Perzia, P., Canese, S., Esposito, V., Battaglia, P., Romeo, T., Andaloro, F., Galgani, F., Castriota, L., 2018b. Composition and abundance of benthic marine litter in a coastal area of the central Mediterranean Sea. *Marine Pollution Bulletin*, 136, 243–247.

Consoli, P., Scotti, G., Romeo, T., Fossi, M.C., Esposito, V., D'Alessandro, M., Battaglia, P., Galgani, F., Figurella, F., Pragnell-Raasch, H., Andaloro, F., 2020. Characterization of seafloor litter on Mediterranean shallow coastal waters: evidence from Dive Against Debris®, a citizen science monitoring approach. *Marine Pollution Bulletin*, 150, 110763.

Courtene-Jones, W., Quinn, B., Ewins, C., Gary, S.F., Narayanaswamy, B.E., 2020. Microplastic accumulation in deep-sea sediments from the Rockall Trough. *Marine Pollution Bulletin*, 154, 111092.

Cózar, A., Echevarría, F., González-Gordillo, J.I., Irigoien, X., Úbeda, B., Hernández-León, S., Palma, Á.T., Navarro, S., García-de-Lomas, J., Ruiz, A., Fernández-de-Puelles, M.L., Duarte, C.M., 2014. Plastic debris in the open ocean. *Proceedings of the National Academy of Sciences of the USA*, 111, 10239–10244.

D'Alessandro, M., Porporato, E.M.D., Esposito, V., Giacobbe, S., Deidun, A., Nasi, F., Ferrante, L., Auriemma, R., Berto, D., Renzi, M., Scotti, G., Consoli, P., Del Negro, P., Andaloro, F., Romeo, T., 2020. Common patterns of functional and biotic indices in response to multiple stressors in marine harbours ecosystems. *Environmental Pollution*, 259, 113959.

D'Onghia, G., Maiorano, P., Sion, L., Giove, A., Capezzuto, F., Carlucci, R., Tursi, A., 2010. Effects of deep-water coral banks on the abundance and size structure of the megafauna in the Mediterranean Sea. *Deep Sea Research Part II: Topical Studies in Oceanography*, 57, 397–411.

Danovaro, R., Fanelli, E., Canals, M., Ciuffardi, T., Fabri, M.C., Taviani, M., Argyrou, M., Azzurro, E., Bianchelli, S., Cantafaro, A., Carugati, L., Corinaldesi, C., de Haan, W.P., Dell'Anno, A., Evans, J., Foglini, F., Galil, B., Gianni, M., Goren, M., Greco, S., Grimalt, J., Güell-Bujons, Q., Jadaud, A., Knittweis, L., Lopez, J.L., Sanchez-Vidal, A., Schembri, P.J., Snelgrove, P., Vaz, S., Angeletti, L., Barsanti, M., Borg, J.A., Bosso, M., Brind'Amour, A., Castellan, G., Conte, F., Delbono, I., Galgani, F., Morgana, G., Prato, S., Schirone, A., Soldevila, E., 2020. Towards a marine strategy for the deep Mediterranean Sea: analysis of current ecological status. *Marine Policy*, 112, 103781.

DATRAS, 2010. *Development of a central database for European trawl survey data*. DATRAS, Database Trawl Surveys. Final report, Project number QLRT-2001-00025 https://archimer.ifremer.fr/doc/2001/rapport-2173.pdf (accessed August 19, 2021).

Davies, A.J., Roberts, J.M., Hall-Spencer, J., 2007. Preserving deep-sea natural heritage: emerging issues in offshore conservation and management. *Biological Conservation*, 138, 299–312.

De Carvalho-Souza, G.F., Llope, M., Tinôco, M.S., Medeiros, D.V., Maia-Nogueira, R., Sampaio, C.L.S., 2018. Marine litter disrupts ecological processes in reef systems. *Marine Pollution Bulletin*, 133, 464–471.

Debrot, A.O., Vinke, E., van der Wende, G., Hylkema, A., Reed, J.K., 2014. Deepwater marine litter densities and composition from submersible video-transects around the ABC-islands, Dutch Caribbean. *Marine Pollution Bulletin*, 88, 361–365.

Deudero, S., Alomar, C., 2015. Mediterranean marine biodiversity under threat: reviewing influence of marine litter on species. *Marine Pollution Bulletin*, 98, 58–68.

Enders, K., Käppler, A., Biniasch, O., Feldens, P., Stollberg, N., Lange, X., Fischer, D., Eichhorn, K.-J., Pollehne, F., Oberbeckmann, S., Labrenz, M., 2019. Tracing microplastics in aquatic environments based on sediment analogies. *Scientific Reports*, 9, 15207.

Enrichetti, F., Bava, S., Bavestrello, G., Betti, F., Lanteri, L., Bo, M., 2019. Artisanal fishing impact on deep coralligenous animal forests: a Mediterranean case study of marine vulnerability. *Ocean & Coastal Management*, 177, 112–126.

Enrichetti, F., Dominguez-Carrió, C., Toma, M., Bavestrello, G., Canese, S., Bo, M., 2020. Assessment and distribution of seafloor litter on the deep Ligurian continental shelf and shelf break (NW Mediterranean Sea). *Marine Pollution Bulletin*, 151, 1–14.

Eriksen, M., Lebreton, L.C.M., Carson, H.S., Thiel, M., Moore, C.J., Borerro, J.C., Galgani, F., Ryan, P.G., Reisser, J., 2014. Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. *PLOS One*, 9, 1–15.

Eryaşar, A.R., Özbilgin, H., Gücü, A.C., Sakınan, S., 2014. Marine debris in bottom trawl catches and their effects on the selectivity grids in the north eastern Mediterranean. *Marine Pollution Bulletin*, 81, 80–84.

FAO. (2016). *Abandoned, Lost or Otherwise Discarded Gillnets and Trammel Nets – Methods to Estimate Ghost Fishing Mortality, and the Status of Regional Monitoring and Management*. FAO Fisheries and Aquaculture Technical Paper 600. Rome, FAO, 79p.

FAO. 2018. *The state of world fisheries and aquaculture 2018 – meeting the sustainable development goals*. Rome, FAO, p. 227 (Licence: CC BY-NC-SA 3.0 IGO).

Filgueiras, A.V., Gago, J., Campillo, J.A., León, V.M., 2019. Microplastic distribution in surface sediments along the Spanish Mediterranean continental shelf. *Environmental Science and Pollution Research*, 26, 21264–21273.

Fischer, V., Elsner, N.O., Brenke, N., Schwabe, E., Brandt, A., 2015. Plastic pollution of the Kuril-Kamchatka Trench area (NW pacific). *Deep Sea Research Part II: Topical Studies in Oceanography* 111, 399.

Fortibuoni, T., Ronchi, F., Mačić, V., Mandić, M., Mazziotti, C., Peterlin, M., Prevenios, M., Prvan, M., Somarakis, S., Tutman, P., Varezić, D.B., Virsek, M.K., Vlachogianni, T., Zeri, C., 2019. A harmonized and coordinated assessment of the abundance and composition of seafloor litter in the Adriatic-Ionian macroregion (Mediterranean Sea). *Marine Pollution Bulletin*, 139, 412–426.

Fulton, M., Hong, J., Islam, M.J., Sattar, J., 2019. Robotic Detection of marine litter using deep visual detection models. *2019 International Conference on Robotics and Automation (ICRA)*, Montreal, Canada (20–24 May 2019), pp. 5752–5758.

Galafassi, S., Nizzetto, L., Volta, P., 2019. Plastic sources: A survey across scientific and grey literature for their inventory and relative contribution to microplastics pollution in natural environments, with an emphasis on surface water. *Science of the Total Environment*, 693, 133499.

Galgani, F., Claro, F., Depledge, M., Fossi, C., 2014. Monitoring the impact of litter in large vertebrates in the Mediterranean Sea within the European Marine Strategy Framework Directive (MSFD): constraints, specificities and recommendations. *Marine Environmental Research*, 100, 3–9.

Galgani, F., Hanke, G., Maes, T., 2015. Global distribution, composition and abundance of marine litter. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), *Marine Anthropogenic Litter*. Springer Open, London, pp. 29–56.

Galgani, F., Hanke, G., Werner, S., Oosterbaan, L., Nilsson, P., Fleet, D., Kinsey, S., Thompson, R.C., Palatinus, A., Van Franeker, J.A., Vlachogianni, T., Scoullos, M., Veiga, J.M., Matiddi, M., Alcaro, L., Maes, T., Korpinen, S., Budziak, A., Leslie, H.A., Gago, J., Liebezeit, G. (2013). *Guidance on Monitoring of Marine Litter in European Seas. MSFD GES Technical Subgroup on Marine Litter (TSG-ML)*. JRC Scientific and Policy Reports. Luxembourg: European Commission, Joint Research Centre, Institute for Environment and Sustainability, p. 124.

Galgani, F., Jaunet, S., Campillo, A., Guenegen, X., His, E., 1995. Distribution and abundance of debris on the contiental shelf of the north-western Mediterranean Sea. *Marine Pollution Bulletin*, 30, 713–717.

Galgani, F., Leaute, J.P., Moguedet, P., Souplet, A., Verin, Y., Carpentier, A., Goraguer, H., Latrouite, D., Andral, B., Cadiou, Y., Mahe, J.C., Poulard, J.C., Nerisson, P., 2000. Litter on the Sea Floor Along European Coasts. *Marine Pollution Bulletin*, 40, 516–527.

Galgani, F., Lecornu, F., 2004. Debris on the sea floor at "Hausgarten": in the expedition ARKTIS XIX/3 of the research vessel POLARSTERN in 2003. *Berichte Polar Meeresforsch*, 488, 260–262.

Galgani, F., Pham, C.K., Claro, F., Consoli, P., 2018. Marine animal forests as useful indicators of entanglement by marine litter. *Marine Pollution Bulletin*, 135, 735–738.

Galgani, F., Souplet, A., Cadiou, Y., 1996. Accumulation of debris on the deep sea floor off the French Mediterranean coast. *Marine Ecology Progress Series*, 142, 225–234.

Galgani, F., Stoefen-o Brien, A., Weis, J., Ioakeimidis, C., Schuyler, Q., Rochman, C., Makarenko, I., Griffiths, H., Bondareff, J., Vethaak, D., Keener, P., Sobral, P., Deidun, A., Topouzelis, K., Vlahos, P., Lana, F., Hassellov, M., Arsonina, B., Gerigny, O., Ambulkar, A., Jambecke, J., João Bebianno, M., 2021. Are litter, plastic and microplastic quantities increasing in the ocean? *Microplastics Nanoplastics*, 1, 1–2.

Galil, B.S., Golik, A., Türkay, M., 1995. Litter at the bottom of the sea: a sea bed survey in the Eastern Mediterranean. *Marine Pollution Bulletin*, 30, 22–24.

García-Rivera, S., Lizaso, J.L.S., Millán, J.M.B., 2017. Composition, spatial distribution and sources of macro-marine litter on the Gulf of Alicante seafloor (Spanish Mediterranean). *Marine Pollution Bulletin*, 121, 249–259.

García-Rivera, S., Lizaso, J.L.S., Millán, J.M.B., 2018. Spatial and temporal trends of marine litter in the Spanish Mediterranean seafloor. *Marine Pollution Bulletin*, 137, 252–261.

Garofalo, G., Quattrocchi, F., Bono, G., Di Lorenzo, M., Di Maio, F., Falsone, F., Gancitano, V., Geraci, M.L., Lauria, V., Massi, D., Scannella, D., Titone, A., Fiorentino, F., 2020. What is in our seas? Assessing anthropogenic litter on the seafloor of the central Mediterranean Sea. *Environmental Pollution*, 266, 115213.

Gerigny, O., Brun, M., Fabri, M.C., Tomasino, C., Le Moigne, M., Jadaud, A., Galgani, F., 2019. Seafloor litter from the continental shelf and canyons in French Mediterranean Water: distribution, typologies and trends. *Marine Pollution Bulletin*, 146, 653–666.

GESAMP. 2016. Sources, fate and effects of microplastics in the marine environment: part two of a global assessment. In: Kershaw, P.J., Rochman, C.M. (Eds.), *IMO/FAO/ UNESCO IOC/UNIDO/WMO/IAEA/ UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection*. Reports and Studies GESAMP 93, 220. http://www.gesamp.org/site/assets/files/1275/sources-fate-and-effects-of-microplastics-in-the-marine-environment-part-2-of-a-global-assessment-en.pdf

GESAMP. 2019. Guidelines for the monitoring and assessment of plastic litter and microplastics in the ocean. In: Kershaw, P.J., Turra, A., Galgani, F. (Eds.). *IMO/FAO/ UNESCO IOC/UNIDO/WMO/ IAEA/UN/UNEP/UNDP/ISA Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection*. Reports and Studies GESAMP 99, p. 130. http://www.gesamp.org/ publications/guidelines-for-the-monitoring-and-assessment-of-plastic-litter-in-the-ocean

GESAMP. 2021. Sea based sources of marine litter. Report of the GESAMP Working Group 43. In: Gilardi, K. (ed.), *IMO/UNESCO6EOC/UNEP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection*. Reports and Studied GESAMP xx, p. 144. http://www.gesamp.org/ work/groups/wg-43-on-sea-based-sources-of-marine-litter

Geyer, R., Jambeck, J.R., Law, K.L., 2017. Production, use, and fate of all plastics ever made. *Science Advances*, 3, e1700782.

Giusti, M., Canese, S., Fourt, M., Bo, M., Innocenti, C., Goujard, A., Daniel, B., Angeletti, L., Taviani, M., Aquilina, L., Tunesi L., 2019. Coral forests and Derelict Fishing Gears in submarine canyon systems of the Ligurian Sea. *Prog. Oceanogr*. 178, 102186.

Goldberg, E.D., 1995. Emerging problems in the coastal zone for the twenty-first century. *Marine Pollution Bulletin*, 31, 152–158.

Gregory, M.R., 2009. Environmental implications of plastic debris in marine settings – entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364, 2013–2025.

Grøsvik, B.E., Prokhorova, T., Eriksen, E., Krivosheya, P., Horneland, P.A., Prozorkevich, D., 2018. Assessment of Marine Litter in the Barents Sea, a Part of the Joint Norwegian–Russian Ecosystem Survey. *Frontiers in Marine Science*, 5, 1–11.

Gutow, L., Ricker, M., Holstein, J.M., Dannheim, J., Stanev, E.V., Wolff, J.-O., 2018. Distribution and trajectories of floating and benthic marine macrolitter in the south-eastern North Sea. *Marine Pollution Bulletin*, 131, 763–772.

Guven, O., Gulyavuz, H., Deval, M., 2013. Benthic debris accumulation in bathyal grounds in the Antalya Bay, Eastern Mediterranean. *Turkish Journal of Fisheries and Aquatic Sciences*, 13, 43–49.

Haave, M., Lorenz, C., Primpke, S., Gerdts, G., 2019. Different stories told by small and large microplastics in sediment – first report of microplastic concentrations in an urban recipient in Norway. *Marine Pollution Bulletin*, 141, 501–513.

Hall, N.M., Berry, K.L.E., Rintoul, L., Hoogenboom, M.O., 2015. Microplastic ingestion by scleractinian corals. *Marine Biology*, 162, 725–732.

Harris, P., Whiteway, T., 2011. Global distribution of large submarine canyons: geomorphic differences between active and passive continental margins. *Marine Geology*, 285, 69–86.

Harris, P.T., 2020. The fate of microplastic in marine sedimentary environments: a review and synthesis. *Marine Pollution Bulletin*, 158, 111398.

Harris, P.T., Macmillan-Lawler, M., Rupp, J., Baker, E.K., 2014. Geomorphology of the oceans. *Marine Geology*, 352, 4–24.

Heezen, B.C., Hollister, C.D., 1971. *The Face of the Deep*. Oxford University Press, New York, London, Toronto. S11.25, p. 669.

HELCOM. (2013). *Chemical Munitions Dumped in the Baltic Sea: Report of the ad hoc Expert Group to Update and Review the Existing Information on Dumped Chemical Munitions in the Baltic Sea (HELCOM MUNI)*. Baltic Sea Environment Proceeding (BSEP) No. 142. Helsinki: Helsinki Commission - Baltic Marine Environment Protection Commission.

Hess, N.A., Ribic, C.A., Vining, I., 1999. Benthic Marine debris, with an emphasis on fishery-related items, surrounding Kodiak Island, Alaska, 1994–1996. *Marine Pollution Bulletin*, 38, 885–890.

Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M., 2012. Microplastics in the marine environment: a review of the methods used for identification and quantification. *Environmental Science & Technology*, 46, 3060–3075.

Holmström, A., 1975. Plastic films on the bottom of the Skagerrak. *Nature*, 255, 622–623.

ICES/IBTS, 2017. Manual for the IBTS North eastern Atlantic Survey (IBTS). *Series of ICES Survey Protocols (SISP)*, 15, 92.

Ioakeimidis, C., Fotopoulou, K.N., Karapanagioti, H.K., Geraga, M., Zeri, C., Papathanassiou, E., Galgani, F., Papatheodorou, G., 2016. The degradation potential of PET bottles in the marine environment: an ATR-FTIR based approach. *Scientific Reports*, 6, 1–8.

Ioakeimidis, C., Papatheodorou, G., Fermeli, G., Streftaris, N., Papathanassiou, E., 2015. Use of ROV for assessing marine litter on the seafloor of Saronikos Gulf (Greece): a way to fill data gaps and deliver environmental education. *Springerplus*, 4, 463–463.

Jalón-Rojas, I., Wang, X.H., Fredj, E., 2019. Technical note: on the importance of a three-dimensional approach for modelling the transport of neustic microplastics. *Ocean Science*, 15, 717–724.

Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. *Science*, 347, 768–771.

Jamieson, A.J., Brooks, L.S.R., Reid, W.D.K., Piertney, S.B., Narayanaswamy, B.E., Linley, T.D., 2019. Microplastics and synthetic particles ingested by deep-sea amphipods in six of the deepest marine ecosystems on Earth. *Royal Society Open Science*, 6, 180667.

June, J.A., 1990. Type, source, and abundance of trawl – caught marine debris off Oregon, in the eastern Bering sea, and in Norton sound in 1988. In: Proceedings of the Second International Conference on Marine Debris, 2–7 April 1989 (ed. R.S. Shomura and M.L. Godfrey). Honolulu, Hawaii: U.S. Dept. Commerce, NOAA Tech. Memo. NMFS, NOAA-TM-NMFS-SWFSC, pp. 279–301.

Kaladharan, P., Singh, V.V., Asha, P.S., Edward, L., Sukhadane, K.S., 2020. Marine plastic litter in certain trawl grounds along the Peninsular coasts of India. *Marine Pollution Bulletin*, 157, 111299.

Kammann, U., Aust, M.-O., Bahl, H., Lang, T., 2018. Marine litter at the seafloor – abundance and composition in the North Sea and the Baltic Sea. *Marine Pollution Bulletin*, 127, 774–780.

Kane, I.A., Clare, M.A., Miramontes, E., Wogelius, R., Rothwell, J.J., Garreau, P., Pohl, F., 2020. Seafloor microplastic hotspots controlled by deep-sea circulation. *Science*, 368, 1140.

Kanhai, L.D.K., Johansson, C., Frias, J.P.G.L., Gardfeldt, K., Thompson, R.C., O'Connor, I., 2019. Deep sea sediments of the Arctic Central Basin: a potential sink for microplastics. *Deep Sea Research Part I: Oceanographic Research Papers*, 145, 137–142.

Kazour, M., Jemaa, S., Issa, C., Khalaf, G., Amara, R., 2019. Microplastics pollution along the Lebanese coast (Eastern Mediterranean Basin): occurrence in surface water, sediments and biota samples. *Science of the Total Environment*, 696, 133933.

Keller, A.A., Fruh, E.L., Johnson, M.M., Simon, V., McGourty, C., 2010. Distribution and abundance of anthropogenic marine debris along the shelf and slope of the US West Coast. *Marine Pollution Bulletin*, 60, 692–700.

KIMO, 2014. *Fishing for Litter Scotland*. Final Report 2011–2014, p. 18. http://www.fishingforlitter.org.uk/assets/file/Report%20FFL%202011%20-%2014.pdf (accessed August 19, 2021).

Kooi, M., Nes, E.H.v., Scheffer, M., Koelmans, A.A., 2017. Ups and downs in the ocean: effects of biofouling on vertical transport of microplastics. *Environmental Science & Technology*, 51, 7963–7971.

Kroodsma, D.A., Mayorga, J., Hochberg, T., Miller, N.A., Boerder, K., Ferretti, F., Wilson, A., Bergman, B., White, T.D., Block, B.A., Woods, P., Sullivan, B., Costello, C., Worm, B., 2018. Tracking the global footprint of fisheries. *Science*, 359, 904–908.

Kühn, S., Bravo Rebolledo, E.L., van Franeker, J.A., 2015. Deleterious effects of litter on marine life. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), *Marine Anthropogenic Litter*. Springer International Publishing, Cham, pp. 75–116.

Kukkola, A.T., Senior, B., Maes, T., Kroger, S., Ag, M., 2020. *Digging Down Into the Detail: A Large-Scale Study of Microplastic Abundance in Sediment Cores From the UK Continental Shelf*. Academic Press, Cambridge.

Kuroda, M., Uchida, K., Tokai, T., Miyamoto, Y., Mukai, T., Imai, K., Shimizu, K., Yagi, M., Yamanaka, Y., Mituhashi, T., 2020. The current state of marine debris on the seafloor in offshore area around Japan. *Marine Pollution Bulletin*, 161, 111670.

Laist, D.W., 1997. Impacts of marine debris: entanglement of marine life in marine debris including a comprehensive list of species with entanglement and ingestion records. In: Coe, J.M., Rogers, D.B. (Eds.), *Marine Debris: Sources, Impacts, and Solutions*. Springer, New York, NY, pp. 99–139.

Lebreton, L.C.M., van der Zwet, J., Damsteeg, J.-W., Slat, B., Andrady, A., Reisser, J., 2017. River plastic emissions to the world's oceans. *Nature Communications*, 8, 15611.

Link, J., Segal, B., Casarini, L.M., 2019. Abandoned, lost or otherwise discarded fishing gear in Brazil: a review. *Perspectives in Ecology and Conservation* 17, 1–8.

Liubartseva, S., Coppini, G., Lecci, R., Clementi, E., 2018. Tracking plastics in the Mediterranean: 2D Lagrangian model. *Marine Pollution Bulletin*, 129, 151–162.

Llorca, M., Álvarez-Muñoz, D., Ábalos, M., Rodríguez-Mozaz, S., Santos, L.H.M.L.M., León, V.M., Campillo, J.A., Martínez-Gómez, C., Abad, E., Farré, M., 2020. Microplastics in Mediterranean coastal area: toxicity and impact for the environment and human health. *Trends in Environmental Analytical Chemistry*, 27, e00090.

Lopez-Lopez, L., González-Irusta, J.M., Punzón, A., Serrano, A., 2017. Benthic litter distribution on circalittoral and deep sea bottoms of the southern Bay of Biscay: analysis of potential drivers. *Continental Shelf Research*, 144, 112–119.

Lorenz, C., Roscher, L., Meyer, M.S., Hildebrandt, L., Prume, J., Löder, M.G.J., Primpke, S., Gerdts, G., 2019. Spatial distribution of microplastics in sediments and surface waters of the southern North Sea. *Environmental Pollution*, 252, 1719–1729.

Loulad, S., Houssa, R., Ouamari, N.E., Rhinane, H., 2019. Quantity and spatial distribution of seafloor marine debris in the Moroccan Mediterranean Sea. *Marine Pollution Bulletin*, 139, 163–173.

Macfadyen, G., Huntington, T., Cappell, R., 2009. Abandoned, lost or otherwise discarded fishing gear. *UNEP Regional Seas Reports and Studies*, 185, 139.

Maes, M., Nicolaus, M., Van Der Molen, J., Barry, J., Kral, F., 2015. *Marine Litter Monitoring. Defra project ME5415*. CEFAS, Lowestoft, p. 61.

Maes, T., Barry, J., Leslie, H.A., Vethaak, A.D., Nicolaus, E.E.M., Law, R.J., Lyons, B.P., Martinez, R., Harley, B., Thain, J.E., 2018. Below the surface: Twenty-five years of seafloor litter monitoring in coastal seas of North West Europe (1992–2017). *Science of the Total Environment*, 630, 790–798.

Maes, T., Barry, J., Stenton, C., Roberts, E., Hicks, R., Bignell, J., Vethaak A. D., Leslie, H., Sanders, M., 2020. The world is your oyster: low-dose, long-term microplastic exposure of juvenile oysters. *Heliyon*, 6, e03103.

Maes, T., Jessop, R., Wellner, N., Haupt, K., Mayes, A.G., 2017a. A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile Red. *Scientific Reports*, 7, 44501.

Maes, T., Van der Meulen, M.D., Devriese, L.I., Leslie, H.A., Huvet, A., Frère, L., Robbens, J., Vethaak, A.D., 2017b. Microplastics baseline surveys at the water surface and in sediments of the North-East Atlantic. *Frontiers in Marine Science*, 4, 1–13.

Martin, C., Baalkhuyur, F., Valluzzi, L., Saderne, V., Cusack, M., Almahasheer, H., Krishnakumar, P.K., Rabaoui, L., Qurban, M.A., Arias-Ortiz, A., Masqué, P., Duarte, C.M., 2020. Exponential increase of plastic burial in mangrove sediments as a major plastic sink. *Science Advances*, 6, eaaz5593.

Maurizio, W., Rovere, M., 2015. *Atlas of the Mediterranean Seamounts and Seamount-like Structures*. Switzerland and Málaga, Spain: IUCN.

Maximenko, N., Corradi, P., Law, K.L., Van Sebille, E., Garaba, S.P., Lampitt, R.S., Galgani, F., Martinez-Vicente, V., Goddijn-Murphy, L., Veiga, J.M., Thompson, R.C., Maes, C., Moller, D., Löscher, C.R., Addamo, A.M., Lamson, M.R., Centurioni, L.R., Posth, N.R., Lumpkin, R., Vinci, M., Martins, A.M., Pieper, C.D., Isobe, A., Hanke, G., Edwards, M., Chubarenko, I.P., Rodriguez, E., Aliani, S., Arias, M., Asner, G.P., Brosich, A., Carlton, J.T., Chao, Y., Cook, A.-M., Cundy, A.B., Galloway, T.S., Giorgetti, A., Goni, G.J., Guichoux, Y., Haram, L.E., Hardesty, B.D., Holdsworth, N., Lebreton, L., Leslie, H.A., Macadam-Somer, I., Mace, T., Manuel, M., Marsh, R., Martinez, E., Mayor, D.J., Le Moigne, M., Molina Jack, M.E., Mowlem, M.C., Obbard, R.W., Pabortsava, K., Robberson, B., Rotaru, A.-E., Ruiz, G.M., Spedicato, M.T., Thiel, M., Turra, A., Wilcox, C., 2019. Toward the integrated marine debris observing system. *Frontiers in Marine Science*, 6, 1–25.

Mecho, A., Francescangeli, M., Ercilla, G., Fanelli, E., Estrada, F., Valencia, J., Sobrino, I., Danovaro, R., Company, J.B., Aguzzi, J., 2020. Deep-sea litter in the Gulf of Cadiz (Northeastern Atlantic, Spain). *Marine Pollution Bulletin*, 153, 110969.

Melli, V., Angiolillo, M., Ronchi, F., Canese, S., Giovanardi, O., Querin, S., Fortibuoni, T., 2017. The first assessment of marine debris in a Site of Community Importance in the north-western Adriatic Sea (Mediterranean Sea). *Marine Pollution Bulletin*, 114, 821–830.

Mifsud, R., Dimech, M., Schembri, P.J., 2013. Marine litter from circalittoral and deeper bottoms off the Maltese islands (Central Mediterranean). *Mediterranean Marine Science*, 14, 298–308.

Mistri, M., Infantini, V., Scoponi, M., Granata, T., Moruzzi, L., Massara, F., De Donati, M., Munari, C., 2017. Small plastic debris in sediments from the Central Adriatic Sea: types, occurrence and distribution. *Marine Pollution Bulletin*, 124, 435–440.

Miyake, H., Shibata, H., Furushima, Y., 2011. Deep-sea litter study using deep-sea observation tools. In: *Interdisciplinary Studies on Environmental Chemistry – Marine Environmental Modeling and Analysis* (ed. K. Omori, X. Guo, N. Yoshie et al.), 261–269. TERRAPUP.

Molina Jack, M.E., Chaves Montero, M.d.M., Galgani, F., Giorgetti, A., Vinci, M., Le Moigne, M., Brosich, A., 2019. EMODnet marine litter data management at pan-European scale. *Ocean & Coastal Management* 181, 104930.

Morales-Caselles, C., Viejo, J., Martí, E., González-Fernández, D., Pragnell-Raasch, H., Gonzalez-Gordillo, J., Montero, E., Arroyo, G., Hanke, G., Salvo, V., Basurko, O., Mallos, N., Lebreton, L., Echevarría, F., Van Emmerik, T., Duarte, C., Gálvez, J., Van Sebille, E., Galgani, F., García, C., Ross, P.S., Bartual, A., Ioakeimidis, C., Markalain, G., Isobe, A., Cózar, A., 2021. An inshore–offshore sorting system sorting system revealed from global classification of ocean litter. *Nature Sustainability*, 4, 484–493.

Mordecai, G., Tyler, P.A., Masson, D.G., Huvenne, V.A.I., 2011a. Litter in submarine canyons off the west coast of Portugal. *Deep Sea Research Part II: Topical Studies in Oceanography*, 58, 2489.

Mordecai, G., Tyler, P.A., Masson, D.G., Huvenne, V.A.I., 2011b. Litter in submarine canyons off the west coast of Portugal. *Deep Sea Research Part II: Topical Studies in Oceanography*, 58, 2489–2496.

Moreno, G., Restrepo, V., Dagorn, L., Hall, M., Murua, J., Sancristobal, I., Grande, M., Le Couls, S., Santiago, J., 2016. *Workshop on the use of biodegradable fish aggregating devices (FADs)*. ISSF Technical Report 2016–18. International Seafood Sustainability Foundation, Washington, D.C.

Moriarty, M., Pedreschi, D., Stokes, D., Dransfeld, L., Reid, D., 2016. Spatial and temporal analysis of litter in the Celtic Sea from Groundfish Survey data: lessons for monitoring. *Marine Pollution Bulletin*, 103, 195–205.

Munari, C., Infantini, V., Scoponi, M., Rastelli, E., Corinaldesi, C., Mistri, M., 2017. Microplastics in the sediments of Terra Nova Bay (Ross Sea, Antarctica). *Marine Pollution Bulletin*, 122, 161–165.

Napper, I.E., Davies, B.F.R., Clifford, H., Elvin, S., Koldewey, H.J., Mayewski, P.A., Miner, K.R., Potocki, M., Elmore, A.C., Gajurel, A.P., Thompson, R.C., 2020. reaching new heights in plastic pollution—preliminary findings of microplastics on Mount Everest. *One Earth*, 3, 621–630.

Neves, D., Sobral, P., Pereira, T., 2015. Marine litter in bottom trawls off the Portuguese coast. *Marine Pollution Bulletin*, 99, 301–304.

Olguner, M.T., Olguner, C., Mutlu, E., Deval, M.C., 2018. Distribution and composition of benthic marine litter on the shelf of Antalya in the eastern Mediterranean. *Marine Pollution Bulletin*, 136, 171–176.

Oliveira, F., Monteiro, P., Bentes, L., Henriques, N., Aguilar, R., Gonçalves, J., 2015. Marine litter in the upper São Vicente submarine canyon (SW Portugal): abundance, distribution, composition and fauna interactions. *Marine Pollution Bulletin*, 97, 401–407.

Pabortsava, K., Lampitt, R.S., 2020. High concentrations of plastic hidden beneath the surface of the Atlantic Ocean. *Nature Communications*, 11, 4073.

Pasquini, G., Ronchi, F., Strafella, P., Scarcella, G., Fortibuoni, T., 2016. Seabed litter composition, distribution and sources in the Northern and Central Adriatic Sea (Mediterranean). *Waste Management*, 58, 41–51.

Peng, L., Fu, D., Qi, H., Lan, C.Q., Yu, H., Ge, C., 2020. Micro- and nano-plastics in marine environment: Source, distribution and threats – a review. *Science of the Total Environment*, 698, 134254.

Peng, X., Chen, M., Chen, S., Dasgupta, S., Xu, H., Ta, K., Du, M., Li, J., Guo, Z., Bai, S., 2018. Microplastics contaminate the deepest part of the world's ocean. *Geochemical Perspectives Letters*, 9, 1–5.

Pham, C.K., Gomes-Pereira, J.N., Isidro, E.J., Santos, R.S., Morato, T., 2013. Abundance of litter on Condor seamount (Azores, Portugal, Northeast Atlantic). *Deep Sea Research Part II: Topical Studies in Oceanography*, 98, 204–208.

Pham, C.K., Ramirez-Llodra, E., Alt, C.H.S., Amaro, T., Bergmann, M., Canals, M., Company, J.B., Davies, J., Duineveld, G., Galgani, F., Howell, K.L., Huvenne, V.A.I., Isidro, E., Jones, D.O.B., Lastras, G., Morato, T., Gomes-Pereira, J.N., Purser, A., Stewart, H., Tojeira, I., Tubau, X., Van Rooij, D., Tyler, P.A., 2014. Marine litter distribution and density in European seas, from the shelves to deep basins. *PLOS One* 9, 1–13.

Pierdomenico, M., Casalbore, D., Chiocci, F.L., 2019. Massive benthic litter funnelled to deep sea by flash-flood generated hyperpycnal flows. *Scientific Reports*, 9, 5330.

Pierdomenico, M., Casalbore, D., Chiocci, F.L., 2020. The key role of canyons in funnelling litter to the deep sea: A study of the Gioia Canyon (Southern Tyrrhenian Sea). *Anthropocene*, 30, 100237.

PlasticsEurope, 2019. *Plastics – The Facts 2018: An Analysis of European Plastics Production, Demand and Waste Data*. Brussel, Belgium: PlasticsEurope Association of Plastics Manufacturers.

Pohl, F., Eggenhuisen, J.T., Kane, I.A., Clare, M.A., 2020. Transport and burial of microplastics in deep-marine sediments by turbidity currents. *Environmental Science & Technology*, 54, 4180–4189.

Primpke, S., Imhof, H., Piehl, S., Lorenz, C., Löder, M., Laforsch, C., Gerdts, G., 2017. *Mikroplastik in der Umwelt. Umweltchemie*, 6, 402–412.

Ramírez-Álvarez, N., Rios Mendoza, L.M., Macías-Zamora, J.V., Oregel-Vázquez, L., Alvarez-Aguilar, A., Hernández-Guzmán, F.A., Sánchez-Osorio, J.L., Moore, C.J., Silva-Jiménez, H., Navarro-Olache, L.F., 2020. Microplastics: sources and distribution in surface waters and sediments of Todos Santos Bay, *Mexico. Science of the Total Environment*, 703, 134838.

Ramirez-Llodra, E., Company Claret, J.B., Sardà, F., De Mol, B., 2013. Distribution of marine litter at bathyal and abyssal depths at the Catalan margin. By-catch of various trawl catches during the expedition PROMETEO 2 on the research vessel Garcia del Cid. *Institut de Ciències del Mar*, PANGAEA. https://doi.org/10.1594/PANGAEA.778309. (In supplement to: Ramirez-Llodra, E., De Mol, B., Company, M., Coll, M., Sardà, F. (2013): Effects of natural and anthropogenic processes in the distribution of marine litter in the deep Mediterranean Sea. *Progress in Oceanography*, 118, 273–287. https://doi.org/10.1016/j.pocean.2013.07.027).

Richardson, K., Gunn, R., Wilcox, C., Hardesty, B.D., 2018. Understanding causes of gear loss provides a sound basis for fisheries management. *Marine Policy*, 96, 278–284.

Richardson, K., Hardesty, B.D., Wilcox, C., 2019. Estimates of fishing gear loss rates at a global scale: a literature review and meta-analysis. *Fish and Fisheries* 20, 1218–1231.

Roberts, J.M., Wheeler, A.J., Freiwald, A., 2006. Reefs of the deep: the biology and geology of cold-water coral ecosystems. *Science*, 312, 543–547.

Rodriguez, Y., Pham, C.K., 2017. Marine litter on the seafloor of the Faial-Pico Passage, Azores Archipelago. *Marine Pollution Bulletin*, 116, 448–453.

Ronchi, F., Galgani, F., Binda, F., Mandić, M., Peterlin, M., Tutman, P., Anastasopoulou, A., Fortibuoni, T., 2019. Fishing for Litter in the Adriatic-Ionian macroregion (Mediterranean Sea): strengths, weaknesses, opportunities and threats. *Marine Policy* 100, 226–237.

Rossi, S., Bramanti, L., Gori, A., Orejas, 2017a. *Marine Animal Forests. The Ecology of Benthic Biodiversity Hotspots*. Cham, Swiss: Springer.

Rossi, S., Bramanti, L., Gori, A., Orejas, C., Rossi, S., 2017b. *An Overview of the Animal Forests of the World*. Cham, Swiss: Springer. pp. 1–26.

Ryan, P.G., Weideman, E.A., Perold, V., Durholtz, D., Fairweather, T.P., 2020. A trawl survey of seafloor macrolitter on the South African continental shelf. *Marine Pollution Bulletin*, 150, 110741.

Sagawa, N., Kawaai, K., Hinata, H., 2018. Abundance and size of microplastics in a coastal sea: comparison among bottom sediment, beach sediment, and surface water. *Marine Pollution Bulletin*, 133, 532–542.

Sanchez-Vidal, A., Thompson, R.C., Canals, M., de Haan, W.P., 2018. The imprint of microfibres in southern European deep seas. *PLOS One*, 13, e0207033.

Sánchez, P., Masó, M., Sáez, R., Juan, S., 2013. Baseline study of the distribution of marine debris on soft-bottom habitats associated with trawling grounds in the northern Mediterranean. *Scientia Marina* 77, 247–255.

Schlining, K., von Thun, S., Kuhnz, L., Schlining, B., Lundsten, L., Jacobsen Stout, N., Chaney, L., Connor, J., 2013. Debris in the deep: using a 22-year video annotation database to survey marine litter in Monterey Canyon, central California, USA. *Deep Sea Research Part I: Oceanographic Research Papers*, 79, 96–105.

Sheehan, E., Rees, A., Bridger, D., Williams, T., Hall-Spencer, J., 2017. Strandings of NE Atlantic gorgonians. *Biological Conservation*, 209, 482–487.

Sinopoli, M., Cillari, T., Andaloro, F., Berti, C., Consoli, P., Galgani, F., Romeo, T., 2020. Are FADs a significant source of marine litter? Assessment of released debris and mitigation strategy in the Mediterranean sea. *Journal of Environmental Management*, 253, 109749.

Spedicato, M.T., Zupa, W., Carbonara, P., Fiorentino, F., Follesa, M., Galgani, F., Garcia, C., Jadaud, A., Ioakeimidis, C., Lazarakis, G., Lembo, G., Mandic, M., Maiorano, P., Sartini, M., Serena, F., Cau, A., Esteban, A., Isajlovic, I., Micallef, R., Thasitis, I., 2019. Spatial distribution of marine macro-litter on the seafloor in the northern Mediterranean Sea: the MEDITS initiative. *Scientia Marina*, 83, 1–14.

Strafella, P., Fabi, G., Spagnolo, A., Grati, F., Polidori, P., Punzo, E., Fortibuoni, T., Marceta, B., Raicevich, S., Cvitkovic, I., Despalatovic, M., Scarcella, G., 2015. Spatial pattern and weight of seabed marine litter in the northern and central Adriatic Sea. *Marine Pollution Bulletin*, 91, 120–127.

Sui, Q., Zhang, L., Xia, B., Chen, B., Sun, X., Zhu, L., Wang, R., Qu, K., 2020. Spatiotemporal distribution, source identification and inventory of microplastics in surface sediments from Sanggou Bay, *China. Science of the Total Environment*, 723, 138064.

Tekman, M.B., Krumpen, T., Bergmann, M., 2017. Marine litter on deep Arctic seafloor continues to increase and spreads to the North at the HAUSGARTEN observatory. *Deep Sea Research Part I: Oceanographic Research Papers*, 120, 88–99.

Tubau, X., Canals, M., Lastras, G., Rayo, X., Rivera, J., Amblas, D., 2015. Marine litter on the floor of deep submarine canyons of the Northwestern Mediterranean Sea: the role of hydrodynamic processes. *Progress in Oceanography*, 134, 379–403.

UNEP, 2015. *Assessment of Marine Litter in the Mediterranean Sea*. United Nations Environment Programme/Mediterranean Action Plan (UNEP/MAP), Italy, p. 94.

UNEP (2021). From Pollution to Solution: A Global Assessment of Marine Litter and Plastic Pollution. Nairobi: UNEP, https://www.grida.no/publications/747.

Urban-Malinga, B., Wodzinowski, T., Witalis, B., Zalewski, M., Radtke, K., Grygiel, W., 2018. Marine litter on the seafloor of the southern Baltic. *Marine Pollution Bulletin*, 127, 612–617.

Van Cauwenberghe, L., Vanreusel, A., Mees, J., Janssen, C., 2013. Microplastic pollution in deep-sea sediments. *Environmental Pollution*, 182, 495–499.

Van Den Beld, I., Guillaumont, B., Menot, L., Bayle, C., Arnaud-Haond, S., Bourillet, J.-F., 2016. Marine litter in submarine canyons of the Bay of Biscay. *Deep Sea Research Part II: Topical Studies in Oceanography*, 145, 142–152.

Van Sebille, E., Wilcox, C., Lebreton, L., Maximenko, N., Hardesty, B.D., van Franeker, J.A., Eriksen, M., Siegel, D., Galgani, F., Law, K.L., 2015. A global inventory of small floating plastic debris. *Environmental Research Letters*, 10, 1–11.

Vieira, R.P., Raposo, I.P., Sobral, P., Gonçalves, J.M.S., Bell, K.L.C., Cunha, M.R., 2015. Lost fishing gear and litter at Gorringe Bank (NE Atlantic). *Journal of Sea Research*, 100, 91–98.

Watters, D.L., Yoklavich, M.M., Love, M.S., Schroeder, D.M., 2010. Assessing marine debris in deep seafloor habitats off California. *Marine Pollution Bulletin*, 60, 131–138.

Wei, C.-L., Rowe, G.T., Nunnally, C.C., Wicksten, M.K., 2012. Anthropogenic "Litter" and macrophyte detritus in the deep Northern Gulf of Mexico. *Marine Pollution Bulletin*, 64, 966–973.

Williams, A.T., Rangel-Buitrago, N., 2019. Marine litter: solutions for a major environmental problem. *Journal of Coastal Research*, 35, 648–663, 616.

Willis, K., Eriksen, R., Wilcox, C., Hardesty, B., 2017. Microplastic distribution at different sediment depths in an urban estuary. *Frontiers in Marine Science*, 4, 1–8.

Woodall, L.C., Robinson, L.F., Rogers, A.D., Narayanaswamy, B.E., Paterson, G.L.J., 2014. The deep sea is a major sink for microplastic debris. *Royal Society Open Science*, 1, 1–8.

Woodall, L.C., Robinson, L.F., Rogers, A.D., Narayanaswamy, B.E., Paterson, G.L.J., 2015. Deep-sea litter: a comparison of seamounts, banks and a ridge in the Atlantic and Indian Oceans reveals both environmental and anthropogenic factors impact accumulation and composition. *Frontiers in Marine Science*, 2, 1–10.

Ye, S., Andrady, A.L., 1991. Fouling of floating plastic debris under Biscayne Bay exposure conditions. *Marine Pollution Bulletin*, 22, 608–613.

Zablotski, Y., Kraak, S., 2019. Marine litter on the Baltic seafloor collected by the international fish-trawl survey. *Marine Pollution Bulletin*, 141, 448–461.

Zhang, C., Zhou, H., Cui, Y., Wang, C., Li, Y., Zhang, D., 2019. Microplastics in offshore sediment in the Yellow Sea and East China Sea, China. *Environmental Pollution*, 244, 827–833.

Zhang, D., Liu, X., Huang, W., Li, J., Wang, C., Zhang, D., Zhang, C., 2020a. Microplastic pollution in deep-sea sediments and organisms of the Western Pacific Ocean. *Environmental Pollution*, 259, 113948.

Zhang, F., Yao, C., Xu, J., Zhu, L., Peng, G., Li, D., 2020b. Composition, spatial distribution and sources of plastic litter on the East China Sea floor. *Science of the Total Environment*, 742, 140525.

Zhao, J., Ran, W., Teng, J., Liu, Y., Liu, H., Yin, X., Cao, R., Wang, Q., 2018. Microplastic pollution in sediments from the Bohai Sea and the Yellow Sea, China. *Science of the Total Environment*, 640–641, 637–645.

Zheng, Y., Li, J., Cao, W., Liu, X., Jiang, F., Ding, J., Yin, X., Sun, C., 2019. Distribution characteristics of microplastics in the seawater and sediment: a case study in Jiaozhou Bay, China. *Science of the Total Environment*, 674, 27–35.

Zhou, P., Huang, C., Fang, H., Cai, W., Li, D., Li, X., Yu, H., 2011. The abundance, composition and sources of marine debris in coastal seawaters or beaches around the northern South China Sea (China). *Marine Pollution Bulletin*, 62, 1998–2007.

Zhu, L., Bai, H., Chen, B., Sun, X., Qu, K., Xia, B., 2018. Microplastic pollution in North Yellow Sea, China: observations on occurrence, distribution and identification. *Science of the Total Environment*, 636, 20–29.

Zobkov, M., Esiukova, E., 2017. Microplastics in Baltic bottom sediments: quantification procedures and first results. *Marine Pollution Bulletin*, 114, 724–732.

7

Plastics in Freshwater Bodies

L. Lebreton[1,2], M. Kooi[3], T. Mani[1], S. M. Mintenig[3], M. B. Tekman[4], Tim van Emmerik[5], and H. Wolter[1]

[1] *The Ocean Cleanup, Rotterdam, The Netherlands*
[2] *The Modelling House, Raglan, New Zealand*
[3] *Aquatic Ecology and Water Quality Management Group, Wageningen University, The Netherlands*
[4] *Deep-Sea Ecology and Technology, Alfred Wegener, Institute Helmholtz Centre for Polar Research, Germany*
[5] *Hydrology and Quantitative Water Management Group, Wageningen University, The Netherlands*

7.1 Introduction

Interest in plastic pollution monitoring and research has rapidly accelerated in recent years; it is, however, widely recognized that freshwater bodies have received far less attention than the marine environment (Blettler et al. 2018). Largely known to play a crucial role in transporting plastics discarded from human activities to the ocean, freshwater bodies may also be directly impacted by plastic pollution (Eerkes-Medrano et al. 2015; Wagner et al. 2014). Just like plastics in the ocean, plastics in freshwater bodies are ubiquitous, persistent, heterogeneously distributed, embedded in the food web, and found in the form of a wide range of debris sizes from several centimeters to millimeters, micrometers, and nanometers. Quantifying the abundance and transport of plastics in freshwater bodies is essential to (i) understand the potential risk for the freshwater environment, (ii) identify and mitigate sources, and (iii) estimate the inputs into the marine environment. However, just like in the ocean, determining the fate of plastics in freshwater bodies is not trivial. The complexity of physical, chemical, and biological processes affecting plastics in rivers and lakes, as well as the diversity in plastic size, shape, and polymer type, results in different transport mechanisms, accumulation, and fate (van Emmerik and Schwarz 2020; Wagner and Lambert 2018). With an increasing amount of evidence building up in recent years showing long-term accumulation, rivers are no longer considered as simple highways for plastics to the ocean. Plastics have been detected in all compartments of freshwater bodies including surface water, water column, sublittoral and littoral sediment, and biota (Burns and Boxall 2018; Sarijan et al. 2020). Further, to date, some of the highest plastic concentrations were observed in water and sediment samples of freshwater bodies across the world (Hurley et al. 2018).

One of the main concerns with plastic pollution in freshwater, as well as in the ocean, is the transport and accumulation of smaller particles referred to as microplastics (MPs) (<5 mm) or nanoplastics (NPs) (<1 μm). From several centimeters to several micrometers, the bioavailability of plastic pollution soars with a larger range of impacted species. Thus, researching MPs in

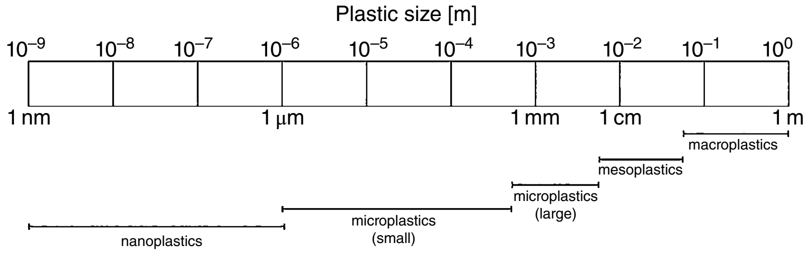
Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

freshwaters has received the most attention. Several comprehensive reviews have recently been published, describing the best practices for monitoring, extraction, and identification of MPs in rivers and lakes, and often suggesting the crucial need for harmonization of methods (Dris et al. 2018; Eerkes-Medrano et al. 2015; Koelmans et al. 2019; Li et al. 2018; Sarijan 2020; Szymańska and Obolewski 2020). Contamination of freshwater bodies by larger pieces of plastics commonly referred to as mesoplastics (5 mm to 5 cm) and macroplastics (>5 cm) has received less attention (van Emmerik and Schwarz 2020). Due to the very high analytical challenges, research on NPs (<1 μm) is still in its infancy (Blettler et al. 2018).

Plastics are found in a wide variety of sizes in different freshwater habitats (e.g. rivers, lakes, and estuaries) and compartments (e.g. surface water, water column, and littoral or sublittoral sediment). Considering everything between macroplastics and nanoplastics (Box 7.1), this chapter aims to (i) provide a comprehensive and detailed assessment of the available methods to monitor and model plastics in freshwater bodies and to (ii) visualize the geographical distribution of studies reporting plastics in rivers and lakes. We aim to depict where international research on plastics in freshwater bodies currently stands, to illustrate the state of the general knowledge, and to highlight remaining research gaps. At first, we discuss considerations that are required and techniques that are employed to monitor a wide range of plastic size classes in different freshwater compartments. We draw a new comprehensive map of the global observational efforts to quantify and characterize plastics in rivers and lakes. Next to this, we discuss different models that have been applied to better understand the sources, transport, and fate of plastics in freshwater bodies and to, eventually, inform on plastic emissions into the global ocean. Finally, we close by discussing new prospects and opportunities for this field of research.

The term "microplastics" is the most common "size class" reported by observational studies (see below the section on observational efforts). Traditionally in the ocean, this term referred to particles larger than 300–500 μm and smaller than 5 mm. The bottom limit was determined by the mesh sizes of neuston trawls deployed at the sea surface. More recently, scientists started to detect and identify plastic particles smaller than a few hundreds of micrometers (particularly in freshwater systems) that are also referred to as microplastics. Eventually, a new size class was defined for

Box 7.1 The importance of defining and reporting upper and lower size detection limits in relation to monitoring methods.



The definition of lower and upper size limit of plastic debris considered by monitoring and modeling methods is critical to allow comparison across studies. Generally, the number of plastic particles found in the environment is inversely proportional to the size classes studied. In addition, the mass per plastic particle/items will increase with larger objects.

particles below 1 micrometer (μm): the nanoplastics. Under this definition, the term microplastics range from 1 to 5000 μm that can lead to misinterpretation of results across studies (Hartmann et al. 2019).

Instead of referring to a simple term such as "microplastics," it is preferable for studies to systematically report the lower and upper size limit of plastics detected by their own sampling methods, so future reviews can accurately compare observational results. In this chapter, we differentiate between nanoplastics (<1 μm), small microplastics (>1 and <500 μm), large microplastics (>500 μm and <5 mm), mesoplastics (>5 mm and <5 cm), and macroplastics (>5 cm).

7.2 Monitoring of Plastics in Freshwater Bodies

Monitoring is essential if we are to better understand the concentration, transport, properties, and risks of plastics in the environment. Plastic concentrations, also referred to as abundances, quantities, amounts, or stocks, can be determined at any specific location and moment in time. The transport of plastics can be assessed by taking into account freshwater system characteristics like flow velocity or discharge. Aside from reporting only plastic number or mass concentrations, detailed information on plastic properties can be included. Knowing properties, like sizes, shapes, and polymer types, is important when studying plastic transport and fate (Kooi and Koelmans 2019) or when aiming at identifying the sources of the plastic waste (van Emmerik et al. 2020a). Traditionally, risks associated to plastics are estimated by comparing exposure concentrations with effect thresholds for specific organisms (Koelmans et al. 2020). However, for a risk to be exerted, plastic items need to be bioavailable for the organisms. A risk assessment is thus more accurate when plastic properties are known. Information on plastic properties is also required to quantify mechanistic risks, such as the blockage of urban drainage infrastructure with soft macroplastics (Honingh et al. 2020).

Independently of the exact research question asked, good monitoring practices are required. However, no standard operating procedures for the sampling and analysis of plastics in the environment exist, and many different approaches have been described in the literature. We do not aim at explaining all methods in detail, since excellent reviews already exist (Elkhatib and Oyanedel-Craver 2020; Hanvey et al. 2017; Hermsen et al. 2018; Hidalgo-Ruz et al. 2012; Klein et al. 2018; Koelmans et al. 2019; Li et al. 2018; Rocha-Santos and Duarte 2015; Shim et al. 2017; van Emmerik and Schwarz 2020). Instead, we want to illustrate the suitability of common methods depending on the targeted plastic sizes and on environmental matrices. The definition of boundaries between different plastic size classes (e.g. between microplastics and macroplastics) is to a certain extent arbitrary (see above Box 7.1). Here, we emphasize that many considerations are generic for the different plastic size classes.

Both in marine or freshwater ecosystems, five steps can be distinguished for monitoring, namely, (i) sampling, (ii) extraction, (iii) analysis, (iv) identification, and (v) extrapolation (Figure 7.1). With sampling, we refer to the sample collection, which can be the collection of actual plastic items, the collection of images, or the collection of visual observation data. Extraction refers to the separation of the plastics from other materials, such as nonplastic debris and natural organic or inorganic matter. During analysis, plastics are analyzed visually (in images or samples), automatically with machine learning, or by using spectroscopic or spectrometric approaches. In the fourth step, analyzed items are counted and properties such as size, shape, mass, polymer type, or item category are identified. The importance of this step has been emphasized in recent years and automated; thus standardized approaches have been developed (Primpke et al. 2020a, 2020b; Wolf

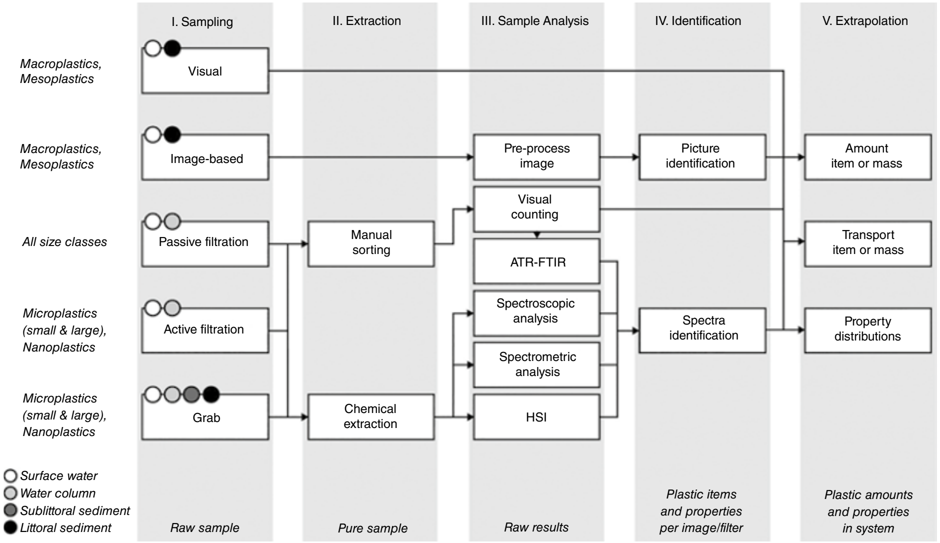


Figure 7.1 Commonly reported steps to monitor different sizes of plastics in the environment, namely, (i) sampling, (ii) extraction, (iii) analysis, (iv) identification, and (v) extrapolation. The applicability of sampling methods is specified for water and sediment samples (shaded spheres representing compartments). Note that littoral refers to both lakeshores and riverbanks. The endproduct of each step is specified at the bottom of each column. For clarity, ATR-FTIR is mentioned individually instead of being grouped into spectroscopic analysis. Further, please note that the direct arrow from visual counting to extrapolation is only advisable for larger plastics (i.e. mesoplastics and macroplastics); for all smaller items, a subsequent analysis using e.g. ATR-FTIR is needed to confirm the presence of a polymer.

et al. 2020). As a last step, generated results are extrapolated to relevant endpoints, such as plastic (numerical and/or mass) concentrations in the study's freshwater system.

7.2.1 Required Steps to Monitor Plastics in the Environment

Although these general steps apply, methods vary depending on the targeted plastic size and environmental matrix (Figure 7.1). In the freshwater environment, the latter can roughly be categorized into surface water, water column, sublittoral sediment, and littoral shores/ riverbanks. Direct visual observations, i.e. counting and image-based sampling, can be applied to quantify the abundance of macroplastics and mesoplastics on shores or floating at the water surface. In the field, or also the laboratory, specific visual counting and identification protocols can be used to determine the item and polymer categories of the observed plastics (van Emmerik et al. 2020a; Vriend et al. 2020a). Image-based sampling can be carried out using drones (Geraeds et al. 2019), fixed cameras (van Lieshout et al. 2020), or spaceborne remote sensing methods (Biermann et al. 2020). Optical methods for the monitoring of riverbanks or the water surface use the visible light (RGB) or other multispectral bands with particular interest in the near and shortwave infrared. Filtration, i.e. volume-reduced sampling, can be applied for all plastic sizes and is specifically needed when low concentrations of plastics are expected (Koelmans et al. 2019; Löder and Gerdts 2015). Here, we differentiated between passive filtration, such as the collection of macroplastics, mesoplastics, or large MPs at existing litter traps or permanent traps (Gasperi et al. 2014; Vriend et al. 2020b), and active filtration, which is mainly applied for (small) MPs (i.e. <500 μm) and will also be likely required for NPs. Plastics down to several micrometers can be retained when filtering water over nets, filter cascades, stacked sieves, or cartridge filters (Carr et al. 2016; Mintenig et al. 2020; Wolff et al. 2019). Sampling methods for NPs are still being developed. To date, the usage of (crossflow) ultrafiltration (Mintenig et al. 2018; Ter Halle et al. 2017) and continuous flow centrifugation (Hildebrandt et al. 2020) has been proposed. In contrast to sampling the water phase, most shore and sublittoral sediment samples are grab samples; are taken using e.g. spoons, sediment corers, or Van Veen grabs (Hanvey et al. 2017); and are often complemented by subsequent sieving. For waters, grab sampling, using e.g. buckets, should only replace filtration when expected plastic concentrations are high, which typically is the case for very small plastics.

For the second step, two forms of extraction are distinguished. Macroplastics, mesoplastics, and larger MPs can be extracted manually from the sample matrix, sometimes using a microscope. This, however, should be avoided for all smaller plastics. These need to be extracted by removing organic materials with the aid of acids, bases, hydrogen peroxide, and/or enzymes and by removing inorganic particles during a density separation (Elkhatib and Oyanedel-Craver, 2020; Hanvey et al. 2017; Klein et al. 2018). Further, MPs have also been separated from natural materials using oil or electrostatic forces (Chrichton et al. 2017; Felsing et al. 2018; Lechthaler et al. 2020a; Mani et al. 2019a). Independently of the chosen method, it is of high importance that the extraction does not affect the MP weights, counts, and shapes (Koelmans et al. 2019).

Various approaches can be applied to analyze extracted plastic items. Images captured in the field can require a preprocessing step, such as atmospheric correction (Biermann et al. 2020). For physically collected samples, targeted plastic sizes largely determine the set of applicable techniques. Previously sorted macroplastics, mesoplastics, and larger MPs can be pointed and counted visually. For large MPs, this must be complemented with a subsequent polymer identification using e.g. attenuated total reflectance (ATR)-FTIR to ensure accurate results (Kroon et al. 2018;

Löder and Gerdts 2015). Any visual analysis of smaller plastics should be avoided (Shim et al. 2017). Instead, applying spectroscopic, e.g. FTIR or Raman microscopy (Cabernard et al. 2018; Löder et al. 2015; Wolff et al. 2019), or spectrometric approaches, e.g. pyrolysis GC-MS, have proven successful (Dümichen et al. 2017; Fischer and Scholz-Böttcher 2017). Less common, but also promising, is the use of (laser-based) hyperspectral imaging (HSI) (Karlsson et al. 2016; Primpke et al. 2020c). NPs, to date, have not yet been quantified in the environment. Here, the usage of nano-FTIR (Meyns et al. 2019) or pyrolysis GC-MS (Fischer and Scholz-Böttcher 2017), best combined with a size fractionation using e.g. field flow fractionation (Mintenig et al. 2018), seems most promising.

The fourth step describes the actual identification of plastic items (shape, dimension, and polymer group or item type) which can be done manually or (semi)automatically. For visually sorted items, this is rather straightforward and also, images are largely inspected manually, as the transferability of machine learning algorithms is still limited (Geraeds et al. 2019; van Lieshout et al. 2020). Analytical techniques for MPs mostly result in large amounts of data that require further steps to really identify the plastics. Here, the automated identification not only has proven to considerably reduce the workload but also the misidentification rate (Primpke et al. 2017). To date, numerous studies analyze FTIR data with the approach and database from Primpke et al. (2018, 2020a), and also, spectrometric results can be analyzed in a (semi)automated approach (Primpke et al. 2020b).

Lastly, once the results on the sample or image level are known, they should be extrapolated to the system level. This provides information on concentrations (i.e. plastic items or mass per length, surface area, volume, or weight), transport fluxes (count or mass of plastics per unit of time), and plastic properties like size distributions or polymer compositions.

7.3 Global Observational Efforts

Plastic pollution research in all habitats is booming more than ever, and its upward, exponential swing in publication output is now outlasting more than a decade (Szymańska and Obolewski 2020; Yao et al. 2019). Today, a title-only search for the popular term “microplastics” will return over 1000 academic publications each for 2019 and 2020 (Google Scholar “allintitle: microplastics”). While marine studies on plastic pollution still vastly outnumber freshwater reports (87% vs. 13%, Blettler et al. 2018), the latter are steadily following the rise in peer-reviewed output, though at still distinctly lower numbers (Szymańska and Obolewski 2020).

Keeping track of all relevant articles continuously emerging has become an honorable challenge. Owing to the large amount of new studies, contemporary literature reviews tend to focus on a specific subdomain such as “microplastics in freshwater sediments” in which a limited selection of studies is presented and discussed in detail (Li et al. 2020; Rezania et al. 2018; Yang et al. 2021; Yao et al. 2019). Few comprehensive attempts have been made to cover the entirety of researched habitats and plastic size ranges, such as by Blettler et al. (2018) and Tekman et al. (2020). However, most recent reviews constrain their scope to MPs (Blair et al. 2017; Li et al., 2018, 2020; Peller et al. 2020; Rezania et al. 2018; Szymańska and Obolewski 2020; Triebskorn et al. 2019; Yang et al. 2021; Yao et al. 2019). In the following section, we attempt to present a current and comprehensive overview of peer-reviewed literature presenting original data on freshwater plastic pollution, covering all environmental compartments and size classes. With this, we shed light on the quantitative development of research output in the field. The findings itself are not discussed in detail (such as the metric particle size ranges or particle concentrations); for this, we refer to other reviews such as by Li et al. (2020), Yang et al. (2021), Szymańska and Obolewski (2020), Li et al. (2018), Peller et al. (2020), Triebskorn et al. (2019), Rezania et al. (2018), Yao et al. (2019), and Blair et al. (2017).

7.3.1 In Search of all the Relevant Literature

To produce a quantitative review of global observational efforts, we started our investigation at LITTERBASE (https://litterbase.awi.de/litter). This database with a web-based public interactive map is curated by the Alfred Wegener Institute (AWI) and, as November 2020, features almost 2500 scientific articles published between 1974 and 2019, of which 1090 studies are on distribution of litter types. Concentrations, distribution, and composition of litter in marine as well as freshwater environments constitute the core (Bergmann et al. 2017a). Joining forces with LITTERBASE to include the most recent relevant publications, we performed an extensive, unrestricted literature search similar to Blettler et al. (2018) in November 2020. Google Scholar (GS) was chosen as the preferred engine known for its vast-scope query algorithm, overlapping and exceeding traditional scientific search tools (Martín-Martín et al. 2018). Using Harzing's Publish or Perish software (Windows GUI Edition, version 7.27.2949.7581), 21 individual GS search requests were run for both 2019 and 2020. The 21 search requests were combinations of the terms "nanoplastic," "microplastic," "mesoplastic," "macroplastic," "river," "lake," "groundwater/aquifer," as well as individual continent and country names. Literature reviews, opinion pieces, laboratory experiments, and biological assessments were not considered. In addition, studies of the cryosphere were not included (e.g. icecaps and glaciers). Search requests for 2020 returned 7579/2242 results (including/excluding duplicates) that were manually distilled to a shortlist of 141 papers containing original data on plastics in freshwater bodies. Combining the freshwater LITTERBASE studies and the newly acquired search results, a total of 379 relevant studies were compiled covering a 36-year period up to November 2020. The recent exponential growth in research is reflected by the fact that 358 of the 379 studies (94%) were published since 2014.

7.3.2 Geographical Distribution of Freshwater Studies

Of the 379 relevant freshwater studies identified since 1974, investigations in Asia (139) take the largest share, followed by Europe (101), North America (63), South America (29), Africa (25) Oceania (14), and intercontinental studies (8) (Figure 7.2). To date, most of these studies have been conducted in China (74) and the United States (48), with research output in the former only recently rocketing with 59 publications since 2018 alone (Szymańska and Obolewski 2020). Further, numerous studies have been conducted in Brazil (21), the United Kingdom and Germany (both 16), India (15), and Indonesia (13). The remaining 176 studies are spread across 59 countries from all continents.

Within research on plastic pollution in freshwater habitats, geographical focal areas are continuously shifting over time. Notably, research on the African continent has rapidly increased from a total of 4 studies up to 2018 (Blettler et al. 2018) to 22 published in 2019 and 2020. While over two-thirds of studies between 2010 and 2018 were conducted in Europe and North America with the remaining minority in Asia, this picture has changed recently (Blettler et al. 2018). Nearly half of the freshwater investigations from 2019 and 2020 were conducted in Asia (45%) and only 21% in Europe and 11% in North America according to our new overview data. Here, we specifically looked at studies presenting original environmental plastic pollution data. It should be noted that a generic literature search, e.g. using the keywords "microplastic" and "freshwater," would return

Figure 7.2 Global observational efforts by the number of studies for the monitoring of plastics in freshwater bodies from 1974 to November 2020. We separate between microplastic only (small or/and large, displayed as circles), microplastic to mesoplastic and/or microplastic to macroplastic (displayed as diamonds), and macroplastic only (displayed as squares). Studies generally focused on four freshwater compartments (sometimes inclusively): surface water (white), water column (light grey), sublittoral sediment (dark grey), and littoral sediment (i.e. riverbanks or lakeshores, black).

a different geographical emphasis, as literature reviews, biological assessments, and laboratory experiments are distributed differently across the globe (Li et al. 2020).

7.3.3 Investigating Different Environmental Compartments

To date, lotic waterbodies, such as rivers and streams, received higher attention than their lentic counterparts, such as lakes and ponds (Blair et al. 2017; Blettler et al. 2018; Eerkes-Medrano et al. 2015; Wagner et al. 2014). Lotic waterbodies play a key role in plastic transport from land toward the oceans; therefore, many freshwater investigations possibly aim at providing a link with marine studies (Lebreton et al. 2017; Meijer et al. 2021; Schmidt et al. 2017). Our quantitative literature review data indicate that, since 1974, studies focusing on rivers, streams, canals, and urban waterways account for 39%, while studies dedicated to lakes and ponds account for 25% of the publications. The remaining studies address coastal environments such as bays and estuaries (20%) or focus on a mix of various freshwater bodies (16%). Between 2019 and 2020, the share of freshwater studies on rivers and streams increased to 49%. Recently, research on groundwater has been taken up (Mintenig et al. 2019; Panno et al. 2019; Selvam et al. 2021), with not yet any conclusive evidence of pollution. Generally, waterbodies have different compartments which can be investigated. These include surface water, shoreline sediments (littoral), subsurface water column (pelagic zone), and sublittoral sediments (benthic zone; MacIntyre and Melack 1995). Surface water investigations dominate in the field of freshwater studies over pelagic and deposited sediment (sublittoral and littoral) research (Peller et al. 2020). This is likely a result of (i) the widespread understanding that a majority of nowadays produced polymers, such as PE, PP, and E-PS (expanded), are positively buoyant in water (Lenaker et al. 2019; Nizzetto et al. 2016; PlasticsEurope 2019); (ii) the historical adoption of marine research methods, such as surface trawling nets (Faure et al. 2012; Hidalgo-Ruz et al. 2012); and (iii) the better debris visibility to observers of surface over submerged or benthic pollution (van Emmerik et al. 2020b). This trend is also reflected by our quantitative literature survey. To date, studies included investigations of the water surface (77%), of sublittoral zones (32%, of which most were published since 2019), and of the water column (8%). Note that many papers study several compartments simultaneously.

7.3.4 Size Class Focus: Dominance of Microplastic, Need for Macroplastic, and Absence of Nanoplastic

The majority of studies in the freshwater environment has focused on investigating MPs (85%), while macroplastic occurrences have been reported by 21% of the studies only. Only very few studies (6%) address both fractions. This strong emphasis on the MPs' size class vs. larger debris is widely attributed to the initial focus on their direct potential detrimental biological, ecological, and human health effects upon ingestion, driven e.g. by (i) several historical United Nations Environmental Programme (UNEP) year books (Kershaw et al. 2011; UNEP 2016), (ii) reported effects on aquatic organisms (Sanchez et al. 2014; Triebskorn et al. 2019; Von Moos et al. 2012), as well as (iii) the bioavailability of these small particles to many organisms (Koelmans et al. 2020). The distinct skew of most reported size frequency distributions toward the smallest available particle sizes demonstrates the relevance of this bioavailable size class, which in terms of particle numbers also outweigh bigger plastic items (Bergmann et al. 2017b; Mani et al. 2019b). In terms of total mass flux, investigating macroplastics is of adamant importance (Lebreton et al. 2017; Mai et al. 2020; Meijer et al. 2021; Schmidt et al. 2017). Mostly, because, they are considered a main environmental source of the most abundant form of MPs: the secondary type derived through fragmentation and abrasion (Andrady 2017). Gradually, we see increasing numbers of observation-based macroplastics studies. Until 2018, there were 31 studies on macroplastics; whereas 2019 and 2020 together already produced 25 of such assessments alone. These studies provide growing evidence that macroplastic pollution and deposition occurs in all freshwater compartments (Ji et al. 2021; van Calcar and van Emmerik 2019; van Emmerik and Schwarz 2020). Considering the current interest in global modeling estimates (see Section 7.4), more macroplastic investigations are needed and also expected in the future (Mai et al. 2020; Meijer et al. 2021).

For overviews of reported freshwater plastic particle concentrations, the reader is referred to Li et al. (2018), van Emmerik and Schwarz (2020), Peller et al. (2020), Triebskorn et al. (2019), Rezania et al. (2018), Lechthaler et al. (2020b), and Blair et al. (2017). Despite a high interest in concentrations and flux of the even smaller NPs (<1 μm), to date, such NPs have yet to be identified in freshwater environments (Blair et al. 2017; Boyle and Örmeci 2020).

7.4 Modeling Plastics in Rivers and Lakes

7.4.1 Predicting Inputs of Plastics in Freshwater Bodies

Many of the factors influencing the quantities of plastics found in environments can be linked to population density (Eerkes-Medrano and Thompson 2018). It is therefore with no surprise that several early attempts at quantifying sources of plastics into freshwater bodies used population density as a predictor (Jang et al. 2014; Lechner et al. 2014). For example, the generation of mismanaged plastic waste can be linked to the number of inhabitants using (i) the average municipal solid waste generation per inhabitant, (ii) the average mass fraction of plastics found in waste, and

(iii) the fraction of waste that is mismanaged (Hoornweg and Bhada-Tata 2012). This method has been widely used to estimate inputs of plastics into rivers and lakes at regional and global scale (Hoffman and Hittinger 2017; Lebreton et al. 2017; Liubartseva et al. 2015; Schmidt et al. 2017). Similarly, considering amounts of mismanaged plastic waste generated by the population living within 50 km of the coastline, Jambeck et al. (2015) estimated for 2010 a global input of plastics into the ocean of 4.8–12.7 million t/y. More recently, two studies estimated global plastic inputs into aquatic ecosystems aiming to evaluate the impact of mitigation strategies and of future commitments from nations. Associating high resolution population density distribution with distance to nearest aquatic environment, including rivers, lakes, and oceans, these two independent studies reported for 2016 an annual input of 9–14 million t/y (Lau et al. 2020) and 19–23 million t/y (Borrelle et al. 2020) into aquatic ecosystems. However, quantifying and mapping where littering occurs on land is difficult. Often population density is used as a predictor, yet it is unclear if people will litter more at the place where they live, where they work, or where they commute. In addition, the role of tourism is poorly investigated.

It is also crucial to realize that regional and global estimates rely on data on the municipal solid waste generation. As these studies generally do not account for plastic degradation, we can assume that they are mostly representative for macroplastic emissions only and that the generation of secondary MPs on land is largely neglected. This is contrasting to the global observational effort that is mostly targeting MPs (Figure 7.2), and it illustrates an evident gap in our knowledge of plastic inputs (and fate) when introduced in freshwater bodies and in the environment in general (Lechthaler et al. 2020b). To overcome this, studies have attempted to develop methods to regionalize emissions of macroplastics and microplastics (Kawecki and Nowak 2020), including the degradation of macroplastics on land to estimate microplastic inputs into rivers with an estimated discharge into the ocean of 14 400 t/y for European rivers (Siegfried et al. 2017) and 47 000 t/y for global rivers (van Wijnen et al. 2019). In the Seine River, Unice et al. (2018) used a traffic-based vehicle emission model to estimate inputs of tire and road wear particles. Van Wezel et al. (2016) conducted a material flow analysis for cosmetics and personal care products, cleaning agents, paint, and coatings for estimating the concentration of MPs in effluent of wastewater treatment plants in the Netherlands. Nizzetto et al. (2016) evaluated emissions of MPs from sewage sludge applications on agricultural land in the Thames River catchment, highlighting the capacity for soils to retain particles. Karlsson et al. (2018) assessed the release of plastic pellets from a polyethylene production site on the Swedish west coast. Finally, MPs may reach the aquatic environment from atmospheric deposition with plastics detected in atmospheric fallout from urban environments (Cai et al. 2017; Dris et al. 2016), but we are not aware of any regional or global estimate of the contribution of atmospheric deposition for the inputs of plastics in freshwater bodies.

7.4.2 Modeling the Processes Influencing Transport and Fate of Plastics in Freshwater

Plastics entering rivers and streams will be subject to the same processes that affect natural particles and items, such as sediments, organic matter, and natural debris (Horton and Dixon 2018; Kooi et al. 2018). These processes include advection, diffusion, settling, resuspension, burial, degradation or weathering, fragmentation, aggregation, biofouling, ingestion by biota, beaching, entrapment by vegetation or artificial structures, wind-induced transport, and tide-induced transport (Figure 7.3). Whether and how these processes influence the transport depends largely on the plastic characteristics, such as size and density. For example, aggregation is known to influence the transport behavior of nanoparticles (Besseling et al. 2017; Quik et al. 2014) but will likely not affect

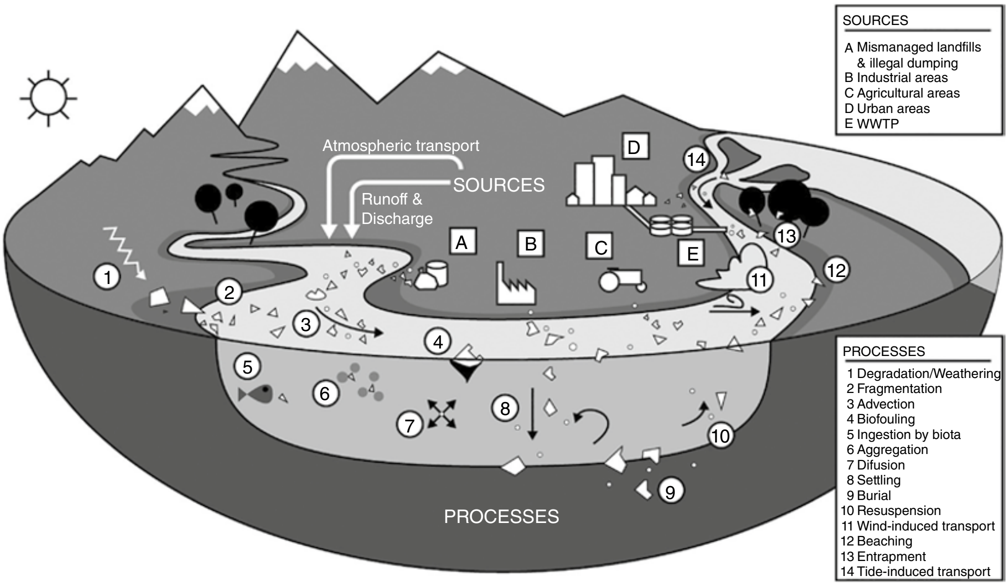


Figure 7.3 Illustration of sources and main processes influencing the transport and fate of plastics in freshwater bodies. (WWTP: wastewater treatment plant)

macroplastic. In addition, the retention in sublittoral sediments will largely be influenced by the plastic sizes (Nizetto et al. 2016) and flow characteristics (Besseling et al. 2017). Under turbulent conditions, cross sectional vertical and horizontal transport of particles is strongly enhanced (Haberstroh et al. 2020). MPs are found in higher quantities in reservoirs of dams than in upstream or downstream locations along the river alimenting the dam (Watkins et al. 2019). Larger plastic debris discarded in rivers can be captured by artificial barriers, beach on riverbanks, or trees bordering the river (Kooi et al. 2018). The transport (and retention) of floating plastics in rivers is further influenced by surface winds with the accumulation of debris on windward banks. Under low turbulence conditions, plastics may be transported rapidly toward the sea; however, turbulence, mixing, river meandering, vegetation, and tidal flow may greatly impact the transport of debris with observations, showing retention for several years in estuarine environments (Tramoy et al. 2020) or in mangrove forests (Ivar do Sul et al. 2014; Martin et al. 2020). Biofilm development can also cause the sinking of floating plastics, particularly in lakes and under warm conditions (Chen et al. 2019; Kaiser et al. 2017). Most of the aforementioned processes have been taken into account in some of the models that currently exist on plastic transport in freshwater bodies (Table 7.1).

The implementation of these processes differs greatly among models. In mass balance models, advection is taken into account simply as the net transport from one cell to the next (Siegfried et al. 2016; van Wijnen et al. 2019). The spatiotemporally explicit models include advection–diffusion equations that are solved in the underlying hydrodynamic models (Besseling et al. 2017; Daily and Hoffman 2020; Unice et al. 2019). Some of the resulting currents are strongly influenced by wind (Hoffman and Hittinger 2017). Further, most models include some form of settling/sedimentation, ranging from simple net-settling factors (Siegfried et al. 2017; van Wijnen et al. 2019) to using particle-settling velocities. These settling velocities have been calculated using Stokes' settling equation (Besseling et al. 2017; Nizzetto et al. 2016) and shape-dependent settling equations that

Table 7.1 Overview of plastic transport models.

	Scale	Spatial	Temporal	Sources[a]	Processes[b]	Particle properties			Underlying model
Spatiotemporally explicit models						Size (μm)	Shape	Density (g/cm)	
Nizzetto et al. (2016)	River catchment	1D	Yes	pt and df	ad, st, and rs	1–5000	Spherical	$\rho > 1.0$	INCA-contaminants
Besseling et al. (2017)	River subcatchment	1D	Yes	pt	ad–df, st, rs, br, dg, ag, and bf	0.1–10 000	Spherical	$\rho \geq 1.0$	NanoDUFLOW
Unice et al. (2019)	River catchment	1D	Yes	pt and df	ad–df, st, dg, ag	5–220	Variable	$\rho > 1.0$	E-HYPE and Delft3D-WAQ
Hoffman and Hittinger (2017)	Lake	2D	Yes	df	ad, and bc	NA	NA	NA	POM
Cable et al. (2017)	Lake	2D	Yes	pt	ad, df, and bc	<1000	NA	$\rho \leq 1.0$	
Mason et al. (2020)	Lake	2D	Yes	df	ad	NA	NA	NA	FVCOM
Daily and Hoffman (2020)	Lake	3D	Yes	df	ad, df, st, and bc	1000–4750	[c]	$1.0 \leq \rho \geq 1.0$[c]	FVCOM
Mass balance models									
Siegfried et al. (2017	Continent	2D	No	pt	st–dg[d]	NA	NA	NA	Global NEWS
van Wijnen et al. (2019)	World	2D	No	pt and df	fr and st–dg[d]	NA	NA	NA	Global NEWS
Multicompartment model									
Kooi et al. (2018)	NA	0D	No	df	st and ag	0.1–1000	NA	1.1	SB4N

[a] Sources: pt = Point, df = diffuse.

[b] Processes: ad = advection, df = diffusion, st = settling, rs = resuspension, br = burial, dg = degradation/weathering, fr = fragmentation, ag = aggregation, bf = biofouling, bc = beaching, en = entrapment, wi = wind-induced transport.

[c] No specific shapes or densities were mentioned, but they use data on settling velocities for nine polymers, with EPS having the lowest reported velocities and PVC and PET the highest.

[d] Combined fragmentation and degradation factor.

take shear stress into account (Unice et al. 2019; Wu and Wang 2006), but direct implementations of measured settling velocities also exist (Daily and Hoffman 2020). Beaching of particles has not yet been modeled directly in freshwater bodies. However, it is implicitly included in some of the lake models, where particles reaching the grid cells near the lake shore are assumed to be beached (Cable et al. 2017; Daily and Hoffman 2020).

Processes that were only included in the spatiotemporal models for rivers include resuspension, burial, degradation, aggregation, and biofouling. Resuspension depends on the shear stress of the river and the critical shear stress that allows entrainment of particles (Besseling et al. 2017; Nizzetto et al. 2016). Burial and degradation have been included as first-order removal processes (Besseling et al. 2017; Unice et al. 2019). Aggregation has been modeled using the von Smoluchowski equation (Besseling et al. 2017; Nizzetto et al. 2016; Unice et al. 2019), and finally, the effect of biofouling has only been included as a simple addition of a thin biofilm layer with a fixed density (Besseling et al. 2017). Other studies pointed out that the effect of biofouling was indirectly taken into account when varying particle sizes and densities (Daily and Hoffman 2020).

7.4.3 Quantifying Plastic Outputs Into the Ocean

A considerable number of studies have attempted to quantify inputs of plastics via rivers into the ocean (Table 7.2). Two different methods have generally been proposed. First, observational studies reported concentrations of plastics in rivers or at wastewater treatment plant outlets, which extrapolate results to a seasonal or annual scale, and commonly use the rivers' discharge as a predictor (van Emmerik et al. 2018). Second, material flow analyses for municipal solid waste and/or other types of emissions (e.g. tire and road wear particles, cosmetics and personal care products, textile fibers, cleaning agents, paint, and coatings, see Section 7.4.1) have been supporting estimates of plastic inputs into the ocean via rivers and waterways.

In most of these material flow analyses, the evaluation of the mismanaged fraction of municipal solid waste is the main predictor to quantify emissions of plastics. This fraction is what is unsoundly disposed (i.e. not recycled, incinerated, or disposed in controlled landfills) and is commonly reported on a country level (Hoornweg and Bhada-Tata 2012). Despite most high-income countries reporting this fraction being 0%, studies have used a minimum threshold of 1–2% to account for littering (Jambeck et al. 2015; Lebreton and Andrady 2019). More recently, Mai et al. (2020) suggested that the human development index could be a better predictor to estimate plastic emissions from rivers into the ocean compared to using waste mismanagement rates. This method thereby presents the advantage to differentiate between rich economies where, instead of an arbitrary minimum threshold to estimate littering, the human development index of a country not only quantifies economic development but also other societal aspects such as education, life expectancy, and income. Using this method, the study noticeably found a lesser contribution of rivers from China for which the dominant input at global scale has been contested by local studies. Particularly, the mismanaged waste fraction in China of 13% (Zhao et al. 2018) is well below previous assessments reporting rates above 70% (Jambeck et al. 2015). The identification of origins of debris found on the South Korean shore, coupled with Lagrangian dispersion modeling in the ocean also suggested that the mismanaged fraction of plastic waste from China is more likely to be below 25% to reflect observations (Seo et al. 2020). Other similar discrepancies between model estimates and observations have been reported in other parts of the world such as in the Mediterranean Sea where inverse Lagrangian modeling also suggested emissions models for the region were likely too high (Kaandorp et al. 2020). The discrepancies between model and field studies highlight a research gap in our understanding of plastic emissions into and from rivers. As this understanding heavily relies

Table 7.2 Existing models and observation-based estimates for river plastic emissions to the ocean.

	Location	Temporal	Date	Source method[a]	Size class	Emission estimate
Local models						
Tramoy et al. (2019)	Seine River	Yes	2007–2017	obs and msw	Meso and macro	1.1–5.9k t/y
Unice et al. (2018)	Seine River	No	2008	rd	Micro (small)	447 t/y
Mani et al. (2015)	Rhine River	No	2014	obs	Micro (large)	70G #/y
Vriend et al. (2020a)	Rhine River	No	2018	obs	Macro	1.3–9.7 kg/day ~0.5 to 3.5k t/y
Mai et al. (2019)	Zhujiang River	Yes	2018	obs	Micro (large)	2.4–3.8k t/y
Zhao et al. (2019)	Yangtze River	Yes	2017	obs	Micro (small and large)	0.54–0.91k t/y
Castro-Jimenez et al. (2019)	Rhone River	No	2016–2017	obs	Meso and macro	0.71 t/y
Miller et al. (2017)	Hudson River	No	2016	obs	Micro (small and large)	109G #/y
Weideman et al. (2020)	Orange and Vaal Rivers	No	2018–2020	obs	Micro (small and large)	1.1–3.1 t/y
Lechner et al. (2014)	Danube River	No	2010–2012	obs	Micro (large)	1.5k t/y
Van Emmerik et al. (2019a)	Jakarta (Ciliwung, Pesanggrahan, Cakung, and other rivers)	Yes	2018	obs	Macro	2100 t/y
Van Emmerik et al. (2019b)	Saigon River	Yes	2018	obs	Macro	1.4–1.6k t/y
Schirinzi et al. (2020)	Barcelona (Llobregat and Besòs Rivers)	Yes	2016–2017	obs	Macro	0.4–0.6 t/y
Schoneich-Argent et al. (2020)	Ems River	No	2017–2018	obs	Macro	0.9–2.8 t/y
Schoneich-Argent et al. (2020)	Weser River	No	2017–2018	obs	Macro	1.3–12.0 t/y
Schoneich-Argent et al. (2020)	Elbe River	No	2017–2018	obs	Macro	14.7–801 t/y
National models						
Van Wezel et al. (2016)	The Netherlands	No	2013	ww	Micro (small)	0.2–66 µg/L
Bai et al. (2018) Bai and Li (2020)	China	Yes	2011–2020	msw	Macro	0.65–0.86m t/y
Jang et al. (2014)	South Korea	No	2012	obs[b]	Macro	26.6k t/y

Regional models						
Liubartseva et al. (2015)	Adriatic Sea	No	2010	msw	Macro	4k t/y
Mihai (2020)	Izvoru Muntelui Lake	No	2008-2012	msw (PET bottles)	Macro	4.2–128.2 t/y
Hoffman and Hittinger (2017)	Great Lakes	No	2010	msw	Macro	9.9k t/y
Boucher et al. (2018)	Lake Geneva	No	2020	obs, msw, rd, and ww	Micro (small and large), meso, and macro	8–193 t/y
Liubartseva et al. (2018)	Med. Sea	No	2010	msw	Macro	30k t/y
Siegfried et al. (2017)	European rivers	No	2000	rd and ww	Micro (small and large)	14.4k t/y
Global models						
Jambeck et al. (2015)	Global	No	2010	msw	Macro	4.8–12.7m t/y
Lebreton et al. (2017)	Global	Yes	2010	obs and msw	Micro (large) and meso	1.15–2.41m t/y
Schmidt et al. (2017)	Global	No	2010	obs and msw	Micro (large) and meso	0.47–2.75m t/y
Van Wijnen et al. (2019)	Global	No	2000	msw, rd, and ww	Micro (small and large)	47k t/y
Meijer et al. (2021)	Global	Yes	2015	obs and msw	Macro	0.8–2.7m t/y
Mai et al. (2020)	Global	No	2018	obs and msw	Micro (large) and meso	57–265k t/y
Roebroek et al. (in press)	Global	No	2015	msw	Macro	0.8–9.6m t/y from floods
Borrelle et al. (2020)	Global	No	2016	msw	Macro	19–23m t/y[c]
Lau et al. (2020)	Global	No	2016	msw	Macro	9–14m t/y[c]

[a] obs: Based or calibrated against observations. msw: based on material flow analysis for municipal solid waste generation. rd: Estimate based on material flow analysis for vehicle traffic and tyre wear particle generation. ww: Estimate based on material flow analysis for microparticles found in wastewater (cosmetics, textile fibres, paint, and abrasive. . .).

[b] Extrapolated using population density.

[c] Emissions to aquatic environments (rivers, lakes, and oceans).

on our knowledge of where, when, and in which form plastics leak into the environment, further research is needed to detect and monitor the accumulation of plastics inland and its potential to leak into waterways over time.

7.5 Prospects and Opportunities

Despite the rapidly increasing number of publications on plastic occurrences in freshwater bodies, several aspects still carry high levels of uncertainty. Here, we highlight four key aspects that deserve more attention when designing and performing monitoring campaigns and when developing and interpreting numerical models. These four aspects are: (i) temporal variation, (ii) transfer between environmental compartments, (iii) harmonization of monitoring and modeling investigations regarding plastic size ranges, and, finally, (iv) data quality control and validation of results.

7.5.1 Temporal Variability

Plastic abundance and transport have been found to vary up to several orders of magnitude during the day, across the river width, along the river length, and during the year (Mani et al. 2015; Mintenig et al. 2020; van Calcar and van Emmerik 2019; van Emmerik et al. 2020; Vriend et al. 2020a). Data from a single sampling event can therefore not be used to estimate meaningful yearly transport fluxes. Although the optimal measurement frequency and strategy are yet to be determined, we emphasize that spatiotemporal variation should be taken into account when developing a monitoring strategy. This is particularly important for the development of numerical models for which we recommend validating against long-term observational and sampling measurement campaigns. While river hydrology and riparian flooding are recognized as a strong cause for mobilization and transport of plastics (Nizzetto et al. 2016; Roebroek et al. 2021) whereby a higher river discharge can increase plastic transport by orders of magnitude (van Emmerik et al. 2019), very few global modeling studies consider temporal variations when calculating emissions into the ocean. Most estimates give annual values while some further offer monthly variations to reflect the seasonal change (Lebreton et al. 2017). Therefore, the contribution of extreme events such as heavy rainfall, fluvial, pluvial, and coastal flooding occurring within hours to several days could be responsible for a significant fraction of emissions (Hurley et al. 2018; Roebroek et al. 2021). Temporal variations of emissions from rivers into the ocean, including the simulation of extreme events, are still largely unconstrained at global scale and will likely change geographically from year to year, in the context of a changing climate shifting and possibly exacerbating the risk of emissions.

7.5.2 Transfer Between Compartments

In this chapter, we have shown that most of the key processes influencing plastic transport in freshwaters have been taken into account in one or more existing numerical models. However, the application of these processes in regional and global emission models is hardly investigated. As such, there is still a lot of room for improvement. Although there is evidence that plastics are transported, e.g. in rivers below the water surface (Haberstroh et al. 2020; Liedermann et al. 2018), subsurface water column inclusion is lacking attention. Such data is, however, highly relevant for understanding the mass flux and dynamics of plastic pollution (Liro et al. 2020; Meijer et al. 2021). The monitoring of plastics below the water surface remains particularly challenging. Too often, samples are taken at the water surface only, but results are either extrapolated over the whole river cross-section, or subsurface plastic concentrations are simply assumed to be negligible. The few studies that did sample below the surface did not only find plastics but also showed that concentrations and properties differed in the water column (Broere et al. 2021; Lenaker et al. 2019; Morritt et al. 2014; van Emmerik et al. 2019b;). In the marine environment, different sampling methods have been used for subsurface sampling (Liu et al. 2020). These should also be tested in freshwaters if we are to better quantify plastic transport in freshwater systems and to the marine environment. Processes like biofouling and degradation influencing the transfer between compartments could be included in numerical models in a dynamic way (Chamas et al. 2020; Kooi et al. 2017; Min et al. 2020). Especially in lakes, where retention times are high, these processes have the potential to strongly influence plastic fate. An improved understanding of beaching would also be of added value since this process can potentially retain or at least delay emissions into the oceans. The contribution of lakeshores and riverbanks as sink for aquatic plastics is largely unknown at a global scale. Knowing where and when beaching occurs could also help to target hotspots that can be the focus of cleanup activities. Further, the interface between rivers and oceans is poorly resolved. The dynamics of transport of plastics from rivers to sea in estuaries are complex and will greatly influence the net plastic emissions from a river into the ocean. Emission models should account for estuarine and coastal dynamics including the influence of tides and waves and the dispersion of freshwater plumes. In reality, the complexity of plastic particles in terms of shape, size, and density significantly limits the accuracy of theoretical formulations to predict the movement of plastics across freshwater compartments. As field observations can contradict theoretical estimations, a harmonization of data collection methodologies for both in situ studies and the development of numerical models will help refine our understanding of plastic emissions from rivers to the ocean.

7.5.3 Plastic Size Investigations

In this review, we have highlighted that observational efforts mostly focus on MPs while most theoretical estimations of river emissions into oceans at national, regional, or global scale derive estimates from municipal solid waste data, thus mostly representing macroplastics. Therefore, we note that these modeled emission estimates do not consider most physical and biological processes affecting the transport and fate of plastics in freshwater environments. Macroplastic transport is challenging to model, since existing sediment transport models cannot form the basis for this large debris, and observational data is scarcer. Thus, researchers have mostly relied on empirical or probabilistic approaches to formulate emission estimates. As such, we emphasize that increasing our understanding of the accumulation and transport of plastics in the environment will require, in addition to aligning sampling locations, durations, intervals, and methods, a homogenization of size classes detected by field measurements and their representation in numerical models. Generally, we would recommend the plastic research community to step away from arbitrary "plastic size classes" like microplastics and macroplastics and simply report upper and lower size detection limits relevant to the methods employed by a study. We have shown that different monitoring steps are suitable for different size ranges, irrespective of the targeted "plastic size class." Plastic properties like size, shape, and density have been shown to follow continuous distributions between 20 and 5000 μm (Kooi and Koelmans 2019). However, we do not expect the continuous nature of plastics to start or stop at the microplastic size range. If we are to fully understand risks associated to plastics in freshwater bodies, we need to let go of these arbitrary names and size classes and focus on the whole spectrum as much as possible.

7.5.4 Data Quality Control and Validation of Results

Finally, we further want to stress the need for high data quality assurance. Recently, several studies have been published that provide rigorous guidelines for both sample handling and reporting (Brander et al. 2020; Cowger et al. 2020; Koelmans et al. 2019). With such guidelines in place, it is time to bring the quality and comparability of future studies to the next level (Provencher et al. 2020). Furthermore, the majority of presented numerical models would benefit from a (better) validation against measured concentrations. However, most studies on plastic transport and fate models presented here did not include any form of validation against measurements. Fortunately, as we have seen, the number of publications on plastic abundances is rapidly increasing internationally. This impressive growth in literature will be the basis of the next generation of numerical models simulating the transport and fate of plastics in rivers, lakes, and eventually the ocean.

References

Andrady, A. L. (2017). The plastic in microplastics: a review. *In Marine Pollution Bulletin*, *119*(1), 12–22.

Bai. M., Zhu. L., An, L., Peng G., Li D. (2018). Estimation and prediction of plastic waste annual input into the sea from China. *Acta Oceanologica Sinica*, *37*(11): 26–39.

Bai, M., & Li, D. (2020). Quantity of plastic waste input into the ocean from China based on a material flow analysis model. *Anthropocene Coasts*, *3*(1), 1–5.

Bellasi, A., Binda, G., Pozzi, A., Galafassi, S., Volta, P., Bettinetti, R. (2020). Microplastic contamination in freshwater environments: a review, focusing on interactions with sediments and benthic organisms. *Environments*, *7*(4), 30.

Bergmann, M., Tekman M. B., Gutow, L. (2017a). Sea change for plastic pollution. *Nature*, *544*(7650), 297–297.

Bergmann, M., Wirzberger, V., Krumpen, T., Lorenz, C., Primpke, S., Tekman, M. B., Gerdts, G. (2017b). High quantities of microplastic in Arctic deep-sea sediments from the HAUSGARTEN observatory. *Environmental Science and Technology*, *51*(19), 11000–11010.

Besseling, E., Quik, J.T.K., Sun, M., Koelmans, A. A. (2017). Fate of nano- and microplastic in freshwater systems: a modeling study. *Environmental Pollution*, 220, 540–548.

Biermann, L., Clewley, D., Martinez-Vicente, V., Topouzelis, K. (2020). Finding plastic patches in coastal Waters using optical Satellite Data. *Scientific Reports*, *10*(1), 1–10.

Blair, R. M., Waldron, S., Phoenix, V., & Gauchotte-Lindsay, C. (2017). Micro- and Nanoplastic Pollution of Freshwater and Wastewater Treatment Systems. *Springer Science Reviews*, *5*(1–2), 19–30.

Blettler, M. C. M., Abrial, E., Khan, F. R., Sivri, N., & Espinola, L. A. (2018). Freshwater plastic pollution: Recognizing research biases and identifying knowledge gaps. *Water Research*, *143*, 416–424.

Borrelle, S. B., Ringma, J., Law, K. L., Monnahan, C. C., Lebreton, L., McGivern, A., Murphy, E., Jambeck, J., Leonard, G. H., Hilleary, M. A., Eriksen, M., Possingham, H. P., De Frond, H., Gerber, L. R., Polidoro, B., Tahir, A., Bernard, M., Mallos, N.s, Barnes, M., Rochman, C. M. (2020). Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. *Science*, 369(6510), 1515–1518.

Boucher J., Faure F., Pompini O., Plummer Z., Wieser O., Felippe de Alencastro L. (2018). (Micro) plastic fluxes in Lake Geneva basin. *Trends in Analytical Chemistry*, *112*, 66–74.

Boyle, K., & Örmeci, B. (2020). Microplastics and nanoplastics in the freshwater and terrestrial environment: a review. *Water*, *12*(9), 2633.

Brander, S. M., Renick, V. C., Foley, M. M., Steele, C., Woo, M., Lusher, A., Carr, S., Helm, P., Box, C., Cherniak, S., Andrews, R.C., Rochman, C.M. (2020). Sampling and quality assurance and quality control: a guide for scientists investigating the occurrence of microplastics across matrices. *Applied Spectroscopy*, *74*(9), 1099–1125.

Broere, S., van Emmerik, T., González-Fernández, D., Luxemburg, W., de Schipper, M., Cózar, A., and van de Giesen, N. (2021). Towards underwater plastic monitoring using echo sounding. *Frontiers in Earth Science*, *9*, 628704. https://doi.org/10.3389/feart.2021.628704.

Burns, E. E., & Boxall, A. B. (2018). Microplastics in the aquatic environment: evidence for or against adverse impacts and major knowledge gaps. *Environmental Toxicology and Chemistry*, 37(11), 2776–2796.

Cabernard, L., Roscher, L., Lorenz, C., Gerdts, G., Primpke, S. (2018). Comparison of Raman and Fourier transform infrared spectroscopy for the quantification of microplastics in the aquatic environment. *Environ Science & Technology*, *52*(22), 13279–13288.

Cable, R. N., Beletsky, D., Beletsky, R., Wigginton, K., Locke, B. W., Duhaime, M. B. (2017). Distribution and modeled transport of plastic pollution in the great lakes, the world's largest freshwater resource. *Frontiers in Environmental Science*, *5*, 45.

Cai, L., Wang, J., Peng, J., Tan, Z., Zhan, Z., Tan, X., Chen, Q. (2017). Characteristic of microplastics in the atmospheric fallout from Dongguan city, China: preliminary research and first evidence. *Environmental Science and Pollution Research*, *24*(32), 24928–24935.

Carr, S.A., Liu, J., Tesoro, A.G. (2016). Transport and fate of microplastic particles in wastewater treatment plants. *Water Research*, *91*, 174–182.

Castro-Jiménez, J., González-Fernández, D., Fornier, M., Schmidt, N., Sempéré, R. (2019). Macro-litter in surface waters from the Rhone River: plastic pollution and loading to the NW Mediterranean Sea. *Marine Pollution Bulletin*, *146*, 60–66.

Chamas, A., Moon, H., Zheng, J., Qiu, Y., Tabassum, T., Jang, J. H., Abu-Omar, M., Scott, S. L., Suh, S. (2020). Degradation rates of plastics in the environment. *ACS Sustainable Chemistry & Engineering*, *8*(9), 3494–3511.

Chen, X., Xiong, X., Jiang, X., Shi, H., Wu, C. (2019). Sinking of floating plastic debris caused by biofilm development in a freshwater lake. *Chemosphere*, *222*, 856–864.

Cowger, W., Booth, A.M., Hamilton, B.M., Thaysen, C., Primpke, S., Munno, K., Lusher, A.L., Dehaut, A., Vaz, V.P., Liboiron, M., Devriese, L.I., Hermabessiere, L., Rochman, C., Athey, S.N., Lynch, J.M., De Frond, H., Gray, A., Jones, O.A.H., Brander, S., Steele, C., Moore, S., Sanchez, A., Nel, H. (2020). Reporting guidelines to increase the reproducibility and comparability of research on microplastics. *Applied Spectroscopy*, doi:10.1177/0003702820930292.

Crichton, E. M., Noël, M., Gies, E. A., & Ross, P. S. (2017). A novel, density-independent and FTIR-compatible approach for the rapid extraction of microplastics from aquatic sediments. *Analytical Methods*, *9*(9), 1419–1428.

Daily, J. & Hoffman, M. J. (2020). Modeling the three-dimensional transport and distribution of multiple microplastic polymer types in Lake Erie. *Marine Pollution Bulletin*, *154*, 111024.

Dris, R., Gasperi, J., Saad, M., Mirande, C., Tassin, B. (2016). Synthetic fibers in atmospheric fallout: A source of microplastics in the environment? *Marine Pollution Bulletin*, *104*(1–2), 290–293.

Dris R., Imhof H. K., Löder M. G. et al. (2018). Microplastic contamination in freshwater systems: methodological challenges, occurrence and sources. In: Zeng, E.Y. (Ed.), *Microplastic Contamination in Aquatic Environments*. Elsevier, Amsterdam, pp. 51–93.

Dümichen, E., Eisentraut, P., Bannick, C.G., Barthel, A.-K., Senz, R. and Braun, U. (2017). Fast identification of microplastics in complex environmental samples by a thermal degradation method. *Chemosphere* 174, 572–584.

Eckert, E. M., Di Cesare, A., Kettner, M. T., Arias-Andres, M., Fontaneto, D., Grossart, H.-P., Corno, G. (2018). Microplastics increase impact of treated wastewater on freshwater microbial community. *Environmental Pollution*, 234, 495–502.

Eerkes-Medrano, D., Thompson, R. C., & Aldridge, D. C. (2015). Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Research*, *75*, 63–82.

Eerkes-Medrano, D. & Thompson, R. C. (2018). Occurrence, fate, and effect of microplastics in freshwater systems. In: Zeng, E.Y. (Ed.), *Microplastic Contamination in Aquatic Environments*, Elsevier, Amsterdam, pp. 95–132.

Elkhatib, D. and Oyanedel-Craver, V. (2020). A critical review of extraction and identification methods of microplastics in wastewater and drinking water. *Environmental Science & Technology*, *54*(12), 7037–7049.

Faure, F., Corbaz, M., Baecher, H., De Alencastro, L. F. (2012). Pollution due to plastics and microplastics in Lake Geneva and in the Mediterranean Sea. *Archives Des Sciences*, *65*(1–2), 157–164.

Felsing, S., Kochleus, C., Buchinger, S., Brennholt, N., Stock, F., Reifferscheid, G. (2018). A new approach in separating microplastics from environmental samples based on their electrostatic behavior. *Environmental Pollution*, *234*, 20–28.

Fischer, M. and Scholz-Böttcher, B.M. (2017). Simultaneous trace identification and quantification of common types of microplastics in environmental samples by pyrolysis-gas chromatography–mass spectrometry. *Environmental Science & Technology*, *51*(9), 5052–5060.

Gall, S.C., Thompson, R.C. (2015). The impact of debris on marine life. *Marine Pollution Bulletin*, *92*(1-2), 170–179.

Gasperi, J., Dris, R., Bonin, T., Rocher, V., Tassin, B. (2014). Assessment of floating plastic debris in surface water along the Seine River. *Environmental Pollution*, *195*, 163–166.

Geraeds, M., van Emmerik, T., de Vries, R., bin Ab Razak, M. S. (2019). Riverine plastic litter monitoring using unmanned aerial vehicles (UAVs). *Remote Sensing*, *11*(17), 2045.

Gregory, M. R. (2009). Environmental implications of plastic debris in marine settings – entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. *Philosophical Transactions of the Royal Society B: Biological Sciences*, *364*(1526), 2013–2025.

Haberstroh, C. J., Arias, M. E., Yin, Z., & Wang, M. C. (2020). Effects of hydrodynamics on the cross-sectional distribution and transport of plastic in an urban coastal river. *Water Environment Research*, 1–15.

Hanvey, J.S., Lewis, P.J., Lavers, J.L., Crosbie, N.D., Pozo, K., Clarke, B.O. (2017). A review of analytical techniques for quantifying microplastics in sediments. *Analytical Methods 9*(9), 1369–1383.

Hartmann, N., Hüffer, T., Thompson, R. C., Hassellöv, M.; Verschoor, A.; Daugaard, A. E.; Rist, S.; Karlsson, T. M.; Brennholt, N.; Cole, M.; Herrling, M. P.; Heß, M.; Ivleva, N. P.; Lusher, A.L.; Wagner, M. (2019). Are we speaking the same language? Recommendations for a definition and categorization framework for plastic debris. *Environmental Science & Technology*, *53*(3), 1039–1047.

Hermsen, E., Mintenig, S.M., Besseling, E. and Koelmans, A.A. (2018). Quality criteria for the analysis of microplastic in biota samples: a critical review. *Environmental Science & Technology*, *52*(18), 10230–10240.

Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M. (2012). Microplastics in the marine environment: a review of the methods used for identification and quantification. *Environmental Science & Technology*, *46*(6), 3060–3075.

Hildebrandt, L., Mitrano, D.M., Zimmermann, T., Pröfrock, D. (2020). A nanoplastic sampling and enrichment approach by continuous flow centrifugation. *Frontiers in Environmental Science*, *8*(89).

Hoffman, M. J., & Hittinger, E. (2017). Inventory and transport of plastic debris in the Laurentian Great Lakes. *Marine Pollution Bulletin*, *115*(1–2), 273–281.

Honingh D, van Emmerik T, Uijttewaal W, Kardhana H, Hoes O and van de Giesen N (2020). Urban river water level increase through plastic waste accumulation at a rack structure. *Frontiers in Earth Science* 8(28).

Hoornweg, D. & Bhada-Tata, P. (2012). *What a Waste: A Global Review of Solid Waste Management*. World Bank. http://hdl.handle.net/10986/17388 (accessed August 21, 2021).

Horton, A. A., Walton, A., Spurgeon, D. J., Lahive, E., Svendsen, C. (2017). Microplastics in freshwater and terrestrial environments: evaluating the current understanding to identify the knowledge gaps and future research priorities. *Science of the Total Environment*, *586*, 127–141.

Horton, A. A. & Dixon, S. J. (2017). Microplastics: an introduction to environmental transport processes. *Wiley Interdisciplinary Reviews: Water*, 5, e1268.

Hurley, Rachel, Woodward, Jamie, Rothwell, James J. (2018). Microplastic contamination of river beds significantly reduced by catchment-wide flooding. *Nature Geoscience*, 11, 251–257.

Ivar do Sul, J.A. and Costa, M.F. (2013). Plastic pollution risks in an estuarine conservation unit. In: Conley, D.C., Masselink, G., Russell, P.E. and O'Hare, T.J. (Eds.), Proceedings 12th International Coastal Symposium (Plymouth, England), *Journal of Coastal Research*, *65*, 48–53.

Ivar do Sul, J. A., Costa, M. F., Silva-Cavalcanti, J. S., Araújo, M. C. B. (2014). Plastic debris retention and exportation by a mangrove forest patch. *Marine Pollution Bulletin 78*(1-2), 252–257.

Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., Narayan, R., Law, K. L. (2015). Plastic waste inputs from land into the ocean. *Science*, 347(6223), 768–771.

Jang, Y. C., Lee, J., Hong, S., Mok, J. Y., Kim, K. S., Lee, Y. J., Choi, H.W., Kang H., Lee, S. (2014). Estimation of the annual flow and stock of marine debris in South Korea for management purposes. *Marine Pollution Bulletin*, 86(1–2), 505–511. doi: 10.1016/j.marpolbul.2014.06.021.

Ji, X., Ma, Y., Zeng, G., Xu, X., Mei, K., Wang, Z., Chen, Z., Dahlgren, R., Zhang, M., Shang, X. (2021). Transport and fate of microplastics from riverine sediment dredge piles: implications for disposal. *Journal of Hazardous Materials*, 404, 124132.

Kaandorp, M., Dijkstra, H. A., van Sebille, E. (2020). Closing the Mediterranean marine floating plastic mass budget: inverse modelling of sources and sinks. *Environmental Science & Technology*, 54(19), 11980–11989.

Kaiser, D., Kowalski, N., Waniek, J. J. (2017). Effects of biofouling on the sinking behavior of microplastics. *Environmental Research Letters*, 12(12), 124003.

Karlsson, T.M., Grahn, H., van Bavel, B., Geladi, P. (2016). Hyperspectral imaging and data analysis for detecting and determining plastic contamination in seawater filtrates. *Journal of near Infrared Spectroscopy*, *24*(2), 141–149.

Karlsson, T. M., Arneborg, L., Broström, G., Almroth, B. C., Gipperth, L., Hassellöv, M. (2018). The unaccountability case of plastic pellet pollution. *Marine Pollution Bulletin*, *129*(1), 52–60.

Kawecki, D., & Nowack, B. (2020). A proxy-based approach to predict spatially resolved emissions of macro- and microplastic to the environment. *Science of the Total Environment*, *748*, 141137.

Kershaw, P., Katsuhiko, S., Lee, S., Samseth, J., Woodring, D., Smith, J. (2011). plastic debris in the ocean. *UNEP Year Book 2011*, 20–33.

Klein, S., Dimzon, I. K., Eubeler, J., Knepper, T. P. (2018). Analysis, occurrence, and degradation of microplastics in the aqueous environment. In: Wagner, M., Lambert, S. (Eds.), *Freshwater Microplastics*. Springer, Cham, pp. 51–67.

Koelmans, A. A., Besseling, E., Foekema, E. M. (2014). Leaching of plastic additives to marine organisms. *Environmental Pollution*, *187*, 49–54.

Koelmans, A.A., Mohamed Nor, N.H., Hermsen, E., Kooi, M., Mintenig, S.M., De France, J. (2019). Microplastics in freshwaters and drinking water: critical review and assessment of data quality. *Water Research*, *155*, 410–422.

Koelmans, A. A., Redondo-Hasselerharm, P. E., Mohamed Nor, N. H., & Kooi, M. (2020). Solving the nonalignment of methods and approaches used in microplastic research to consistently characterize risk. *Environmental science & technology*, *54*(19), 12307–12315.

Kooi, M., Van Nes, E. H., Scheffer, M., Koelmans, A. A. (2017). Ups and downs in the ocean: effects of biofouling on the vertical transport of microplastics. *Environmental Science & Technology*, *51*, 14, 7963–7971.

Kooi, M., Besseling, E., Carolien, K., van Wezel, P. A., Koelmans, A. A (2018). Modeling the fate and transport of plastic debris in freshwaters: review and guidance. In: Wagner M, Lambert S (Eds.) *Freshwater Microplastics* (vol 58). Springer, Cham, pp. 125–152.

Kooi, M., & Koelmans, A. A. (2019). Simplifying microplastic via continuous probability distributions for size, shape, and density. *Environmental Science & Technology Letters*, *6*(9), 551–557.

Kroon, F., Motti, C., Talbot, S., Sobral, P., Puotinen, M. (2018). A workflow for improving estimates of microplastic contamination in marine waters: a case study from North-Western Australia. *Environmental Pollution*, *238*, 26–38.

Lau, W. W. Y., Shiran, Y., Bailey, R. M., Cook, E., Stuchtey, M. R. et al. (2020). Evaluating scenarios toward zero plastic pollution. *Science*, *369*(6510), 1455–1461.

Lebreton, L., Van Der Zwet, J., Damsteeg, J. W., Slat, B., Andrady, A., Reisser, J. (2017). River plastic emissions to the world's oceans. *Nature Communications*, *8*, 1–10.

Lebreton, L., Slat, B., Ferrari, F., Sainte-Rose, B., Aitken, J., Marthouse, R., Hajbane, S., Cunsolo, S., Schwarz, A., Levivier, A., Noble, K., Debeljak, P., Maral, H., Schoeneich-Argent, R., Brambini, R., Reisser, J. (2018). Evidence that the Great Pacific Garbage Patch is rapidly accumulating plastic. *Scientific Reports*, *8*(1), 4666.

Lebreton, L. & Andrady, A. (2019). Future scenarios of global plastic waste generation and disposal. *Palgrave Communications* *5*, 6.

Lechner, A., Keckeis, H., Lumesberger-Loisl, F., Zens, B., Krusch, R., Tritthart, M., Glas, M., Schludermann, E. (2014). The Danube so colourful: A potpourri of plastic litter outnumbers fish larvae in Europe's second largest river. *Environmental Pollution*, *188*, 177—181.

Lechner A. (2020). "Down by the River": (Micro-) plastic pollution of running freshwaters with special emphasis on the Austrian Danube. In: Streit-Bianchi M., Cimadevila M., Trettnak W. (Eds.) *Mare Plasticum – The Plastic Sea*. Springer, Cham, pp. 141–185.

Lechthaler, S. E., Hildebrandt, L., Stauch, G., Schüttrumpf, H. (2020a). Canola oil extraction in conjunction with a plastic free separation unit optimises microplastics monitoring in water and sediment. *Analytical Methods*, *12*, 5128–5139.

Lechthaler, S., Waldschläger, K., Stauch, G., Schüttrumpf, H. (2020b). The way of macroplastic through the environment. *Environments* *7*(10), 1–30.

Lenaker, P. L., Baldwin, A. K., Corsi, S. R., Mason, S. A., Reneau, P. C., Scott, J. W. (2019). Vertical distribution of microplastics in the water column and surficial sediment from the Milwaukee River Basin to Lake Michigan. *Environmental Science and Technology*, *53*(21), 12227–12237.

Li, J., Liu H., Chen P. (2018). Microplastics in freshwater systems: a review on occurrence, envirionmental effects, and methods for microplastics detection. *Water Research*, *137*, 362–374.

Li, C., Busquets, R., Campos, L. C. (2020). Assessment of microplastics in freshwater systems: a review. *Science of the Total Environment*, *707*, 135578.

Liedermann, M., Gmeiner, P., Pessenlehner, S., Haimann, M., Hohenblum, P., Habersack, H. (2018). A methodology for measuring microplastic transport in large or medium rivers. *Water (Switzerland)*, *10*(4), 1–12.

Liro, M., van Emmerik, T., Wyzga, B., Liro, J., Mikuś, P. (2020). Macroplastic storage and remobilization in rivers. *Water (Switzerland)*, *12*(7), 2055.

Liu, K., Courtene-Jones, W., Wang, X., Song, Z., Wei, N., Li, D. (2020). Elucidating the vertical transport of microplastics in the water column: a review of sampling methodologies and distributions. *Water Research*, 186, 116403.

Liubartseva, S., Coppini, G., Lecci, R., Creti, S. (2016). Regional approach to modeling the transport of floating plastic debris in the Adriatic Sea. *Marine Pollution Bulletin*, *103*(1–2), 115–127.

Löder, M.G.J., Gerdts, G. (2015). Methodology used for the detection and identification of microplastics – a critical appraisal. In: Bergmann, M., Gutow, L. and Klages, M. (Eds.), *Marine Anthropogenic Litter*. Springer International Publishing, Berlin, pp. 201–227.

Martin, C., Baalkhuyur, F., Valluzzi, L., Saderne, V., Cusack, M., Almahasheer, H., Krishnakumar, P. K., Rabaoui, L., Qurban, M.A., Arias-Ortiz, A., Masqué, P., Duarte, C. M. (2020). Exponential increase of plastic burial in mangrove sediments as a major plastic sink. *Science Advances*, *6*(44), eaaz5593.

MacIntyre, S., & Melack, J. M. (1995). Vertical and horizontal transport in lakes: Linking littoral, benthic, and pelagic habitats. *Journal of the North American Benthological Society*, *14*(4), 599–615.

Mai, L., You, S.-N., He, H., Bao, L.-J., Liu, L., Zeng, E. Y. (2019). Riverine microplastic pollution in the Pearl River Delta, China: are modeled estimates accurate? *Environmental Science & Technology*, *53*, 11810–11817.

Mai, L., Sun, X. F., Xia, L. L., Bao, L. J., Liu, L. Y., Zeng, E. Y. (2020). Global riverine plastic outflows. *Environmental Science and Technology*, *54*(16), 10049–10056.

Mani, T., Hauk, A., Walter, U., Burkhardt-Holm, P. (2015). Microplastics profile along the Rhine River. *Scientific Reports*, *5*(17988), 1–7.

Mani, T., Frehland, S., Kalberer, A., Burkhardt-Holm, P. (2019a). Using castor oil to separate microplastics from four different environmental matrices. *Analytical Methods*, *11*(13), 1788–1794.

Mani, T., Primpke, S., Lorenz, C., Gerdts, G., Burkhardt-Holm, P. (2019b). Microplastic pollution in benthic midstream sediments of the Rhine River. *Environmental Science and Technology*, *53*(10), 6053–6062.

Martín-Martín, A., Orduna-Malea, E., Thelwall, M., Delgado López-Cózar, E. (2018). Google Scholar, Web of Science, and Scopus: a systematic comparison of citations in 252 subject categories. *Journal of Infometrics*, *12*(4), 1160–1177.

Mason, S. A., Daily, J., Aleid, G., Ricotta, R., Smith, M., Donnelly, K., Knauff, R., Edwards, W. & Hoffman, M. J. (2020). High levels of pelagic plastic pollution within the surface waters of Lakes Erie and Ontario. *Journal of Great Lakes Research*, *46,* 2.

Meijer, L. J., van Emmerik, T., van der Ent, R., Schmidt, C., Lebreton, L. (2021). More than 1000 rivers account for 80% of global riverine plastic emissions into the ocean. *Science Advances*, 7(18), eaaz5803, doi: 10.1126/sciadv.aaz5803

Meyns, M., Primpke, S. and Gerdts, G. (2019). Library based identification and characterisation of polymers with nano-FTIR and IR-sSNOM imaging. *Analytical Methods*, *11*(40), 5195–5202.

Miller, R. Z., Watts, A. J. R., Winslow, B. O., Galloway, T. S., Barrows, A. P. W. (2017). Mountains to the sea: river study of plastic and non-plastic microfiber pollution in the northeast USA. *Marine Pollution Bulletin*, *124*(1), 245–251.

Mihai F-C. (2018). Rural plastic emissions into the largest mountain lake of the Eastern Carpathians. *Royal Society Open Science*, *5*, 172396.

Min, K., Cuiffi, J.D., Mathers, R.T. (2020). Ranking environmental degradation trends of plastic marine debris based on physical properties and molecular structure. *Nature Communications*, *11*, 727.

Mintenig, S.M., Bauerlein, P.S., Koelmans, A.A., Dekker, S.C., van Wezel, A.P. (2018). Closing the gap between small and smaller: towards a framework to analyse nano- and microplastics in aqueous environmental samples. *Environmental Science: Nano*, *5*, 1640–1649.

Mintenig, S. M., Löder, M. G. J., Primpke, S., Gerdts, G. (2019). Low numbers of microplastics detected in drinking water from ground water sources. *Science of the Total Environment*, *648*, 631–635.

Mintenig, S.M., Kooi, M., Erich, M.W., Primpke, S., Redondo-Hasselerharm, P.E., Dekker, S.C., Koelmans, A.A., van Wezel, A.P. (2020). A systems approach to understand microplastic occurrence and variability in Dutch riverine surface waters. *Water Research*, 176, 115723.

Moore, C., Lattin, G., Zellers, A. (2011). Quantity and type of plastic debris flowing from two urban rivers to coastal waters and beaches of southern California. *Journal of Integrated Coastal Zone Management*, *11*, 65–73.

Morritt, D., Stefanoudis, P. V., Pearce, D., Crimmen, O. A., Clark, P. F. (2014). Plastic in the Thames: a river runs through it. *Marine Pollution Bulletin*, *78*(1–2), 196–200.

Munier B & Bendell L.I. (2018). Macro and micro plastics sorb and desorb metals and act as a point source of trace metals to coastal ecosystems. *PloS One*, *13*(2), e0191759.

Nizzetto, L., Bussi, G., Futter, M. N., Butterfield, D., Whitehead, P. G. (2016). A theoretical assessment of microplastic transport in river catchments and their retention by soils and river sediments. *Environmental Science: Processes and Impacts*, *18*(8), 1050–1059.

Panno, S. V., Kelly, W. R., Scott, J., Zheng, W., McNeish, R. E., Holm, N., Hoellein, T. J., Baranski, E. L. (2019) Microplastic Contamination in Karst Groundwater Systems. *Groundwater*, *57*(2), 189–196.

Peller, J. R., Nelson, C. R., Babu, B. G., Iceman, C., Kostelnik, E. (2020). A review of microplastics in freshwater environments: locations, methods, and pollution loads (Chapter 4). In: Ahuja, S., Loganathan, B.G. (Eds.), *Contaminants in Our Water: Identification and Remediation Methods*, Part 4 – A Review of Microplastics in Freshwater Environments: Locations, Methods, and Pollution Loads. American Chemical Society, Washington, pp. 65–90.

PlasticsEurope (2019). *Plastics – The Facts 2019*. PlasticsEurope. https://www.plasticseurope.org/en/resources/market-data (accessed August 21, 2021).

Primpke, S., Cross, R.K., Mintenig, S.M., Simon, M., Vianello, A., Gerdts, G. Vollertsen, J. (2020a). EXPRESS: toward the systematic identification of microplastics in the environment: evaluation of a new independent software tool (siMPle) for spectroscopic analysis. *Applied Spectroscopy*, https://doi.org/10.1177/0003702820917760.

Primpke, S., Fischer, M., Lorenz, C., Gerdts, G., Scholz-Böttcher, B.M. (2020b). Comparison of pyrolysis gas chromatography/mass spectrometry and hyperspectral FTIR imaging spectroscopy for the analysis of microplastics. *Analytical and Bioanalytical Chemistry*, *412*, 8283–8298.

Primpke, S., Godejohann, M., Gerdts, G. (2020c). Rapid identification and quantification of microplastics in the environment by quantum cascade laser-based hyperspectral infrared chemical imaging. *Environmental Science & Technology*, *54*(24), 15893–15903.

Primpke, S., Wirth, M., Lorenz, C., Gerdts, G. (2018). Reference database design for the automated analysis of microplastic samples based on Fourier transform infrared (FTIR) spectroscopy. *Analytical and Bioanalytical Chemistry*, *410*, 5131–5141.

Primpke, S., Lorenz, C., Rascher-Friesenhausen, R., Gerdts, G. (2017). An automated approach for microplastics analysis using focal plane array (FPA) FTIR microscopy and image analysis. *Analytical Methods*, *9*(9), 1499–1511.

Provencher, J. F., Covernton, G. A., Moore, R. C., Horn, D. A., Conkle, J. L., Lusher, A. L. (2020). Proceed with caution: The need to raise the publication bar for microplastics research. *Science of the Total Environment*, *748*, 141426.

Quik, J. T. K., Velzeboer, I., Wouterse, M., Koelmans, A. A., van de Meent, D. (2014). Heteroaggregation and sedimentation rates for nanomaterials in natural waters, *Water Research*, *48*, 269–279.

Rezania, S., Park, J., Md Din, M. F., Mat Taib, S., Talaiekhozani, A., Kumar Yadav, K., Kamyab, H. (2018). Microplastics pollution in different aquatic environments and biota: a review of recent studies. *Marine Pollution Bulletin*, *133*, 191–208.

Rocha-Santos, T. & Duarte, A.C. (2015). A critical overview of the analytical approaches to the occurrence, the fate and the behavior of microplastics in the environment. *Trac-Trends in Analytical Chemistry 65*, 47–53.

Rochman, C. M., Hoh, E., Kurobe, T., Teh, S. J. (2013). Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress. *Scientific Reports*, *3*, 3263.

Roebroek, C.T.J., Harrigan, S., van Emmerik, T., Baugh, C., Eilander, D. Prudhomme, C., Pappenberger, F. (2021). Plastic in global rivers: Are floods making it worse? *Environmental Research Letters*, 16, 025003, https://doi.org/10.1088/1748-9326/abd5df

Sanchez, W., Bender, C., Porcher, J. M. (2014). Wild gudgeons (*Gobio gobio*) from French rivers are contaminated by microplastics: preliminary study and first evidence. *Environmental Research*, *128*, 98–100.

Sarijan, S., Azman, S., Said, M. I. M., Jamal, M. H. (2020). Microplastics in freshwater ecosystems: a recent review of occurrence, analysis, potential impacts, and research needs. *Environmental Science and Pollution Research*, *28*(2), 1341–1356.

Seo, S., & Park, Y.-G. (2020). Destination of floating plastic debris released from ten major rivers around the Korean Peninsula. *Environment International*, *138*, 105655.

Shim, W.J., Hong, S.H., Eo, S.E. (2017) Identification methods in microplastic analysis: a review. *Analytical Methods*, *9*(9), 1384–1391.

Schirinzi, G. F., Köck-Schulmeyer, M., Cabrera, M., González-Fernández, D., Hanke, G., Farré, M., Barceló, D. (2020). Riverine anthropogenic litter load to the Mediterranean Sea near the metropolitan area of Barcelona, *Spain. Science of the Total Environment*, *714*, 136807.

Schmidt, C., Krauth, T., Wagner, S. (2017). Export of plastic debris by rivers into the sea. *Environmental Science and Technology*, *51*(21), 12246–12253.

Schoneich-Argent, R. I., Dau, K., Freund, H. (2020). Wasting the North Sea? A field-based assessment of anthropogenic macrolitter loads and emission rates of three German tributaries. *Environmental Pollution*, *263*, 114367.

Schwarz, A. E., Ligthart, T. N., Boukris, E., van Harmelen, T. (2019). Sources, transport, and accumulation of different types of plastic litter in aquatic environments: a review study. *Marine Pollution Bulletin*, *143*, 92–100.

Selvam, S., Jesuraja, K., Venkatramanan, S., Roy, P. D., Jeyanthi Kumari, V. (2021). Hazardous microplastic characteristics and its role as a vector of heavy metal in groundwater and surface water of coastal south India. *Journal of Hazardous Materials*, *402*, 123786.

Siegfried, M., Koelmans, A.A., Besseling, E., Kroeze, C. (2017). Export of microplastics from land to sea. *A modelling approach, Water Research*, *127*, 249–257.

Szymańska, M., & Obolewski, K. (2020). Microplastics as contaminants in freshwater environments: a multidisciplinary review. *Ecohydrology and Hydrobiology*, *20*(3), 333–345.

Tekman, M. B., Gutow, L., Macario, A., Haas, A., Walter, A., Bergmann, M. (2020). *Distribution of Litter Types in Different Realms (1,336 Publications)*. AWI-LITTERBASE. https://litterbase.awi.de/litter (accessed August 21, 2021).

Ter Halle, A., Jeanneau, L., Martignac, M., Jardé, E., Pedrono, B., Brach, L., Gigault, J. (2017). Nanoplastic in the North Atlantic Subtropical Gyre. *Environmental Science & Technology*, *51*(23), 13689–13697.

Teuten, E. L., Saquing, J. M., Knappe, D. R. U., Barlaz, M. A., Jonsson, S., Björn, A., Rowland, S. J., Thompson, R. C., Galloway, T. S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P. H., Tana, T. S., Prudente, M., Boonyatumanond, R., Zakaria, M. P., Akkhavong, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H. (2009). Transport and release of chemicals from plastics to the environment and to wildlife. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526), 2027–2045.

Triebskorn, R., Braunbeck, T., Grummt, T., Hanslik, L., Huppertsberg, S., Jekel, M., Knepper, T. P., Krais, S., Müller, Y. K., Pittroff, M., Ruhl, A. S., Schmieg, H., Schür, C., Strobel, C., Wagner, M., Zumbülte, N., & Köhler, H. R. (2019). Relevance of nano- and microplastics for freshwater ecosystems: a critical review. *TrAC – Trends in Analytical Chemistry*, *110*, 375–392.

Tramoy, R., Gasperi, J., Dris, R., Colasse, L., Fisson, C., Sananes, S., Rocher, V., Tassin, B. (2019). Assessment of the plastic inputs from the Seine basin to the sea using statistical and field approaches. *Frontiers Marine Science*, *6*, 151.

Tramoy, R., Gasperi, J., Colasse, L., Tassin, B. (2020). Transfer dynamic of macroplastics in estuaries – new insights from the Seine estuary: Part 1. Long term dynamic based on date-prints on stranded debris. *Marine Pollution Bulletin*, *152,* 110894.

UNEP (2016). *Marine Plastic Debris and Microplastics – Global Lessons and Research to Inspire Action and Guide Policy Change*. United Nations Environment Programme, Nairobi.

Unice, K.M., Weeber, M.P., Abramson, M.M., Reid, R.C.D., van Gils, J.A.G., Markus, A.A., Vethaak, A.D., Panko, J.M. (2019). Characterizing export of land-based microplastics to the estuary – Part I: application of integrated geospatial microplastic transport models to assess tire and road wear particles in the Seine watershed. *Science of the Total Environment*, *646*, 1639–1649.

van Calcar, C. J., & van Emmerik, T. H. M. (2019). Abundance of plastic debris across European and Asian rivers. *Environmental Research Letters*, *14*(12), 124051.

van Emmerik, T, Kieu-Le, T-C, Loozen, M, van Oeveren, K, Strady, E, Bui, X-T, Egger, M, Gasperi, J, Lebreton, L, Nguyen, P-D, Schwarz, A, Slat, B, Tassin, B. (2018). A Methodology to Characterize Riverine Macroplastic Emission Into the Ocean. *Front. Mar. Sci.*, 5:372.

van Emmerik, T., Loozen, M., van Oeveren, K., Buschman, F., Prinsen, G. (2019a). Riverine plastic emission from Jakarta into the ocean. *Environmental Research Letters*, *14*, 084033.

van Emmerik, T., Strady, E., Kieu-Le, TC. et al. (2019b). Seasonality of riverine macroplastic transport. *Scientific Reports*, *9*, 13549.

van Emmerik, T., & Schwarz, A. (2020). Plastic debris in rivers. *WIREs Water*, *7*(1). https://doi.org/10.1002/wat2.1398.

van Emmerik, T., Roebroek, C., De Winter, W., Vriend, P., Boonstra, M., Hougee, M. (2020a). Riverbank macrolitter in the Dutch Rhine–Meuse delta. *Environmental Research Letters*, *15*(10), 104087.

van Emmerik, T., Seibert, J., Strobl, B., Etter, S., den Oudendammer, T., Rutten, M., bin Ab Razak, M. S., van Meerveld, I. (2020b). Crowd-based observations of riverine macroplastic pollution. *Frontiers in Earth Science*, *8*, 1–12.

van Lieshout, C., van Oeveren, K., van Emmerik, T., Postma, E. (2020). Automated river plastic monitoring using deep learning and cameras. *Earth and Space Science*, *7*(8), e2019EA000960.

von Moos, N., Burkhardt-Holm, P., Köhler, A. (2012). Uptake and effects of microplastics on cells and tissue of the blue mussel *Mytilus edulis* L. after an experimental exposure. *Environmental Science & Technology*, *46*(20), 11327–11335.

van Wezel, A., Caris, I., Kools, S. A. E. (2016). Release of primary microplastics from consumer products to wastewater in the Netherlands. *Environmental Toxicology and Chemistry*, *35*(7), 1627–1631.

van Wijnen, J., Ragas, A.M.J., Kroeze, C. (2019). Modelling global river export of microplastics to the marine environment: sources and future trends. *Science of the Total Environment*, *673*, 392–401.

Vriend, P., Van Calcar, C., Kooi, M., Landman, H., Pikaar, R., Van Emmerik, T. (2020a). Rapid assessment of floating macroplastic transport in the Rhine. *Frontiers in Marine Science*, *7*, 10.

Vriend P, Roebroek CTJ and van Emmerik T (2020b). Same but different: a framework to design and compare riverbank plastic monitoring strategies. *Frontiers in Water*, *2*, 563791.

Wagner, M., & Lambert, S. (2018). Freshwater microplastics. In M. Wagner & S. Lambert (Eds.), *Handbook of Environmental Chemistry* (Vol. 58). Springer Nature, Cham, Switzerland. https://doi.org/10.1007/978-3-319-61615-5.

Wagner, M., Scherer, C., Alvarez-Muñoz, D., Brennholt, N., Bourrain, X., Buchinger, S., Fries, E., Grosbois, C., Klasmeier, J., Marti, T., Rodriguez-Mozaz, S., Urbatzka, R., Vethaak, A. D., Winther-Nielsen, M., Reifferscheid, G. (2014). Microplastics in freshwater ecosystems: what we know and what we need to know. *Environmental Sciences Europe*, *26*(1), 1–9.

Watkins L, McGrattan S, Sullivan PJ, Walter MT (2019). The effect of dams on river transport of microplastic pollution. *Science of the Total Environment*, *664*, 834–840.

Weideman, E. A., Perold, V., Ryan, P. G. (2020). Limited long-distance transport of plastic pollution by the Orange-Vaal river system, South Africa. *Science of the Total Environment*, 727, 138653.

Wolf, M., van den Berg, K., Garaba, S. P., Gnann, N., Sattler, K., Stahl, F., Zielinski, O. (2020). Machine learning for aquatic plastic litter detection, classification and quantification (APLASTIC-Q). *Environmental Research Letters*, *15*(11), 114042.

Wolff, S., Kerpen, J., Prediger, J., Barkmann, L., Müller, L. (2019). Determination of the microplastics emission in the effluent of a municipal waste water treatment plant using Raman microspectroscopy. *Water Research X*, *2*, 100014.

Wright S.L., Thompson R.C., Galloway T.S. (2013). The physical impacts of microplastics on marine organisms: a review. *Environmental Pollution*, *178*, 483–492.

Wu, W., Wang, S. S. Y. (2006). Formulas for sediment porosity and settling velocity. *Journal of Hydraulic Engineering*, *132*(8), 858–862.

Yang, L., Zhang, Y., Kang, S., Wang, Z., Wu, C. (2021). Microplastics in freshwater sediment: a review on methods, occurrence, and sources. *Science of the Total Environment*, *754*, 141948.

Yao, P., Zhou, B., Lu, Y. H., Yin, Y., Zong, Y. Q., Chen, M. Te, O'Donnell, Z. (2019). A review of microplastics in sediments: spatial and temporal occurrences, biological effects, and analytic methods. *Quaternary International*, *519*, 274–281.

Zbyszewski, M. & Corcoran, P.L. (2011). Distribution and degradation of fresh water plastic particles along the beaches of Lake Huron, Canada. *Water Air Soil Pollution*, *220*, 365–372.

Zhao, S., Wang, T., Zhu, L., Xu, P., Wang, X., Gao, L., Li, D. (2019). Analysis of suspended microplastics in the Changjiang Estuary: implications for riverine plastic input to the ocean. *Water Research*, 161, 560–569.

8

Degradation and Fragmentation of Microplastics

Anthony L. Andrady[1] *and Bimali Koongolla*[2]

[1] *Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC, USA*
[2] *Guangdong Provincial Key Laboratory of Applied Marine Biology, South China Sea Institute of Oceanology, Institution of South China; and Sea Ecology and Environmental Engineering, Chinese Academy of Sciences (CAS), Guangzhou, China*

The term *degradation* generally refers to changes that result in the loss of desirable properties of a material such as plastics. However, here we use a narrower meaning for the term to include only those changes caused by chemical reactions in the plastic material. Physical changes, such as crystallization or annealing can also negatively affect useful properties of plastics, but not being chemical changes these are not referred to as degradations but instead as deteriorations. In outdoor environments where the plastic[1] is routinely exposed to sunlight, degradation occurs particularly rapidly due to chemical changes caused by solar ultraviolet radiation (UVR). Over time, the useful properties of the plastic product such as color or mechanical integrity gradually decrease as a result of degradation, impairing its utility and shortening the useful lifetime of the product (Anderson et al. 2015; Gewert et al., 2018; Singh and Sharma 2008). Chemical changes that occur in the degradation of plastics are often accompanied by chain scission events that shorten the average chain length of polymer molecules. Useful mechanical properties of polymers rely primarily on their long-chain architecture that obtains very high inter-molecular attractive forces and chain entanglement to deliver their superior performance (see Chapter 1). Shortening the average chain length, therefore, weakens the material, often limiting its outdoor service life. While degradation of plastics on land environments has been extensively studied, degradation of plastics in the ocean environment has not received the same research attention. Understanding the fate of plastics litter in the marine environment, especially the mechanisms that lead to their invariable oxidation and fragmentation into microparticles, is important to mitigate the problem of plastic pollution of the ocean (Andrady 2015; Wypych 2015).

The degradation of plastics in the ocean environment is especially interesting because it is believed to be the primary mechanism leading to fragmentation that generates secondary microplastics (MPs) from plastic macro-litter. Not only are secondary MPs far more abundant in the ocean compared to primary MPs, but being generated in that environment, as opposed to being introduced from outside, their abundance in the ocean cannot be directly controlled or regulated. While the sources of influx of MPs into oceans have been identified (see Chapter 3), there appears to be no natural mechanism that removes them from the ocean within any practical timescale. Their interaction with marine life

---

[1] Plastics is a subset of the larger group of compounds called polymers. Here, we use the term interchangeably even though all polymers are not plastics (See Chapter 1).

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

through entanglement and particularly their ingestion is well known (see Chapter 12). With over 700 marine species (Kühn and van Franeker 2020) as well as numerous zooplankton species (Botterell et al. 2019) now reported to ingest MPs, the topic is of increasing ecological interest. MPs and possibly nanoplastics (NPs) are found in freshwater bodies as well (Eerkes-Medrano et al. 2015). Riverine transport is a major route of plastic debris into the ocean (Lebreton et al. 2017) (see Chapter 7). MPs exposed to solar UVR would continue to degrade and fragment yielding NPs (Zhu et al. 2020), but the latter have not been found in the ocean environment. A good understanding of the chemistry of fragmentation of common plastics found as debris in both freshwater and ocean environment is therefore critical to developing strategies to keep MPs out of the world's ocean.

Plastics are organic compounds[2] that will invariably degrade under long-term exposure to any outdoor environment including the ocean. The service lifetimes of outdoor plastics such as cladding (or siding) in buildings or marine engineering materials, routinely exposed to solar radiation during use, are limited by their rates of environmental photo-degradation. Generally, several environmental agents or stressors are responsible for the degradation process. Of these, solar UVR is the primary agent, while other factors include mechanical stresses, high temperature (Fairbrother et al. 2019), humidity (James et al. 2013), biological agents (Welden and Cowie 2017), and atmospheric pollutants (Pospíšil et al. 2004). In addition to the already-mentioned chain scission that weakens the plastic progressively, other concurrent changes such as discoloration, cracking, out-gassing, and increased crystallinity also commonly result from degradation.

The service lifetimes of plastics used outdoors or in marine applications, however, are not completely at the mercy of solar UV irradiance and high sample temperatures; plastic products intended for outdoor use are generally compounded with potent UV stabilizers (Petukhova and Fedorov 2019; Wypych 2020) or chemicals that retard photo-degradation, in addition to the thermal stabilizers typically used to protect them from degradation during high-temperature processing (Gugumus 2000). The UV stabilizers can be inorganic pigments such as TiO_2 (rutile) that absorb solar UVR shielding the underlying plastic material (Turton and White 2001), organic UV absorbers, or compounds that interfere with degradation reactions (Gijsman 2017). Particularly effective are compounds that are added to the plastic at very low levels (<0.5%) to efficiently deactivate the reactive free-radical intermediates responsible for oxidation and chain scission. Among these, especially popular are the hindered amine light stabilizers (HALSs). In plastics that degrade *via* free-radical mediated chemical pathways, such as PE, PP, and PS, these radical quenchers mop up the propagating radicals converting them into less reactive or unreactive products. Stabilizers not being covalently linked to the polymer molecules can, however, leach out from the plastic in contact with seawater (Rani et al. 2017) or themselves photodegrade (Wypych 2020) and therefore have a finite effective lifetime in plastics in the ocean.

In this chapter, a summary introduction to mechanisms of photo-degradation of common plastics will be described followed by how these might be modified when degradation takes place in the marine environment. Finally, the available data on fragmentation of common plastics during photo-oxidation will be discussed.

8.1 Classifying Degradation

Degradation processes are generally classified according to the primary causative agent as shown in Figure 8.1. With plastics typically encountered in the marine environment, PE, PP, PS, and PET (see Chapter 1), it is photo-oxidation initiated by solar UVR that is mostly responsible for

---

[2] Common plastics found in the ocean environment are organic, but inorganic polymers such as polyphosphazenes, polysilanes, and polysilazanes are known.

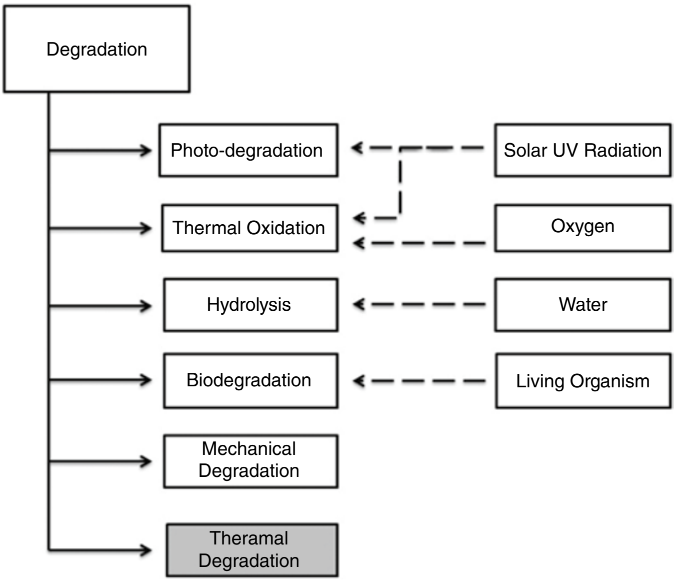


Figure 8.1 Agents that bring about degradation and fragmentation of plastics.

degradation (Klemchuk 1990). Often, it is accompanied by thermally initiated oxidation as well, but compared to photo-oxidation, it progresses at a relatively slower rate. Mechanical degradation generally occurs at the high shear forces encountered by plastics in processing operations but not in outdoor exposure. Unique to the ocean environment is mechanical fragmentation (Chubarenko et al. 2020; Efimova et al. 2018; Song et al. 2017) of both degraded and undegraded plastics leading to fracture of plastics. The mechanical forces generated by wave action in the "swash zone" on beaches, where the waves break, with plastics abraded by sand, can fragment plastic debris in the ocean. Given that the slamming pressure of waves on sloping beaches (Yang 2017) is in the range of 18–32 kPa, this can be a significant fragmentation mechanism (White and Turnbull 1994). Note that this is not a degradation but a mechanical deterioration that interestingly yields thin ribbon-like fragments of plastics (Chubarenko et al. 2020) that might be mistaken for short fibers. Importantly, the same mechanical forces in the ocean also help loosen up and release fragments from the surface of highly-weathered plastics, as will be described later. While some hydrolysis (Arhant et al. 2019; Davies and Evrad 2007) and biodegradation (see Chapter 11) also occur under marine conditions, they proceed at an appreciable rate with only a few types of plastics (Lucas et al. 2008; Sudhakar et al. 2008), including some thermosets such as polyurethanes (PUs) (Davies and Evrad 2007) and aliphatic polyesters (Albertsson and Karlsson 1993). Biodegradation and hydrolysis do not contribute appreciably to the degradation of common thermoplastics found in marine debris. Not operative at all in the marine environment is thermal degradation that usually requires very high temperatures to break down polymer chains (Çit et al. 2009).

The classification in Figure 8.1, however, is for convenience of description and simplifies the complex interplay of different degradative agents that plastics are simultaneously subjected to in real environments. Several of these agents, especially solar UVR, high temperatures, and mechanical stresses (Winkler et al. 2019) acting in concert bring about degradation in the environment, the combined effect of which is referred to as natural weathering (Feldman 2002). The term "aging" is sometimes used interchangeably with weathering in the literature (White 2006), but as it also includes annealing, the term "weathering" is preferred. Laboratory weathering degradation in general, and that of plastics in the oceans in particular, cannot duplicate the complexities of real environments and often focus on a few of the pertinent agents.

Different plastics degrade in the environment at different rates, and these rates are always determined by both the chemical structure of the polymer and the nature of the environment the material is exposed to.

8.2 Weathering Under Laboratory Accelerated Conditions

Natural weathering of plastics on land environments is quite a slow process even under harsh exposure conditions of a sandy beach. For instance, PE or PP plastic films (which do not contain any UV stabilizer), exposed to harsh conditions at Arizona or, Florida, take about a year or so to weaken to the point of embrittlement (Fayolle et al. 2007; Jabarin and Lofgren 1994). When embrittled, the tensile elongation at break of the friable plastic is reduced to <5%, and the material is too fragile to even handle without fragmenting. The same extent of degradation can, however, be reached in only a few weeks or months of exposure in laboratory-accelerated weathering. Accelerated weathering also allows for closer control of temperature and the radiation dose received by the plastic. In laboratory-accelerated weathering the plastic is typically exposed to a high-intensity light source ideally with a spectral irradiance distribution matching that of solar radiation received on the Earth's surface (Hiejima et al. 2018), and maintained at an elevated temperature to accelerate the degradation. Commercial equipment to conveniently carry out laboratory-accelerated weathering exposures of materials is available.

8.2.1 The Light Source

The rates and mechanisms of degradation are highly dependent on the spectral quality of the light source used in accelerated exposures (François-Heude et al. 2015; Pickett et al. 2008; Gok et al. 2019). Therefore, the source used should always be indicated when reporting accelerated weathering data. The spectral irradiance distribution (E_λ) ($\mathrm{W/m^2}$) of the source used should ideally match that of solar radiation to ensure that identical chemical pathways are obtained in both natural and accelerated exposures. Borosilicate-filtered xenon source radiation closely matches solar radiation (air mass 1), compared to, for instance, with that for a UV-340 fluorescent source and ASTM G173-03 standard, as shown in Figure 8.2. The photon dose received by the sample is given by the following equation:

$$D = \int_{0}^{t} \int_{\mathrm{All}\,\lambda} E_\lambda \, d\lambda \tag{I}$$

where D is the dose of radiation, E_λ is the irradiance ($\mathrm{W/m^2}$) at wavelength λ, and t is the duration of exposure. The second integral in Equation (I) covers the entire wavelength range of the source. Estimating equivalent months of outside exposure (based on the dose alone) when calculated for a source that is not spectrally similar to sunlight, is therefore not useful.

Figure 8.3 illustrates the very different spectral features of radiation from mercury vapor and metal halide lamps, both extensively used in accelerated-weathering studies under marine conditions. With these sources the UVR region of the spectrum, which is mostly responsible for polymer degradation, is very different from that of the solar ultraviolet spectrum. It is also critical to ensure that no UVC ($\lambda < 290$ nm) radiation is emitted by the source. The germicidal wavelengths in UVC, not typically found in sunlight reaching the Earth's surface, have very high photon energy and are the most damaging radiation to plastics. Photodamage suffered by the sample is given by the

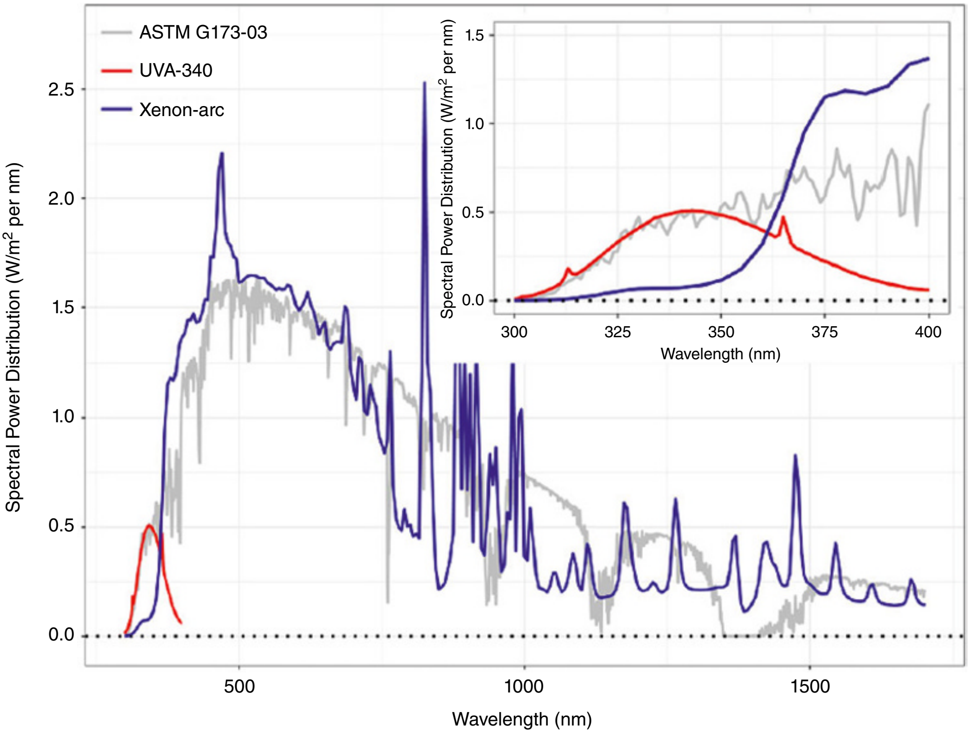


Figure 8.2 Spectral power distributions of the ASTM G173-03 standard (AM 1.5), xenon-arc full spectrum, and fluorescent UVA-340 light sources. The inset shows the UV region between 300 and 400 nm. Reproduced with permission from Gok et al. (2019).

wavelength sensitivity distribution *F*(λ) for a given plastic compound for a specified mode of damage such as discoloration or surface cracking. The wavelength sensitivity spectrum *F*(λ) is a weighting function and cannot be generalized for different compounds of the same plastic or for different modes of damage. Photodamage D is then given by:

$$D = \int_0^t \int_{\text{All }\lambda} F(\lambda) E_\lambda \, d\lambda \qquad \text{(II)}$$

The exceptional sensitivity of photodegradation of plastics to the wavelength λ of radiation is illustrated in Figure 8.4 that shows the change in tensile extensibility (%) of strip samples (0.42 mm thick) of photodegradable[3] PE (copolymer of ethylene with 1% carbon monoxide) laminates exposed to a xenon light source at 77 °C for 117 hours. Sample films were exposed to light behind a series of cut-on filter each transmitting only a part of the source spectrum as illustrated in Figure 8.4 (left). Each sample therefore receives only a part of the solar-simulated source spectrum. In Figure 8.4 (left), the horizontal axis of the plot gives the wavelength corresponding to 5% transmittance of each of the filters and the vertical axis is the average tensile extensibility (%) of the degraded PE samples exposed behind each filter. The samples exposed behind the cut-on filter that transmitted radiation of λ > about 328 nm (or only wavelengths longer than UVB) showed little or

---

[3] Photodegradable copolymer of PE from ITW HiCone Inc. was used in this experiment to obtain results in a short exposure time.

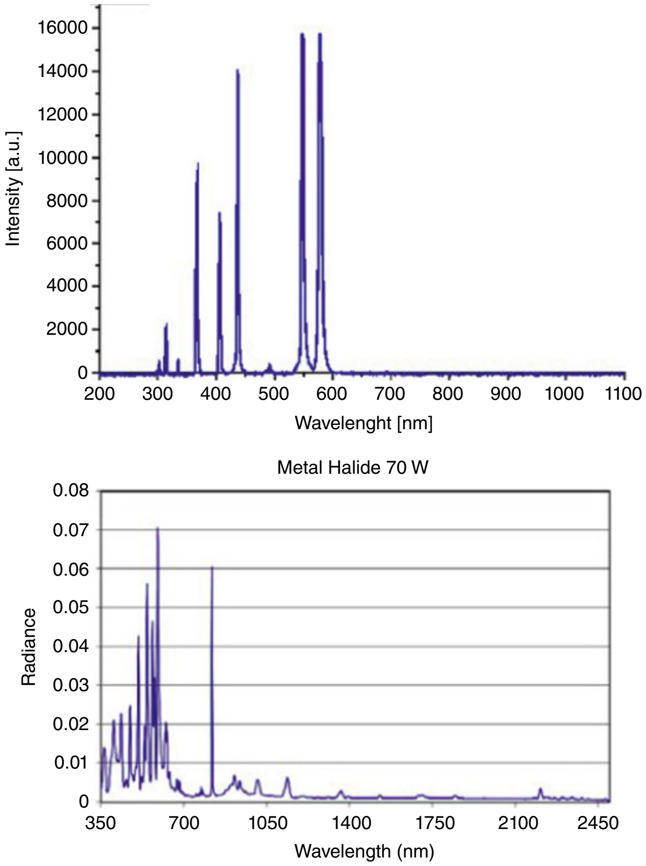


Figure 8.3 Comparison of the spectral features of a mercury vapor lamp with that of a metal halide lamp. Reproduced with permission from Elvidge et al. (2010).

no change in extensibility (Andrady 1996). Whenever any UVB reached the sample through the appropriate cut-on filter, degradation ensued. Similar results were reported by Hu Xingzhou (1997) for 100-μm polyethylene films exposed to a xenon source for 280 hours. The fraction of UVA and UVB in the source radiation and therefore the spectral features of the source primarily determine the degradation rate of the plastic.

Table 8.1 gives selected values of the irradiance of different light sources used in laboratory weathering (François-Heude et al. 2015), illustrating the differences in the irradiance (W/m^2) between the xenon arc mercury lamp (SEPAP 14.24) and two types of UVA fluorescent lamps. Since their overall light output is higher than that of sunlight (for Shanghai), exposure to them obtains accelerated weathering. Also shown is the overlap of the absorption spectrum of two important chromophores in PE and PP oxidation, the hydroperoxide [–ROOH] and ketone [>C=O] moieties, with the source spectra. The overlap function is given in Table 8.1, for example, for [–ROOH] groups is

$$J_{\mathrm{ROOH}} = I_{(\mathrm{absev})} / \left[\mathrm{ROOH}\right] \tag{III}$$

where $I_{(\mathrm{absv})}$ is the volumic absorbed energy and [ROOH] is the hydroperoxide concentration. At a given irradiance (W/m^2) the value of the concentration-independent overlap, depends strongly on the source spectrum. The formulations in Equations (II) and (III) implicitly assume reciprocity (as discussed below) because of the differences in irradiance distributions of sources, but the different impacts of the effective radiation are evident from Table 8.1.

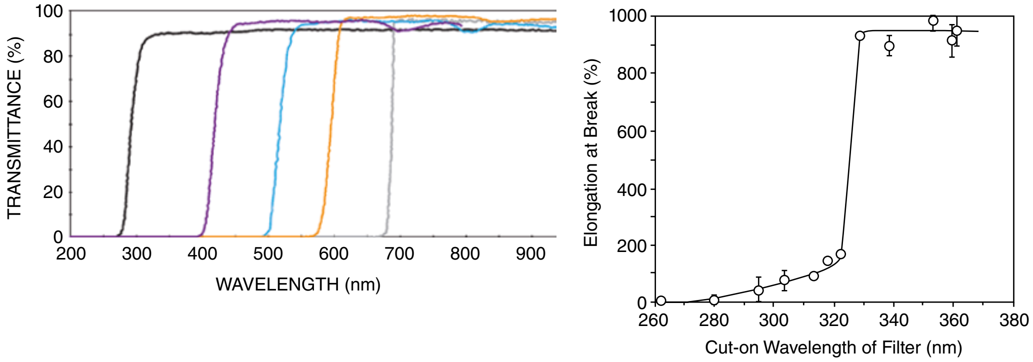


Figure 8.4 (Left) Transmittance spectra for several cut-on filters. (Right) Change in average tensile extensibility (%) for photodegradable polyethylene material exposed behind a series of cut-on filters. Filter wavelengths are those at 5% transmission and standard error of the mean is indicated by the bars. Courtesy: Andrady et al., JAPS (1996).

Table 8.1 A comparison of radiation sources used in laboratory-accelerated weathering of PP.

Source (lamp)	Irradiance (W/m^2) In (300 > λ < 400 nm	Overlap with [ROOH] (E/mol.s)	Overlap with [>C=O] (E/mol.s)
Sunlight*	3.0	8.92×10^{-8}	1.51×10^{-6}
Xenon	35	9.45×10^{-7}	1.47×10^{-5}
Xenon	42	7.87×10^{-7}	1.20×10^{-5}
Xenon	55	1.45×10^{-6}	2.25×10^{-5}
UVA-351	82	$2,84 \times 10^{-6}$	$4,75 \times 10^{-5}$
UVA-351	163	5.66×10^{-6}	9.47×10^{-5}
UVA TLK-40	6	1.45×10^{-7}	2.31×10^{-6}
SEPAP14/24	66	8.45×10^{-6}	1.25×10^{-4}
SEPAP14/24	86	1.10×10^{-5}	1.64×10^{-4}

*Shanghai Sunlight. Data selected from (François-Heude et al. 2015).

8.2.2 Light Intensity and Temperature

Photo-oxidative degradation is readily accelerated by combining a higher intensity of radiation (compared to solar radiation) and maintaining a high sample temperature, often with cycling (between hot/light and cold/dark conditions [Copinet et al. 2004]). Sometimes an intermittent water spray is also used in such exposures that are typically carried out in commercially available environmental chambers. Of these, increasing the temperature has the greatest effect on the rate of degradation (Bandow et al. 2017). The Arrhenius relationship between the rate of chemical reactions and the temperature is well known and how much acceleration might be achieved depends on the activation energies of the damage processes. With activation energy for photoreactions of aliphatic polymers ~27–50 kcal/mol and aromatic polymers ~12–20 kcal/mol (Pickett 2020), even a small increase in temperature can obtain significant acceleration in degradation rates. Increasing the intensity of the UV radiation (by using multiple lamps) at higher temperatures, obtain accelerated degradation of plastics, as demonstrated in the photodegradation of polycarbonates (Pickett et al. 2019), PET (Gok et al. 2019), and PE (Bigger et al. 1992; Fairbrother et al. 2019).

Care must be taken, however, to ensure that neither the high intensity of radiation (Hsueh et al. 2020) nor the high temperatures result in degradation chemistries not typically obtained in field exposure to solar UVR at ambient temperature (Therias et al. 2020). Increasing the intensity of UVR to accelerate degradation assumes reciprocity between the intensity I ($\mathrm{MJ/m^2}$) and the duration of exposure t, so that photo-damage is given by Equation (IV) (Chin et al. 2005; Martin et al. 2003; White et al. 2009).

$$\text{Photo-damage} = I.t^{n} \tag{IV}$$

where $n = 1$.

This relationship (also called the Schwarzchild's law) need not hold for all plastics that undergo weathering or for changes in different properties of the same plastic, during accelerated weathering. The exponent n in the equation can have values other than unity for different plastics and for various modes of photo-damage (Kollmann and Wood 1980). For instance, on photodegradation of HDPE, the change in bulk stiffness showed good reciprocity at different light intensities while that for change crystallinity in the same exposure, did not (Fairbrother et al. 2019). Equation (II) implicitly assumes reciprocity ($n \sim 1.0$) in its formulation as $F(\lambda)$ is generally determined in a separate experiment using monochromatic radiation. This function does not take into account any synergism or mutual suppression of degradation reactions at different wavelengths acting together nor does it accommodate potential temperature dependence of reciprocity.

8.3 Photo-Oxidation Pathways of Common Plastics

This section reviews the chemistry of photo-oxidation of common polymers found in the ocean environment, especially those that float in seawater. PE is reported to be the predominant plastic in both beach debris and surface waters (Erni-Cassola et al. 2019; Wilcox et al. 2020) in a majority of studies. It is also the resin manufactured in the highest volume globally and being popular in packaging uses, more likely to turn up in beach and urban litter. The chemistry behind the photodegradation of PE therefore deserves detailed attention. Polypropylene (PP) is generally the second-most frequent plastic material found in the ocean, followed by PS foam and nylon used in fishing gear (Hess et al. 1999). Both PP and PS generally follow the autoxidation scheme described for the case of PE (Gijsman 2008) with some modifications that arise from their structural differences. Oxidation chemistry for PE is discussed in detail here, with differences for PP and PS pointed out subsequently. This is a descriptive discussion of the basic chemistry of known degradation pathways in air for these three plastics, with the kinetics of degradation left out because of space constraints. Though not included here, even negatively buoyant plastics such as nylon, cellulose acetate, PVC, and PET can undergo weathering in the dry sediment or the beach environment.

8.3.1 Photo-degradation of Polyethylene

Solar UV-initiated oxidative degradation of PE in air has been well studied and the basic chemistry discussed in the early literature (Reich and Stivala 1971; Stivala et al. 1983). Basic photochemistry teaches that only the radiation that is absorbed by the plastic can cause any photoreaction, but neither PE nor PP has structural features (or chromophores) that allow them to absorb solar UVR. However, they invariably have a suite of impurities that can act as chromophores that do absorb UVR. These include low levels of chain unsaturation (Chabira et al. 2008; Rajakumar et al. 2009) and hydroperoxide or carbonyl functionalities (Gijsman, P. 2008) that result from high temperature (which can reach up to 300 °C), and high-shear processing of the plastic into pellets or products (Yanai et al. 1995). Catalyst residues, traces of metals, and environmental pollutants can also facilitate the absorption of solar UV radiation by these aliphatic polymers.

Environmental photo-oxidation of plastics is a free-radical process best described under three stages: initiation, propagation, and termination (Gijsman 2008). Initiation is the stage where free-radicals are photolytically generated to initiate oxidation reactions. Solar radiation reaching the earth's surface contains only 4–6% of UVR (290–400 nm) that is sufficiently energetic (72–97 kcal/mol) to directly photolyze covalent bonds in the polymer (Rånby 1989) to generate secondary (and some primary) macro-alkyl radicals [R•] that serve as initiators of oxidation (see reaction (1); Karlsson et al. 2018). Most of the [R•] radicals formed in reaction (1) and (5) will tend to be secondary macro-radicals in the case of PE, except at branch points where a tertiary radical may be possible. Tertiary radicals formed in branched PE are known to facilitate faster degradation compared to their secondary analogs (Decker et al. 1973). The radicals are macro- or chain-radicals in polymers in the solid-state and therefore have very limited mobility. Only small radicals such as [•OH] can move about in the medium and bulk of the polymer. Those such as [R•] secondary radicals being relatively large and have limited mobility.

Initiation

$$\text{Polymer}\left[\text{RH}\right] \rightarrow \text{Mainly R}\bullet \tag{1}$$

Propagation

$$\text{R}\bullet + \text{O}_2 \rightarrow \text{ROO}\bullet \tag{2}$$

$$\text{ROO}\bullet + \text{RH} \rightarrow \text{ROOH} + \text{R}\bullet \tag{3}$$

$$\text{ROOH} \rightarrow \text{RO}\bullet + \bullet\text{OH} \tag{4}$$

$$\text{HO}\bullet + \text{RH} \rightarrow \text{R}\bullet + \text{H}_2\text{O} \tag{5}$$

Termination

$$\left.\begin{array}{l}2\text{R}\bullet \\ \text{ROO}\bullet \ + \text{ROO}\bullet \\ 2\text{ROO}\bullet\end{array}\right\} \rightarrow \text{Non-radical products} \tag{6}$$

Propagation reactions that continue the oxidation process are of special interest because the scission of long polymer chains that decreases the mechanical integrity of PE, are associated with this step. The chemistry of propagation has been well studied in alkanes and starts with the highly reactive secondary macro-alkyl [R•] radicals that typically have short lifetimes (Pilař et al. 2017). These react with oxygen (reaction (2)) yielding polymer-peroxy [ROO•] radicals, provided there is sufficient oxygen dissolved in the polymer. Alternatively, the [R•] radical may abstract a hydrogen atom from another LDPE chain nearby, essentially shifting the radical to a different location in the bulk or to another chain, by a process called "radical hopping" (Hicks 2007) ($\text{R}\bullet + \text{R}'\text{H} \rightarrow \text{RH} + \text{R}'\bullet$). When adequate oxygen is available, reaction (2) is at least two orders of magnitude faster than the "hopping" reaction and is preferred (Bracco et al. 2018). The oxygen that diffuses into the polymer from air or seawater is consumed by this single reaction; dissolved oxygen in plastics must be replenished by fast enough diffusion from air (or sewater) if propagation is to continue. This is not always the case, especially with thick samples that become oxygen-starved especially in the interior, resulting in diffusion-controlled oxidation. As diffusion is from the surface into the bulk (in the z-direction), the rate of oxidation will depend on the thickness of the sample (Cunliffe and Davis 1982; Furneaux et al. 1981).

The resulting [ROO•] radical abstracts a hydrogen atom and is converted into a polymer hydroperoxide [ROOH] (reaction (3)) in a relatively slow reaction that determines the rate of propagation. Decomposition of this hydroperoxide [ROOH] *via* reaction (4) into [RO•] and hydroxyl radicals [•OH] occurs photolytically by solar UVR of $\lambda < 340$ nm and also thermally. This dissociation generates more free radicals, making the sequence autocatalytic or an autoxidation (Gryn'ova et al. 2011). Unimolecular decomposition of [ROOH] into radicals has relatively high activation energy, but the alternative route of bimolecular dissociation is unlikely in solid polymers as chains have very limited mobility making encounters of a pair of [ROOH] groups quite rare. The radical pair (RO• and •OH) resulting from dissociation is strongly associated with each other and in solid polymers is said to exist in a "cage", and some degree of "cage recombination" of the radical pair is to be expected (Selonke et al. 2012). For solid PP, Garton (1980) estimated that only 4.5% of radicals escape cage recombination to continue on propagation. These radicals, however, are very efficient and repeat the propagation reaction cycle numerous times before terminating, creating a long kinetic chain of propagation. The repeating cycle of propagation is illustrated in Figure 8.5 and is well established for polyolefins (Mayo 1978; Niki et al. 1973).

In the oxidizing polymer, there will be three types of chain-radicals, [R•], [RO•], and [ROO•], and these may interact with each other leading to biradical termination. Under diffusion-controlled conditions, crosslinking or chain extension through [R•] radical reactions is likely. The reaction of the [ROO•] radical with an alkyl [R•] radical (by the Russell mechanism) (Russel 1957) yielding a macro-ketone

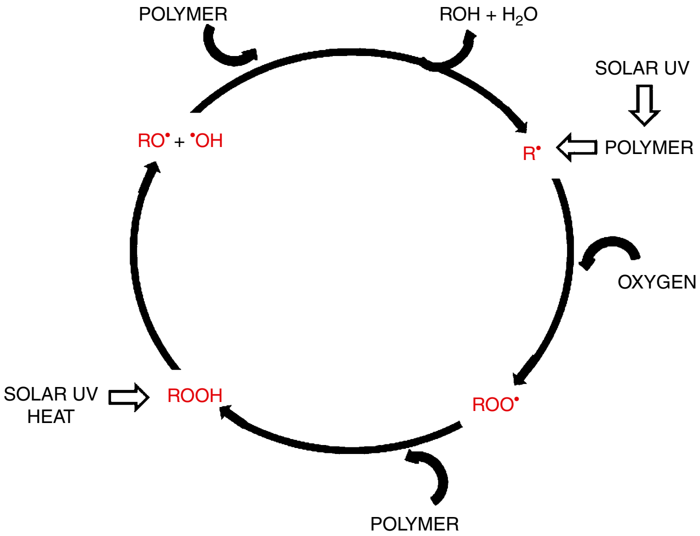
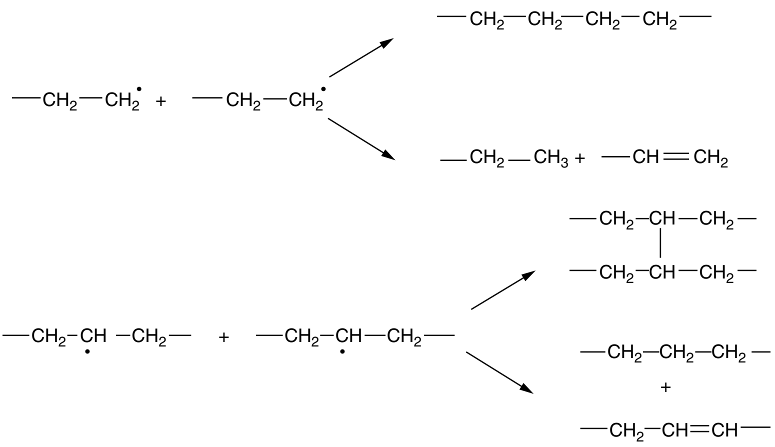


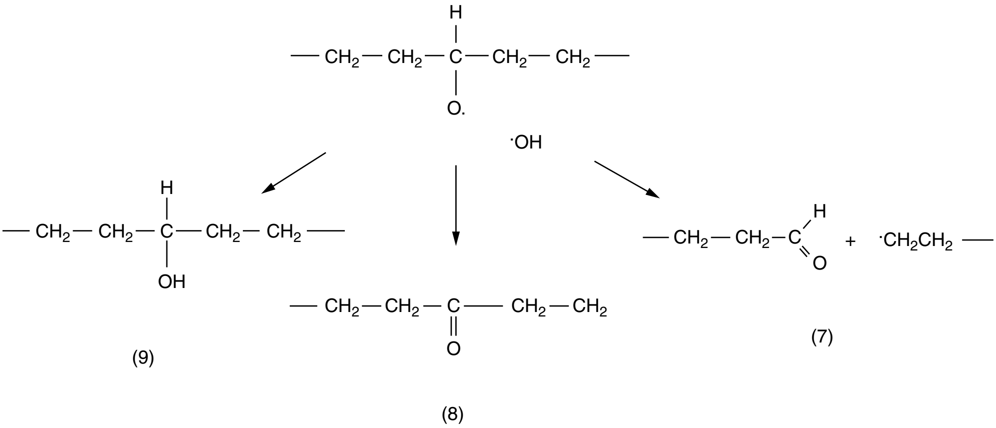
Figure 8.5 Photo-oxidation of polyolefins illustrating the autocatalytic nature of the process.

and a macro-alcohol is also possible as the [R•] radical moves about by radical hopping. A unimolecular termination resulting in terminal unsaturation is possible in theory, but is less likely.



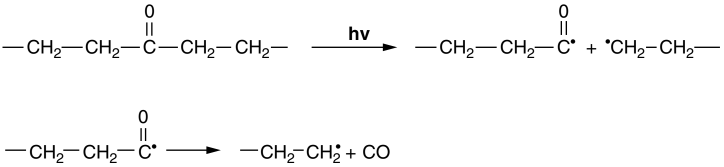
8.3.1.1 Carbonyl Compound Products

Most reaction products observed during PE oxidation are believed to arise from various reactions of the macro-alkoxy [RO•] radicals. The long-chain [RO•] radical may (i) undergo β-scission, forming a chain-terminal aldehyde (reaction (7)) (Hartley and Guillet 1968); (ii) form an in-chain ketone (reaction (8)), or (iii) abstract hydrogen to form alcohol (reaction (9)). The β-scission reaction is the primary mechanism that obtains chain scission in oxidation of most polymers of interest to this discussion and produces a terminal aldehyde on the chain at the point of scission, that may lose a carbon monoxide (CO) molecule to form another alkyl [R•] radical.



The ketone produced in reaction (8) is a strong chromophore that undergoes photolysis *via* Norrish I and II reactions shown below. In Norrish II photo-conversion, which does not yield radicals, the macro-ketone (>R=O) abstracts a hydrogen from a γ-carbon atom, resulting in chain scission. The secondary macro-alcohol formed in reaction (9), as well as all aldehydes and ketones formed in these reactions, may oxidize further to form carboxylic acids and esters (Hakkarainen and Albertsson 2004). Carboxylic acid is therefore, a major product in PE oxidation (Yagoubi et al. 2015), and the low molecular weight acids are volatilized during photo-initiated oxidation of LDPE (Lomonaco et al. 2020). Chain scission by Norrish photoreactions (reactions (10) and (11)) generates chain unsaturation. The generation of the carbonyl compounds can be readily monitored spectroscopically.

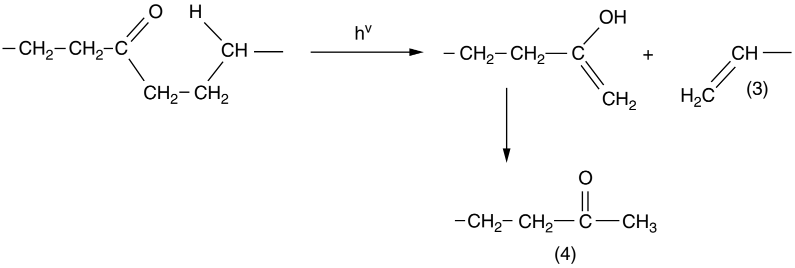
The broad carbonyl absorption band between 1640 and 1840 cm^{-1} in FTIR spectra of oxidized PE evolves with the duration of exposure and is a complex band with overlapping peaks of different oxidation products with a carbonyl functionality in their structure. The carbonyl index (CI), the ratio of the >C=O band intensity to that of an oxidation-invariant peak (e.g. the band at 2020 cm^{-1}) in the spectra, is often used to quantify the extent of photo-oxidation. The evolution of the carbonyl absorption band with the duration of exposure in LDPE, is shown in Figure 8.6 (left) with the de-convolution of the band into its components by Gaussian curve fitting shown in Figure 8.6 (right). The intensity of this peak increases linearly with the duration of exposure.



$$-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2- \xrightarrow{h\nu} -CH_2-CH_2-\overset{O}{\overset{\|}{C}}{}^{\bullet} + {}^{\bullet}CH_2-CH_2-$$

$$-CH_2-CH_2-\overset{O}{\overset{\|}{C}}{}^{\bullet} \longrightarrow -CH_2-CH_2^{\bullet} + CO$$

Norrish I reaction (10)



Norrish II reaction (11)

In a multi-laboratory study of accelerated degradation of PE under xenon-source as well as carbon-arc source radiation, the carbonyl index of the weathered plastic correlated well with exposure duration (Shimizu et al. 2016). Changes in, and the development of, new functional groups during exposure are conveniently monitored using Fourier Transform Infra-Red (FTIR) spectroscopy, carried out in the Attenuated Total Reflectance (ATR) mode with thick samples such as MPs. As might be expected from Norrish reaction mechanisms, the intensity of carbonyl absorption in FTIR spectra correlates well with that of the –C=C– unsaturation peaks (Yagoubi et al., 2020) and with the decrease in the tensile extensibility of polyethylene (PE) films (Andrady et al. 1993). Figure 8.6 shows the increase in the area of carbonyl absorption in FTIR spectra during natural weathering of LDPE, and the mathematical deconvolution of the complex peak into component functionalities. The assignments of the major peaks in the band suggested by Yagoubi et al. (2020) is given in Table 8.2.

8.3.2 Photodegradation of Polypropylene (PP)

For the most part, photo-oxidation of PP follows the same general reaction sequence described for PE, similarly increasing in fractional crystallinity (Gallo and Severini 2013; Rabello and White 1997) and decreasing the average molecular weight due to chain scission (Ni et al. 2015), as oxidation progresses. However, a few important differences from the oxidation of PE need to be appreciated.

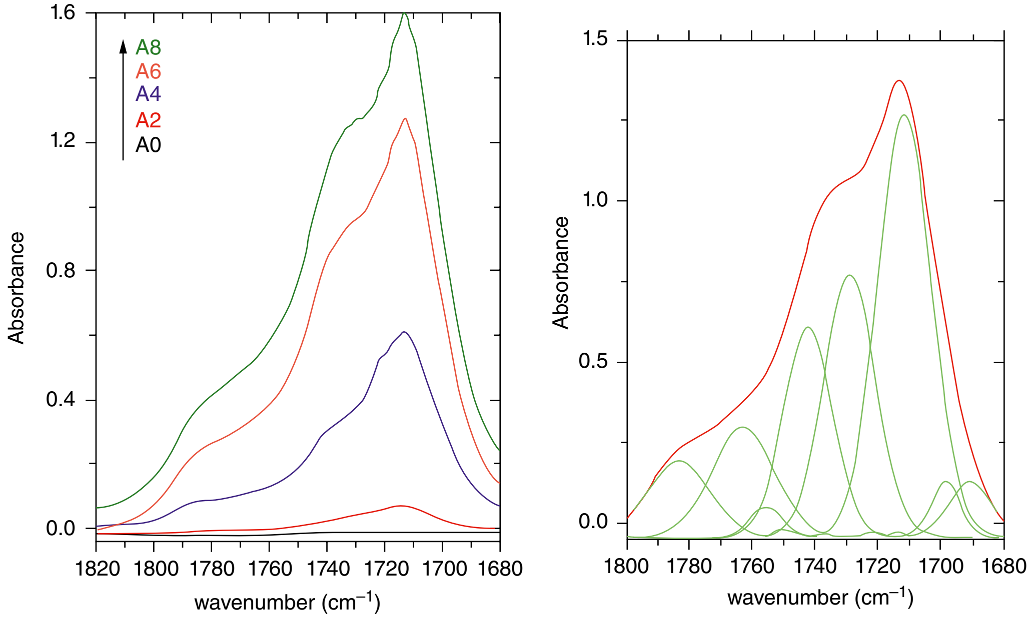


Figure 8.6 (Left) Evolution of the carbonyl band in FTIR spectra of the LDPE film during natural weathering for different durations. (Courtesy of Rodriguez et al. 2020). (Right) Mathematical deconvolution of the complex carbonyl absorption band into components (Courtesy of Yagoubi et al. 2015).

Table 8.2 Position of component peaks that compose the broad carbonyl absorption band in FTIR spectra of naturally weathered of an LDPE film with no UV stabilizer (thickness 180 micron).

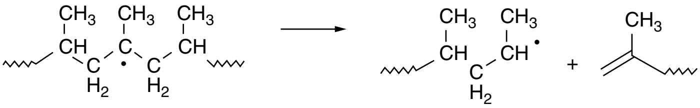
Peak position (per cm)	Assignment
1686	Ketones and α, β unsaturated carboxylic acids
1714	Carboxylic acids
1722	Ketones
1733	Aldehydes
1739	Esters
1750	Per-acids
1756	Free monocarboxylic acid
1777	Per-esters
1785	γ Lactone

Values based on Yagoubi et al. (2015).

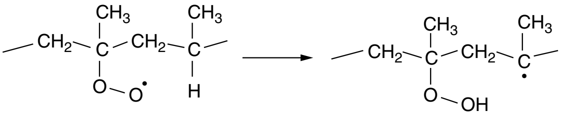
These arise mostly from the structural feature of PP having a tertiary carbon atom in each repeat unit; in fact, about a third of the carbon atoms in PP are tertiary. This feature modifies the oxidative reactions described above for PE. Initiation as in the case of PE is by the action of solar UVR absorbed by trace chromophoric impurities, but the generated chain-alkyl radicals [R•] are tertiary macro-radicals, as the hydrogens attached to the tertiary carbon are particularly photo-labile (Duvall 2014). The –C–H bond energy in alkanes for tertiary carbons (396–400 kJ/mol) is significantly lower than that for secondary carbons (413–416 kJ/mol). While the generation of some secondary alkyl radicals cannot be ruled out, the analysis of weathered PP shows predominantly tertiary hydroperoxides

(Tidjani 1997). In addition, the tertiary [R•] radicals are relatively more stable and have longer lifetimes compared to the primary or secondary chain-radicals of PE.

The tertiary [R•] radicals also readily participates in "radical hopping" as they are longer-lived (relative to those of PE) and as PP has abundant labile tertiary hydrogens (Gallo et al. 2006; Grause et al. 2020) to abstract in hopping reactions. In addition, the long-lived tertiary alkyl radicals of PP can undergo β-scission into an unsaturated end group and a radical, as shown in reaction (12).



Beta-scission in tertiary alkyl radical (12)



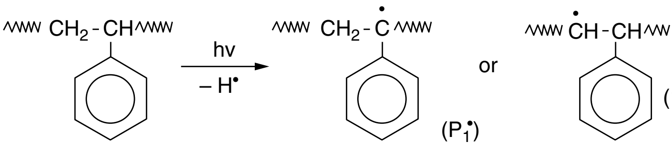
Creation of adjacent hydroperoxides (13)

However, the more likely reaction of the alkyl radical is with oxygen to form a tertiary [ROO•] radical that can readily abstract a tertiary H atom from an adjacent repeat unit to form a [ROOH] group (reaction (13)). Unlike in PE, the high local availability of labile hydrogens in PP creates clusters of tertiary radicals in close proximity, introducing a high degree of spatial heterogeneity to the oxidation process. Consequently, unlike in PE, the tertiary [ROO•] moieties in PP can react *via* energetically favorable bimolecular reactions despite their limited mobility. This phenomenon also contributes to high surface heterogeneity, that is even microscopically discernible in the case of PP (Billingham 1989; Richters 1970). The [ROOH] groups dissociate to form alkoxy [RO•] and [•OH] radicals as in the case of PE or may react to form in-chain lactones (Tidjani 1997) or trans-vinylene groups (Mendes et al. 2003). The hydroxyl radicals formed are reactive and abstract labile H atoms from the PP chains. Even though the role of [•OH] radicals in PP degradation is often ignored, its removal from the system retards degradation, showing its crucial role in the process (Wu et al. 2020). The tertiary alkoxy [RO•] radicals may undergo chain scission, yielding a terminal chain ketone (or acetone) (Grossetete et al. 2002) or a tertiary alcohol by abstracting an H atom. With the build-up of carbonyl functionalities, Norrish photoreactions occur with additional chain scission. The reported (Rajakumar et al. 2009) abundance of carbonyl products for PP is as follows: carboxylic acid > ketone > ester > lactone.

PP tends to degrade more by chain scission with very limited crosslinking during oxidation, reacting more easily (as in H-abstraction reactions) compared to PE, and therefore oxidizes and degrades relatively faster. For instance, the development of carbonyl functionalities in weathering of PP under a UV-340 lamp ($0.89\,W/m^2$) in air was found to be nine times faster compared to in PE (Almond et al. 2020). Termination in PP is also by combination of radicals. Any allylic hydrogens formed in the termination of PP and PE are particularly labile (with low –C–H bond dissociation energies) and can readily participate in propagation reactions.

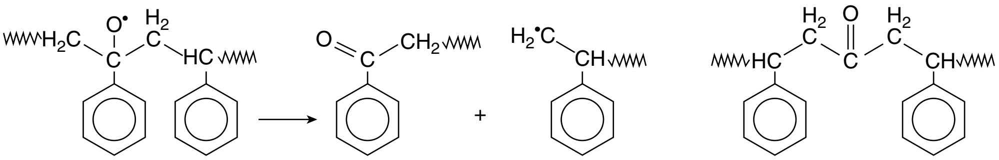
8.3.3 Photodegradation of Polystyrene (PS)

Polystyrene (PS) can sometimes be denser than seawater but can undergo degradation on beaches, but expanded PS foam (EPS) used in packaging as well as in marine floats, is much lower in density and floats in sea water. PS also follows the same basic oxidation pathway as above, but two structural features make it's photo-degradation different from that of either PE or PP. These are as follows: (i) the structure of PS has phenyl groups, that are good UV-absorbing chromophores, in each repeat unit of the chain; and (ii) commonly used atactic PS is wholly amorphous because of structural constraints that interfere with crystallization. On exposure to UVR the phenyl rings are excited first into an excited singlet state and then into a triplet state (by intersystem crossing), transferring the absorbed radiant energy to bonds, photolyzing them (Allen, 1985). Oxygen can form a charge-transfer complex helping initiation. It is the tertiary –C-H bond in the polymer that is more likely to undergo scission as the resulting radical is particularly stable (Dulog and David 1971), though this preference still depends on the energy or the wavelength of irradiation.



(14)

As with PE, the [R•] radical of PS also reacts with oxygen to form [ROO•] radicals that may abstract a tertiary H atom from a nearby (or the same) polymer chain to form [ROOH] groups (Weir 1978). These hydroperoxides are photo-labile and homolytically dissociate by UVR or heat into a pair of radicals, introducing an autocatalytic nature to the oxidation of PS as well. The polystyrene-oxy radical can also undergo β-scission, breaking up the main polymer chain (Kuzina and Mikhailov 1998).



As with PE and PP plastics discussed above, the average molecular weight of PS also decreases on photo-oxidation as reported in the literature for natural (Andrady and Pegram 1991) and for laboratory-accelerated weathering (Shah et al. 2017). Since PS is soluble in organic solvents, either Gel Permeation Chromatography (GPC) or solution viscosity [using the Mark-Houwink empirical equation (Fujita 1988)] can be used to assess the decrease in its average molecular weight during photodegradation. This decrease in the average molecular weight of the soluble fraction was found to vary linearly with the duration of exposure (Shah et al. 2017).

A common observation in the weathering of PS or EPS foam is that on extended exposure the surface of polymer undergoes marked yellowing (Andrady and Pegram 1991). The discoloration, however, is localized to a surface layer and is accompanied by embrittlement, with the surface reduced to a crosslinked brittle powdery material (Pegram and Andrady 1992). The yellow coloration is believed to be due to the development of conjugated unsaturation. If left undisturbed, the yellow embrittled layer on PS and EPS surfaces protects the underlying plastic material from further photodegradation (Yousif and Haddad 2013). A contributing secondary reaction to yellowing discoloration is the formation of quinone methanes (Rabek 1987).

8.4 Changes Accompanying Weathering of Plastics

1) Weathering reactions generally result in the formation of oxygenation functional groups on the polymer chains. These, especially with PE and PP, primarily include carbonyl groups (>C=O), carboxylic acid groups (-COOH), unsaturation (-C=C-), and hydroxyl groups (-OH) (Gardette et al. 2013). All of these are easily observed using FTIR spectroscopy. The presence of the polar functional groups on degraded surfaces can encourage faster biofouling (Karlsson et al. 2018).
2) By far the most important consequence of weathering, however, is chain scission (Jabarin and Lofgren 1994). While both crosslinking and chain scission occur in oxidizing plastics (Gulmine et al. 2006),[4] it is usually chain scission that dominates (Naddeo et al. 2004; Sudhakar et al. 2008), reducing the average molecular weight, Mn (g/mol) of the polymer and broadening its molecular weight distribution (see Figure 8.7). Even the scission of a small fraction of the long polymer chains in a sample is sufficient to compromise it's mechanical integrity. Experimentally, this decrease in Mn (g/mol) can be monitored using GPC (Andrady et al. 1991), while its effects are also reflected as changes in tensile properties (Dilara and Briassoulis 1998) especially a decrease in uniaxial extensibility (Benítez et al. 2013; Hsu et al. 2012; Ojeda et al. 2011).

   At higher extents of degradation, surface pits or micro-cracks appear and these may become wide enough to be noticed even under a low-power microscope. It is the propagation of these cracks into the bulk of plastics that invariably results in fragmentation during weathering. Fragmentation of plastics in the ocean still requires the help of mechanical stress to loosen the

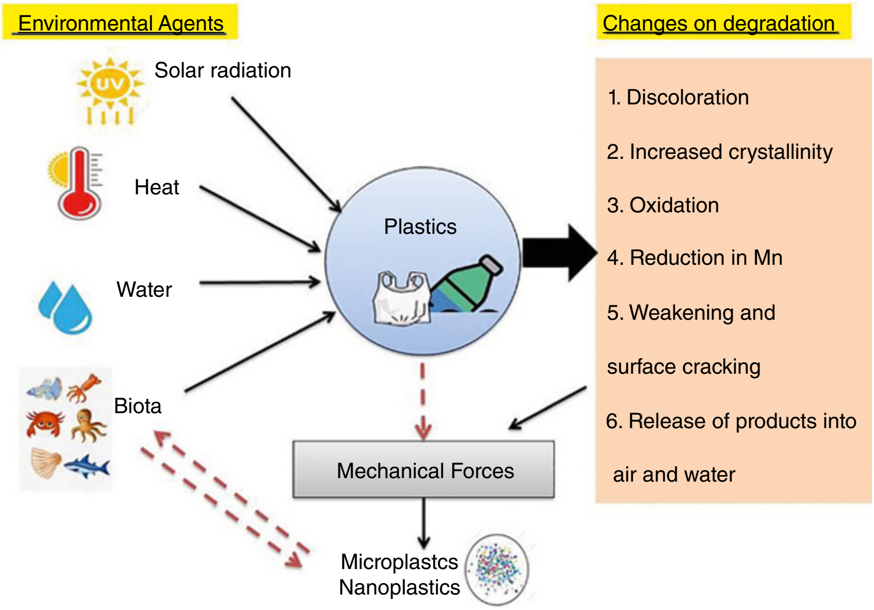


Figure 8.7 Summary of agents and effects associated with weathering of plastics in the marine environment.

---

[4] Some polymer degradation reactions change the chemical structure of the main chain or a side chain of the polymer without causing any scission of the chains.

daughters from the degrading plastic fragment. The reduction in the average molecular weight, Mn (g/mol) is reflected in the loss of mechanical properties, particularly the tensile extensibility of the PE (Carrasco et al. 1996; Andrady et al., 2022; Pabiot and Verdu 1981).

3) In semi-crystalline polymers, photo-oxidation occurs almost exclusively in the amorphous domains. In addition, the short chains formed as a result of chain scission that accompanies oxidation, can migrate through the plastic and often add on to existing crystallites or form new crystallites, by chemo-crystallization (Chabira et al. 2008; Fayolle et al. 2007; Gulmine et al. 2003). The consequent increase in percent crystallinity with oxidation of PE or PP can be measured by calorimetry or X-ray diffraction techniques. Because of the high attenuation of UVR in the polymer, most of the initiation occurs in the surface layers, yielding a heterogeneous surface with pits and cracks within the volume occupied by the degraded amorphous fraction.
4) Common plastics undergo discoloration, usually yellowing, on weathering due to the formation of surface chromophores. With polyolefins these can also arise due to the photodegradation of thermal stabilizer additives. However, with PS, PC, or PVC, the photoreactions of the base polymer that give rise to colored products have been elucidated. For instance, with PVC, photo-dehydrochlorination results in the formation of conjugated unsaturation sequences in the main chain of the polymer with the evolution of HCl. As conjugated sequences absorb blue wavelengths in the sunlight spectrum the weathered PVC appear yellow in reflected light. Oxidative changes may also affect the permeability of the weathered plastic, resulting in faster release of additives from the MP to water (Bandow et al. 2017; Gewert et al. 2018; Paluselli et al. 2019) (or even within biota).

8.5 Weathering of Plastics in the Marine Environment

The ocean environment consists of several zones that are very different in their ability to promote natural weathering of plastic litter. For the present purpose, it is convenient to compare the relative efficacy of oxidative degradation or fragmentation in each of the zones.

1) Beach or dry sediment: Beaches can be of different types including sandy beaches, pebble beaches or rocky beaches, and shell/glass beaches.
2) Tidal or "swash zone" is the beach region that is kept moist by wave action or tidal movements.
3) Surface water generally refers to the visible surface at the air/water interface but can also include a layer a few meters below the surface because of mixing. It is also a photic zone.
4) Water column: The deep water column below the photic zone down to the bottom sediment.
5) The bottom sediment.

Figure 8.8 summarizes the effects of weathering on plastics in the marine environment. The intensity of the principal agents that facilitate weathering of polymers in these zones are qualitatively described in Table 8.3. Clearly, the efficacy of degradation of plastics decreases with zones, starting from the first zone in column 1.

Beaches: The degradation rates of plastics exposed to solar UVR on beaches would be the same or even faster than that on land at the same location (Corcoran et al. 2009). Given the low specific heat of rocks or quartz sand (only a fifth of that of water), sunlight heats these up quickly to high temperatures (Sumner et al. 2007). Compared to air temperature, that of plastic litter exposed to sunlight on sand can often be much higher, by as much as 20 °C, depending on its color. Polymer oxidative reactions have only moderate activation energies (20–50 kcal/mol) (Pickett 2020) and are

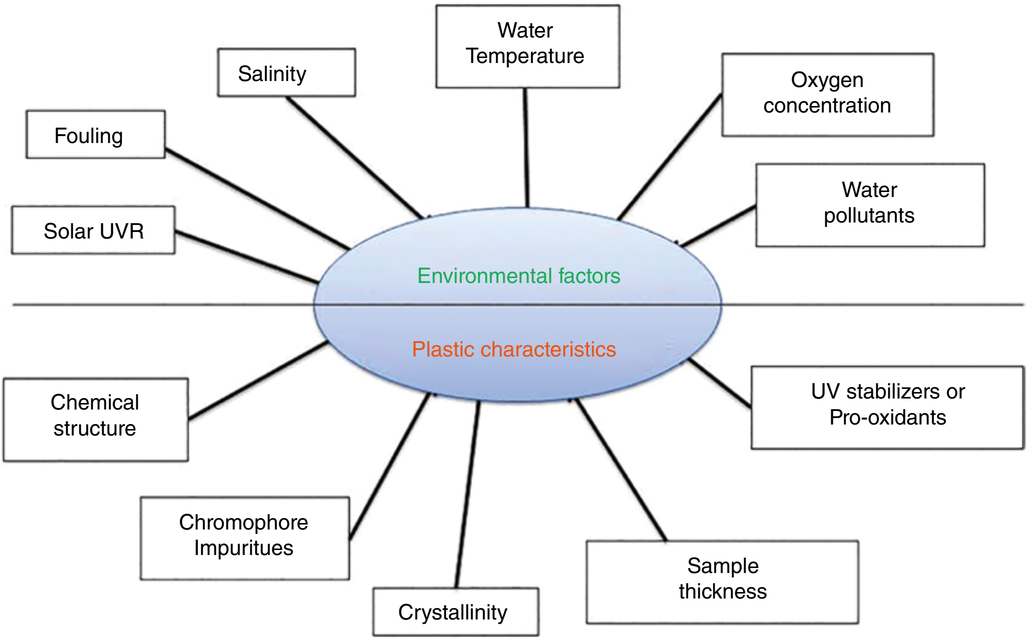


Figure 8.8 Factors that control the mechanism and kinetics of photodegradation of plastics in the marine environment.

Table 8.3 Factors that control photodegradation of plastics in different oceanic zones.

Zone	Solar UVR	Temperature	Oxygen	Fouling
Beach (dry sediment)	+++ 3.4–6.6 kWh/m^2/d	+++ up to 56 °C	+++ ~200 mg/L (~20%)	None
Tidal zone or the swash zone	+++ 3.4–6.6 kWh/m^2/d	++ 22–56 °C	+++ ~200 mg/L (~20%)	Possible
Surface water	+++ 3.4–6.6 kWh/m^2/d	++ 22–30 °C	++ 8 mg/L (< 0.5%)	High
Water column	None	Cold	Very low	Low
Bottom sediment	None	Very cold	Very low	Moderate

Note: Values in columns 2 and 3 are typical only for Miami Beach, Florida, and those in column 4 are for seawater in general.

accelerated significantly at higher temperatures. This combination of factors makes the beach environment the most conducive marine zone for weathering and fragmentation of plastic debris.

Tidal zone: Plastic debris in the intertidal zone receives the same insolation as those on beaches but is maintained at the relatively lower water temperature, at least a part of the time, as this zone is wetted intermittently by wave action or tidal movements. Debris in this zone is also subjected to mechanical agitation by tidal movements as well as abrasion by sand, encouraging their fragmentation. This serves to generate fragments from both virgin plastics and already highly-degraded plastics where fragments weakly adhering to the plastic are separated by mechanical force. Recent evidence suggests that unweathered virgin plastic pellets can also undergo mechanical fragmentation into at least mesoscale particles due to abrasion by sand and aggregate (Chubarenko et al. 2020). Fragmentation in this study was independent of any photodegradation. In the study, plastic debris was placed in a modified concrete mixer with sand and water (2 kg/m^3) and rotated to simulate swash-zone conditions. However, the conditions in the swash zone on a sloping beach can be even more aggressive; the suspended sediment concentration in the water in the zone is around 100 kg/m^3, and water velocities are around 1.5 m/s in the uprush of wave (Aagaard and Hughes 2006). Plastic debris caught up in this field of turbulence likely experiences considerable friction with sand particles, mechanically generating MPs.

Water surface: Plastics floating on the surface of the ocean receive the same insolation as those on the beaches but are maintained at the relatively lower temperature of seawater. Also, the availability of oxygen to the floating samples, especially those submerged, is limited by the low oxygen solubility in seawater. Still, surface waters are relatively richer in oxygen compared to the deep-water column mainly due to the photosynthetic activity of phytoplankton in this zone, as seen in Table 8.3. Abiotic degradation therefore progresses faster in floating plastic debris compared to that submerged at a level that received, for instance, only about 50% of UV radiation relative to that in air (Leonas and Gorden 1993). More importantly, surface biofouling of plastic debris screens the underlying material from insolation, further decreasing the rate of degradation in this zone. Some or all of these factors (low temperature, low oxygen levels, and screening by surface foulants) contribute to the retardation of oxidative degradation in plastics floating in seawater, relative to that on beaches.

Water column: Plastics deeper in the water column, well below the photic zone, cannot undergo any photodegradation. The most potent wavelength to initiate photo-oxidation of plastics, the short wavelength solar UV, is absorbed by seawater and does not reach depths below about 5 m from the surface (Dunne et al. 1996). Water temperature also gradually drops with depth until the thermocline is reached, below which it drops even faster, again contributing to the retardation of all chemical reactions. In a recent study, plastic geotextile samples were subjected to weathering in air and in the aphotic water column over a 12-month period (Hsieh et al. 2016). The tensile strength and puncture resistance of the geotextiles decreased in outdoor exposure (reduction factors of 1.31 and 4.06 for PP and PET respectively), while those exposed in the aphotic zone showed a minimal change (reduction factors of 0.93 and 1.02, respectively) for the same two plastics).

Bottom sediment: The anoxic, aphotic, low-temperature, bottom sediment environment inhibits any oxidative degradation but still may support anaerobic degradation depending on the biotic composition of sediment and the type of plastic. The sediment is rich in MPs as well (Cordova and Wahyudi 2016), but these likely originated in other zones and reached the sediment through vertical migration (Clark et al. 2016) or *via* fecal pellets and marine snow. Barett et al. (2020) estimated 14 MMT of MPs to be accumulated in the bottom sediment worldwide. The degradation of plastics under these conditions is not well understood, but there is an urgent need to research the topic as the bottom sediment invariably collects all the plastics that enter the ocean.

Fouling or surface colonization of plastic litter by algae and marine invertebrates (discussed in Chapter 10) is likely a key determinant of the rate of weathering degradation of plastics in surface water. The duration over which the litter floats, and therefore exposed to solar radiation, is invariably determined by how rapidly the litter will undergo fouling (Ye and Andrady 1991). Fouling influences photodegradation rates of litter in two ways: (a) by shielding the plastic from solar UVR that initiates photodegradation; and (b) by increasing the effective density of debris sufficiently to sink them beyond the photic zone, arresting photo-initiation (Barnes and Milner 2004). Early studies of the phenomenon suggested, however, that floating plastic debris after sinking under the weight of foulants will re-float because of predation of foulants on submerged plastics by fish (Kooi et al. 2016; Ye and Andrady 1991). The reduced density makes the debris float again, and litter may undergo several such "bobbing" movements, surfacing and sinking a few times before they permanently settle into the sediment (Zhang et al. 2020). Other plastics such as PS, PVC, or Nylon, are denser than seawater and sink beyond the photic zone to invariably settle on the bottom sediment.

This vertical migration in the water column also occurs with floating micro- or nanoparticulate debris but due to their aggregation and adhesion to algae and bacteria *via* the transparent exopolymer (TEPs) exuded by these organisms. Adhering to debris or other marine life can increase the density of agglomerates, encouraging their vertical migration (Kooi et al. 2016; Long et al. 2015). Kvale et al. (2020) modeled the process and based on global surface counts of MPs estimated 7.3×10^3 to 4.2×10^5 MT of MPs to migrate to the bottom sediment annually.

The complexity of the natural weathering in the seawater environment makes it difficult to reliably simulate it in the laboratory. Using natural seawater under UV lamps, will drastically alter its biotic profile and will be biotically similar to the synthetic seawater often used in laboaratory studies. The latter is prepared by dissolving a salt mixture in water to get a solution similar in its inorganic composition to seawater. Accelerating the degradation is especially complicated because it is difficult to ensure laboratory conditions that are relevant to natural exposure. Several factors need to be taken into account in designing accelerated exposures. The primary issue is that oxidation of plastic samples, except thin films, will be diffusion-controlled even in air and especially in seawater with a much lower dissolved oxygen concentration relative to air. Therefore, only a thin surface layer of the plastic will be oxidized in seawater exposures of plastics to UVR. While surface oxidation measurements of samples weathered in seawater may yield information on oxidation at the surface, bulk mechanical tests will be insensitive to such surface changes (Andrady et al. 2022). The figure 8.8 summarizes the factors that influence weathering of plastics in the ocean environment.

Two strategies are typically employed to accelerate degradation in the laboratory; elevated sample temperatures and higher UVR relative to that in sunlight. Increasing the temperature in seawater exposures, however, further decreases the solubility of oxygen, making the oxidation even more diffusion-controlled compared to natural exposure. The second consequence of higher temperatures is the faster leaching of reaction products formed (as well as any additives in the plastic) at the plastic/water interface, that will affect the rates of degradation. Increasing UVR levels relative to outdoor sunlight by employing higher intensity UV lamps or multiple lamps in accelerated tests will increases the rate of photo-initiation. However, despite the abundant initiating radicals produced, the propagation reactions will be limited to a thin surface layer by the low oxygen availability in seawater. Consequently, the high concentration of radicals may increase radical–radical reactions relative to propagation reactions (Gugumus 1990), creating a reaction environment that is very different from that occurring in natural seawater exposures. Both strategies used to accelerate degradation in the laboratory in fact alter the natural oxidation kinetics and limit degradation to even a thinner surface layer relative to natural weathering. High levels of UVR under laboratory-accelerated conditions also exclude the crucial variable of surface fouling that occur in natural seawater environments. Fouling, that shields the plastic surface from sunlight, is discouraged by high UVR levels as well as by the high temperatures.

A way around some of these difficulties is to use thin samples where oxidation is less likely to be diffusion-controlled even under accelerated test conditions. Generally, studies using thinner samples obtain rapid fragmentation or weight loss even in natural exposures (see Table 8.5), when using products such as plastic bags that are made from thin films of plastic. Where degradation is monitored using bulk mechanical properties, natural and accelerated seawater exposures will show no apparent change in properties of the plastics in seawater (Andrady et al. 2022). However, surface techniques such as X-ray photoelectron spectroscopy (XPS) or Energy Dispersive X-ray Spectrometry (EDAX) may still show chemical signatures of oxidation on the surface of plastics weathered in seawater (Andrady et al. 2022; Rowenczyk et al. 2020).

8.6 Studies on Weathering of Plastics in Seawater

Reports on weathering of plastics in the marine environment first appeared in 1990s, at a time when the beach litter problem received public attention and enhanced photodegradable plastic technologies (now used in photodegradable six-pack rings) were being first proposed by the plastics industry to address the concern. The first paper on photo-degradation of plastics in seawater was presented in the United States at a symposium held by the Society of Plastics Industry in 1987 and included preliminary data on the photodegradable PEs (Andrady 1987).

8.6.1 Retardation of Degradation in Seawater Relative to Air

Early research on the natural weathering of plastics floating in seawater at several US locations indicated the rates of their degradation to be much slower compared to that of the same plastic exposed in air at the same location (Andrady 1990; Andrady et al. 1993; Pegram and Andrady 1989). These studies assessed the extent of degradation in terms of the decrease in tensile properties of the material, especially extensibility under uniaxial strain. Table 8.4 summarizes data from a paper that illustrates this phenomenon, where several plastic products typically found in marine debris were exposed while floating in sea water and in air (on wooden frames) at the same location and

Table 8.4 Comparison of natural weathering data for plastic material exposed in air and floating in seawater at the same location in Beaufort, NC.

	Duration (mos.)	Extensibility in air (%)	Extensibility in seawater (%)	Tensile strength in air (kg/sq. cm)	Tensile strength in seawater (kg/sq. cm)
LDPE film	0	548 [29]	548 [29]	124.1 [6.1]	124.1 [6.1]
	6	27 [9]	601 [114]	132.3 [13.7]	115 [3.3]
	12	na	541 [39]	118.7 [3.4]	na
PP tape	0	82 [1.0}	82 [1.0]	75.5 [1.0]	75.5 [1.0]
	6	19 [2.0]	82 [1.0]	74.3 [1.3]	20.1 [1.6]
	12	8 [1.0]	61 [4.0]	67.2 [1.6]	11.3 [0.4]
Latex Rubber Balloons	0	986 [50]	986 [50]	96.7 [3.6]]	96.7 [3.6]
	6	63	611 [34]	1.4	16.0 [3.1]
	12	na	513 [15]	na	9.1 [1.0]

Tabulation is based on data from Andrady and Pegram, 1989. The original reference provides detailed data for the variation of the measured parameters at 2-month intervals. The standard error of the mean value is shown in parentheses.

their degradation followed by tensile testing. The marked retardation in seawater exposures is evident in the data. This retardation of degradation obtained in natural weathering in seawater has since been confirmed in recent studies (Andrady et al. 2022; Aria-Villamizar et al. 2018; Leonas and Gordan 1993; Ranjan and Goel 2019; Resmeriță et al. 2018; Tang et al. 2019), both in terms of the loss in mechanical properties and the rate of development of (>C=O) absorption bands in FTIR spectra.

For instance, Tang et al. (2019) working with PP pellets exposed to sunlight for 12–18 months found their surface carbonyl index to increase from 0 to 3.92 in air exposures, but only up to 0.78 when exposed floating in artificial seawater, for the same duration at the same location. The surface hydroxyl index also showed a similar change: 0–2.61 in air and only 0–1.21 in seawater. In another study, geotextiles made of PP, and PET showed slower degradation as measured by the loss of tensile properties for weathering in seawater, compared to that in air (Hsieh et al. 2016). In a more recent study, Biber et al. (2019) investigating natural weathering of PE, PET, and PS films also reported a similar retardation.

The cause of this retardation in both oxidation and chain-scission obtained with samples exposed floating in seawater was explained as being due to a combination of factors: (i) lower seawater temperatures relative to that in air, (ii) lower dissolved oxygen concentration in water, and (iii) surface fouling of samples that shield the surface from solar UV irradiation (Andrady 2011; Andrady et al. 1993). Of these, the diffusion-controlled kinetics due to low oxygen levels is particularly important (Andrady et al., 2022). An interesting unresolved question, however, is if the highly oxidative radical species, especially halogen radicals, generated in solar UV-irradiated seawater, also plays a role in retarding degradation by changing the chemistry of propagation reactions.

An exception to this general observation was found with EPS foam. With foam samples weathered in Beaufort, NC, exposed floating in seawater for a one-year period, a faster rate of degradation relative to samples exposed in air at the same location was observed, based on a reduction in sample thickness or mass loss (Andrady et al. 1991). This loss in the thickness of the foam observed in seawater was not merely due to expanded cells coming apart and being dispersed in water, which would be primarily a mechanical fragmentation. But, the average molecular weight Mn (g/mol) (determined by GPC) of the EPS samples (see Figure 8.9) also decreased with the duration of exposure in seawater, indicating chain scission. This is likely due to the very thin walls of the closed-cell

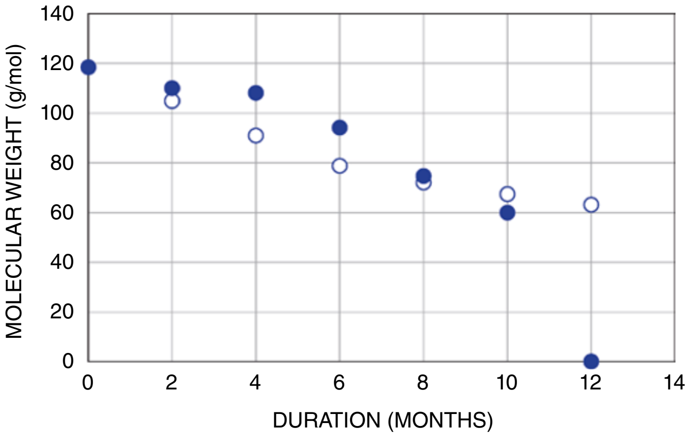


Figure 8.9 Change in the average number-average molecular weight Mn (g/mol), of expanded polystyrene (EPS) foam exposed to outdoor weathering in air (open symbols) and while floating in seawater, as determined by GPC. (filled symbols) (plotted using data from Andrady et al. 1991).

PS foam (average thickness 9.2 μm) resulting in oxidation that is not diffusion-controlled and allowing the entire thickness to undergo oxidation and scission. Biber et al. (2019) working with the thicker (46 μm) PS laminates, however, did not find faster degradation in seawater. Furthermore, the protective yellow reaction products on the fragile surface are washed away in floating samples, leaving the surface exposed for further photo-reaction (Andrady et al. 1991; Gewert et al. 2018). However, if all the degradation products are subsequently mineralized by biodegradation is not known. Environmental degradation to be ecologically meaningful requires the plastic material to be completely converted into CO_2 and water by biotic action.

8.6.2 Recent Research on Weathering in Seawater

Recent research on the degradation of plastics in the ocean environment includes several natural weathering studies (in Table 8.5), but for the most part are laboratory studies. These have used different types of UV sources and different temperatures, making it difficult to directly compare the data to each other or to that from natural weathering. Especially valuable are the long-term exposure studies where the exposure conditions and durations are known and to some extent controlled.

The data from accelerated weathering studies summarized in Table 8.6 confirmed the retardation of photodegradation of plastics observed for natural weathering in seawater. Among them, an interesting study on accelerated weathering of PE found higher extents of degradation when PE samples were first exposed to seawater in the dark followed by UV radiation in air, compared to irradiating them while floating in seawater for the same duration (Carneiro et al. 2018). This is a consequence of the same retardation phenomenon. Karlsson et al. (2018) found LDPE films that were thermally pre-degraded at 90 °C for up to a month, followed by 12 weeks of natural weathering in seawater, to be completely fragmented. Control samples that were not pre-degraded showed only a ~ 20% decrease in tensile extensibility but no fragmentation within the same duration exposure. The pre-degraded plastic will carry high surface concentrations of chromophores, and therefore undergo ready oxidation-scission *via* Norrish reactions. Some of the fragments already formed in pre-oxidation, may have also separated out in water. Interestingly, however, the >C=O absorption band in FTIR spectra of pre-degraded samples, decreased during seawater exposure, indicative of no further oxidation. This was explained as being due to bio-assimilation of degradation products, but some of the products in LDPE oxidation are in any case water soluble and may also account for some of the decrease. Weathering of multilayer film samples of PE/PET and compostable PLA/cellulose films, under natural weathering in seawater and in bottom sediment exposure, was reported by Beltran-Sanahuja et al. (2020). Only minimal weight loss of the PE/PET films was observed in aphotic deep water and the sediment. The biodegradable PLA polymer underwent marked degradation under sediment exposure with a fivefold increase in weight loss, compared to that in deep water over the 12-month exposure. The bottom anaerobic sediment supported the biodegradation of at least this "biodegradable" plastic.

8.7 Fragmentation of Plastics in Marine Weathering

Fragmentation is a mechanical process where an already weathered plastic material is broken up into several daughter pieces because of stresses acting on it. The stress causing fragmentation might be due to physical causes, such as wave action and abrasion by sand (Chubarenko et al. 2020; Ren et al. 2020), action of wind and human interactions with debris, or biological, as with attrition of ingested MPs in the gut of organisms (Dawson et al. 2018; Fairbrother et al. 2019; Jang et al. 2018).

Table 8.5 Summary of recent publications on natural weathering of common plastics in seawater environments.

Plastic	Thickness	Duration/days	FTIR	Tensile	Crystallinity	SEM	Other	Reference
LDPE	40–50 μm	84	X	X	X	X	Fouling	Karlsson et al. (2018)
LDPE/starch LDPE	20–22 μm	720		X			Respirometry	Tosin et al. (2012)
LDPE, PET, PS	43–60 μm	600	X	X				Biber et al. (2019)
HDPE	100 μm	180				X	Weight loss	Kalogerakis et al. (2017)
HDPE	190 μm	180	X	X				Arias-Villamizar et al. (2018)
PE	50 μm primary MPs	21	X	X				Brate et al. (2018)
PE, PS	43–60 μm	540		X			Loss of area	O'Brine et al. (2010)
PE	300–364 μm	-	X		X	X	X-ray tomography	ter Halle et al. (2016)
PP	Plastic cup	60	X			X	EDX, Fouling	Khoironi et al. (2020)
PE	Films (plastic bag)	15–33		X		X	Biofoulant species	Eich et al. (2015)
HDPE	Plastic bag	~1000	X	X		X		Napper and Thompson (2019)
PE, PP	Debris pieces** 300–364 μm	F	X		X	X	Microtomography	ter Halle et al. (2016)
PE, PP	Debris pieces**	F	X		X	X	Molecular weight	ter Halle et al. (2017)
PP	Geotextile 30–40 μm fiber	180		X				Carnerio et al. (2018)
PP	Pellets	1080	X			X		Tang et al. (2019)
PP, PE, nylon	Braided rope	360		X			Weight loss	Welden and Cowie (2017)
PET, PE, PVC, PP, PS	Pellets	1080	X		X		Yellowness	Brandon et al. (2016)

PS, EPS		720				X	Particle size analysis	Song et al. (2020)
PA/PP/EVOH PET/PE, and PLA/cell	Variable multilayer film	360	X		X			Beltran-Sanahuja et al. (2020)
PE, PP,PS, PET, PLA	Variable (products)	720	X	X	X		Molecular weight	
HDPE, PP, PS (intertidal zone)	0.38 mm	224					UV transmittance, weight loss	Weinstein et al. (2016)
ABS	1500 µm**	-	X		X	X		Tuner et al. (2020)
HDPE	110 µm film	180	X	X				Aria-Viamissaret al. (2018)

** Characterization of debris from ocean or beaches.

Table 8.6 Summary of publications on laboratory-accelerated weathering of common plastics in seawater and freshwater environments.

Plastic	Source	Thickness	Seawater	Temp/°C	Maximum duration/days$^{\#}$	Characterization	Reference
PP	Mercury vapor lamp	Pellets	-	30	21	Microscopy, contact angle, Energy-Dispersive X-ray Spectroscopy. EDX, FTIR spectroscopy, tensile properties, DSC, weight loss	Resmeriță et al. (2018)
PP	T5L345-C22-10W (UVB) 10.25 W/m2	Pellets (100μ)	Artificial	25	360	Microscopy, EDX, FTIR spectroscopy, porosimetry	Tang et al. (2018)
PP	Fluorescent UV	Geotextile 30–40 μm fiber	Natural	60 Spray	21 (UV~367 h.)	Tensile tests only. Retardation of degradation in seawater	Carnerio et al. (2018)
PP	T5L345-C22-10W (UVB) l (10.25 W/sq.m)	Pellets	Synthetic	25	360	Microscopy and FTIR spectroscopy. Retardation of degradation in seawater. Interior not degraded	Tang et al. (2019)
PP	Mercury vapor lamp $UV_{365} = 100W/m^2$	400–500 μm	Synthetic	25	200–360	Microscopy, contact angle, EDX, FTIR spectroscopy, XRD, Total organic carbon (TOC) and OH radicals. Shows increased TOC. Also	Wu et al. (2020)
PP, PS	Metal halide HQI-TS 250W/NDL Osram	Pellets		23–28	63	FTIR spectroscopy. Continuous saturation of water with air and agitation	Andrade et al. (2019)
PS	UVA/B lamp	Plastic cup lid	Fresh water	30	56	NTA particle size distribution	Lambert and Wagner (2016)
PE	Mercury vapor 256 nm	Pellets	Synthetic	19	56	Microscopy, TGA EDX, FTIR, and Raman spectroscopy. Exposure to salt water in dark shows spectral change > exposed to UV	Da costa et al. (2018)
PP, PE, PS	UV-340	Pellets	Synthetic	-	90	FTIR, Raman spectroscopy, and microscopy	Cai et al. (2018)
LDPE	Xenon 60 W/m2	23 μm Film	Freshwater	32–44	175	Microscopy, FTIR spectroscopy, topography (AFM), microindentation, fragment study	Julienne et al. (2019)

LDPE	UV light (280–320)	35 µm film	Synthetic	30	90	FTIR, microscopy, AFM and EDX spectroscopy. Retardation of degradation in freshwater as well as seawater	Ranjan and Goel (2019)
LDPE, PET	UVB 200	Powder		25	28 days	Nanoparticle Tracking Analysis (NTA), XRD, dynamic image analysis	Oelschla et al. (2017)
LDPE, ECO, PS		4–7 mm film	Natural	24	10	Tensile tests only. Retardation of degradation in seawater	Leonas and Gordan (1993)
LDPE, HDPE, PS, PP, PET, CA, latex rubber	T8 Ocean Sun lamps and Repti Sun 5.0 UVB lamps	Product mix with rubber balloon	Natural	29	389	Weight loss, change in electrical resistance, microscopy.	Gerritse et al. (2020)
LDPE, HDPE, PP, PET, PS	HQI-TS2510W/NDL	Pellets, powder	Natural	-	70	FTIR spectroscopy only	Fernández et al. (2020)
PE, PP, EPS	Metal halide	Pellets	None	43–45	360	FTIR and fragmentation	Song et al. (2017)
PE, PP, PET, Nylon	TUV PL-L 36W/4P[a]	Mixed litter ~ 1 mm	Natural		195	Tensile, microscopy, AFM, and thermogravimetry. Surface pits, cracks and roughening for samples exposed to UV+ seawater	Iñiguez et al. (2018)
PE, PP, PS, PET, PLA	UVA/B Lamp	Pellets	Freshwater	30	112	NTA particle size distribution	Lambert and Wagner (2016)
PVC with organotin	UVL-21, Analytik Jena	Fragment	Synthetic	ambient	2	Measurement of organotin released on weathering	Chen et al. (2019)
PS, PE, PP, CA, PET	UV-340	Various	Freshwater	19	56	Particle count (Coulter counter) and microscopy	Svendin, (2020)

Duration is the total duration including any dark time if one was used; a lamp with some <290 nm UV in the emission spectrum. AFM - Atomic Force Microscopy. XRD - X-ray Diffreaction

MPs that are 31.5 μm in size (average), for instance, were reduced to particles <1 μm in size in the gut of the detritivorous species, the Pacific krill (which incidentally also ingests silicaceous diatoms providing an effective abrasive medium). Hodgson et al. (2018) found amphipods to fragment ingested biodegradable plastic bags into MPs of average diameter 489 μm. Human intervention can also promote fragmentation of beach plastic litter.

Fragmentation of virgin or relatively un-weathered plastics is possible under mechanical stress in turbulent water as illustrated by the release of textile fibers in the laundering of synthetic fabric. Weathering, however, encourages the process by weakening or embrittling the material, allowing a much smaller mechanical force to bring about fragmentation. Karlsson et al. (2018), for instance, found pre-degradation (thermo-oxidation at 90 °C) to facilitate subsequent fragmentation of the samples during natural weathering. Oxidation of plastics initiated by solar UVR and/or high temperatures in air, can result in embrittlement, making the plastic fragile. Yet, it takes some mechanical force (such as wave or wind action) to dislodge the weakened, loosely-attached, daughters from the parent plastic (Chubarenko et al. 2020; Ren et al. 2020; Resmeriță et al. 2018). Weathering-assisted fragmentation, therefore, generally involves two agents: (a) solar UVR that brings about oxidative degradation; and (b) mechanical stress that breaks up the weakened material. Higher the extent of degradation, lower will be the force needed to fragment the material. With composite plastics containing additives such as starch, the biodegradation of additives renders the polymer fragile and assists in fragmentation as well as the subsequent biodegradation of the polymer (Tosin et al. 2012). Fragmentation of HDPE exposed to the intertidal zone for 224 days followed by 48 hrs of agitation (rotation in contact with seawater at 3 rpm) yielded low counts (< 100 per 30 sq cm strip) of MPs in the size range of 63–500 μm (Weinstein et al. 2016); the particles were visually identified, and being in the intertidal zone some of the particles formed by weathering would have been washed away.

Laboratory-accelerated studies on fragmentation generally include applying a suitable mechanical stress on photodegraded plastics to reflect natural weathering conditions. Usually, agitation with sand, which is relevant to wind or wave action on beaches, is employed. Kalogerakis et al. (2017), Song et al. (2017), and (2020) used this approach with both virgin and weathered plastics. Kalogerakis et al. (2017) placed weathered plastic strip samples in 250 mL bottles half filled with sand and rotated them horizontally for 12 hrs at 13 rpm at 30 °C to release the adhering fragments. Song et al. (2017) used a similar procedure, rotating instead at 37 rpm for two months. The stress needed to remove micro-fragments from the embrittled surface layer is much smaller than that for generating fragments from virgin plastics. For instance, with a highly weathered PP rope sample from beach debris, merely shaking with water was adequate to release a population of NPs that could be characterized by flow cytometry (Andrady 2010). However, the nature of the stress field (rpm and grain size of sand) as well as the duration of agitation should be selected (Kalogerakis et al. 2017) to merely remove existing MPs from photodegradation, rather than generate new MPs or NPs mechanically from the un-weathered bulk of material.

8.7.1 Macro-Fragmentation Into Mesoscale fragments

During weathering, plastics invariably crack and break up into large visible fragments that include mesoplastic or larger daughter fragments. Weathering of LDPE films (Biber et al. 2019; Napper and Thompson 2019; O'Brine et al. 2010) and braided ropes (Welden and Cowie 2017) illustrate macro-fragmentation. In the latter study, even with mild photic exposure conditions (marine silt sediment at 10 m depth at an average temperature of 10 °C), the rate of material loss was 0.62 wt% a month.

Weather-assisted fragmentation of plastics mostly occurs in the beach zone as suggested by the size distribution of debris (Fok et al. 2017). But, in accelerated studies, fragmentation takes place in sea water exposures as well. A microcosm study of common plastic items in seawater, exposed to UVR (using a combination of UV fluorescent and Reptilamps) over a period of 378–427 days, resulted in the formation of mesoplastics (Gerritse et al. 2020). It is easier to observe macro-fragmentation with thin-film samples as the surface cracks on them are deep relative to the sample thickness. It is reasonable to expect plastics extensively weathered either on land (and carried by rivers) or on beaches, to undergo fragmentation on reaching water, by the mechanical forces of wave action. This emphasizes the importance of regular beach cleaning in controlling ocean MPs. However, plastic debris disposed directly into water are unlikely to photo-degrade sufficiently to reach the point of embrittlement prior to their sinking to aphotic depths.

With semi-crystalline plastics, oxidative degradation resuls in material loss that occurs nearly exclusively in the inter-crystalline amorphous domains. Gulmine et al. (2003), for instance, found both the percent crystallinity and surface hardness of LDPE, LLDPE, and HDPE to increase nearly linearly with the duration of exposure to xenon or UV-340 sources in air. This has the important consequence of internal stresses developing in the polymer, initiating microcracks visible on the surface (Skrypnyk and Spoormaker 1999) as reported for both natural and accelerated weathering (Craig and White 2006). SEM micrographs typically show uniformly spread cracks and pits on the surface of weathered samples, that increases their brittleness. It is the propagation of these cracks into the bulk of the plastic in the z-direction, assisted by environmental mechanical stresses, that obtain macro-fragmentation. Models of macro-fragmentation based on these concepts was recently published (Meides et al. 2020; ter Halle et al. 2016) and is illustrated in Figure 8.10 (left); Figure 8.10 (right) shows an image of macro-fragmentation of litter.

Figure 8.10 illustrates the maco-fragmentation process. Fragments will tend to have a higher degree of crystallinity than the parent material. Garvey et al. (2020) finds that in addition to an increase in fractional crystallinity, the lamellar structure of the crystalline domains in PE is disrupted during natural weathering, based on wide-angle X-ray diffraction and low-frequency Raman spectroscopic data. Such a disruption in crystalline lamellae will invariably impact oxygen solubility and therefore lead to diffusion control of the oxidation.

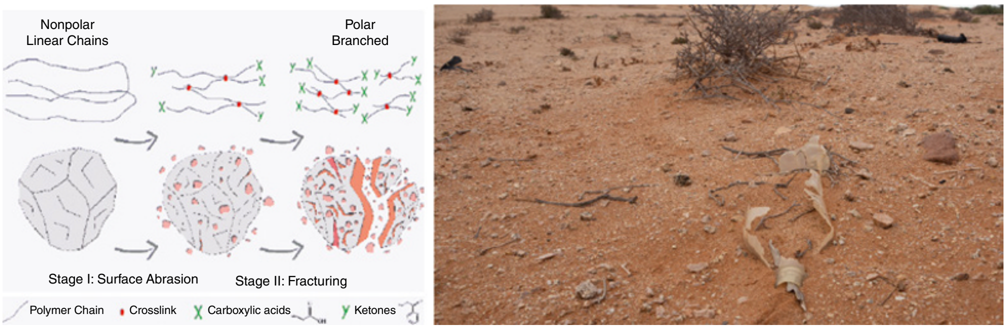


Figure 8.10 (Left) Two-stage macro-fragmentation model for plastic objects exposed to the solar radiation and mechanical stress (Courtesy Meides et al. 2020). (Right) Macro-fragmentation of a plastic cup. (AdobeStock.com).

8.7.2 Micro-Fragmentation by Surface Ablation

Based on the chemistry of photo-oxidation in solid polymers under oxygen-starved conditions obtained in seawater, a second concurrent mode of fragmentation is likely. This second mode is fragmentation by surface ablation (Andrady 2017a; Kalogerakis et al. 2017; Tang et al. 2019) that is also a two-stage process requiring extensive photo- or thermal degradation followed by some mechanical stress to release daughter particles formed into the water. However, in contrast to the few large daughters visible to the naked eye, formed in macro-fragmentation, surface ablation obtains much larger numbers (10^3 to 10^5 per cm^2 area of plastic) of microscale and nanoscale daughters with a more uniform size distribution. Song et al. (2018) exposed plastic pellets to a halide lamp UV source for 12 months followed by 2 months of abrasion by sand to obtain 6×10^3 particles/pellet. This mode of fragmentation, the surface ablation model (SAM), illustrated in Figure 8.11, was expected based on theoretical considerations (Andrady 2017b). The model is qualitatively consistent with the formation of numerous sub-micron particles during laboratory accelerated photo-oxidation of PP in air Andrady (2010), Song et al. (2018), Andrady et al. (2017b), Svedin (2020), and Julienne et al. (2018).

Studies on the photo-oxidation of plastics while in contact with water are limited. That nanoscale particles could be generated in such exposures was first shown by Gigault et al. (2016) in further weathering of already naturally-weathered MPs collected from the gyre in ultrapure water (under a metal halide UV source). However, if the fragments were generated in photo-oxidation in air or in water is not clear. Samples of plastics exposed to UVR while in contact demineralized water was reported by Lambert and Wagner (2016). Seven types of plastic pellets and sheets in water were exposed to a UV source ($\lambda = 320 - 340$ nm) for up to 112 days, and NPs generated were studied using Nanoparticle Tracking Analysis (NTA). All plastic types showed an increase in particle counts with weathering exposure; the particle counts ranged from 10^5 to 10^8 particles/pellet with PS and PLA yielding the highest particle concentration. Studying the photodegradation of PP in seawater, using a mercury vapor source, Resmeriță et al. (2018) (as well as Julienne et al. 2018) confirmed surface erosion to be a possible mechanism of fragmentation. Surface ablation occurs to some small extent in all oxidations of plastics, especially under diffusion-controlled conditions; that it contributes significantly to fragmentation of floating plastics exposed to solar UVR, in the ocean is, however, unlikely. In a recent study, Svendin (2020) exposed five types of common plastics to UVB fluorescent lamps in air or in deionized water, followed by exposure for 10 min in an ultrasonic

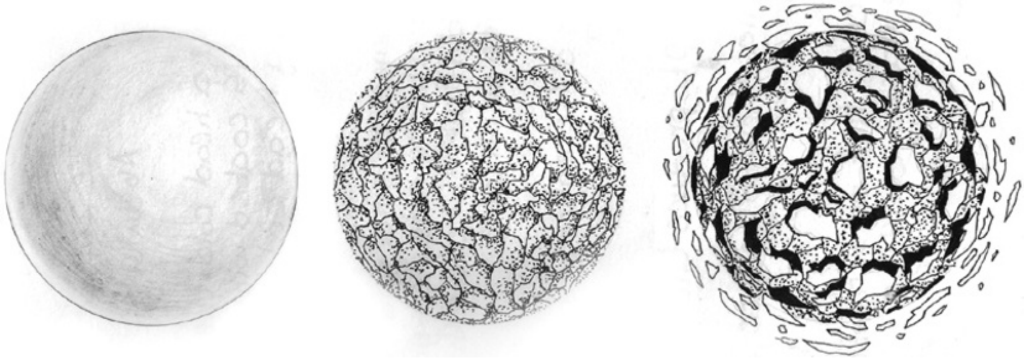


Figure 8.11 A schematic of fragmentation by surface ablation. (Left) A spherical virgin pellet. (Middle) Extensively photo-oxidized pellet with surface micro-cracks. (Right) The oxidized pellet fragmenting (Courtesy: Andrady 2017b).

bath. The fragmentation of plastics increased non-linearly with duration and for PP and PS were the fastest and PE was the slowest to fragment. At a given duration of exposure the NP concentrations were generally higher in samples weathered in water relative to that in air.

Diffusion-controlled oxidation of plastics typically results in a concentration gradient of dissolved oxygen from the surface to interior of the plastic and limits oxidation to a surface layer that is typically several 100 μm in thickness (Andrady et al., 2022). The chemistry of this layer will be very different from that of the underlying bulk plastic in that it (a) is more highly oxidized and richer in hydrophilic polar groups, (b) has a higher percent crystallinity, and (c) has a different average molecular weight, compared to the underlying bulk plastic material. It is convenient to think of an extensively photodegraded plastic pellet as one being coated by a thin layer of a covalently bonded hydrophilic polymer that might even be crosslinked. The strength as well as swelling characteristics of this layer in seawater, will be very different from that of the underlying plastic, and once swollen, the layer can "de-laminate" under even mild mechanical stress. Routine wet–dry cycles experienced by plastics debris on beaches due to wave action or tidal movements that may facilitate this process. In addition, seawater drying within the cracks on the weathered plastic into halite crystals, may expand and contract thermally, adding to the stress on the material surface. The volume expansion of water freezing inside cracks would similarly contribute to micro-fragmentation. These changes occur at different rates in the surface layer of polymer compared to the bulk and, as shown in Figure 8.10, and results in the surface breaking up into numerous daughter particles. The number of expected spherical daughters N of diameter d yielded by a spherical plastic pellet of radius D can be calculated from geometric considerations.[5] In real environments, the fragments need not be spherical and their thicknesses would be variable, but still influenced by the thickness of the degraded layer. In fragments from plastic products, where antioxidant stabilizers might be present, these additives compounds are also depleted more easily from the surface layers by leaching out into water.

Scanning electron microscopy (SEM) images from recent studies of PS beads (0.1 μm) weathered under UV-340 lamps have surface features that are qualitatively consistent with what might be expected by the model illustrated in Figure 8.11 (see Figure 8.12). Verifying the formation of MPs and NPs by the surface ablation mechanism relies on accelerated laboratory exposure data employing particle-counting techniques such as Coulter counter, NTA, or the more recent ncS1 technology, which yield particle size distributions in aqueous media. However, the size-scale of daughters formed and the difficulty in detecting NPs in complex media preclude their detection in nature. These MP/NPs can aggregate on interacting with marine exo-polymer present in seawater, adhere to surfaces, or even be in the biomass. A number of studies on fragmentation in general and surface abrasion in particular, are summarized in Table 8.6.

Both modes of fragmentation are likely to operate concurrently in plastics weathering in the marine environment, especially on the beach zones. Some of the smaller-sized daughter particles produced by surface ablation, though numerous, can readily pass through the gut of most marine species to enter systemic circulation (Al-Sid-Cheikh et al. 2018; Chae et al. 2018; Ding et al. 2018; Mattson et al. 2017; Pitt et al. 2018). The physiological consequences and behavioral modifications these can induce in marine species, or in human consumers of seafood carrying MPs/NPs, are unclear at the present time. Also unknown is the ultimate fate of very small MPs and NPs in the environment; it is reasonable to expect them to keep degrading photothermally and given their very high specific surface area undergo biodegradation as well to mineralize in the long term.

---

[5] $N = 8 + (6D2/d2) - (12D/d)$

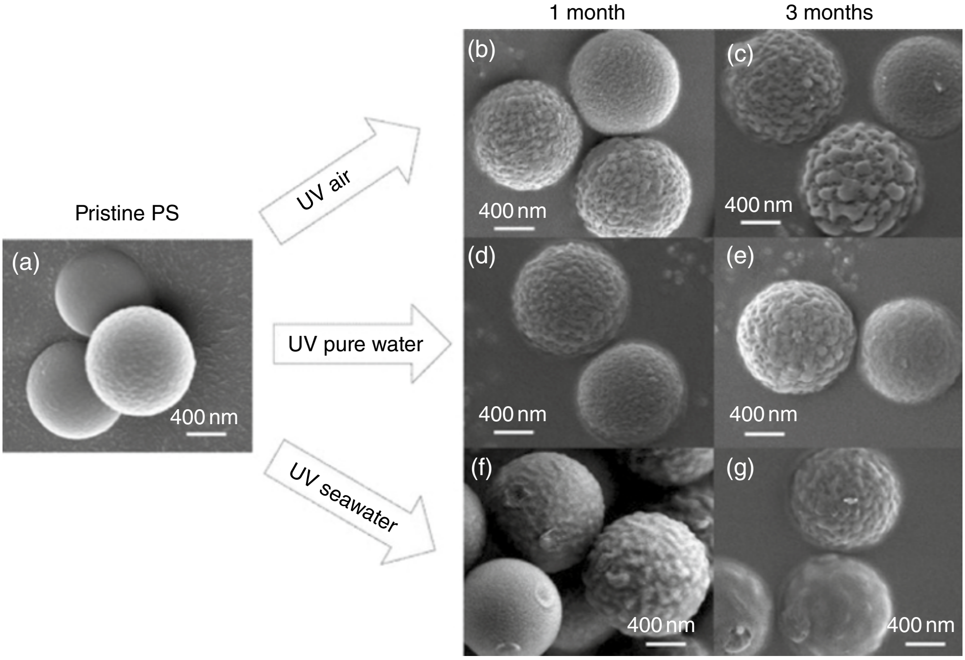


Figure 8.12 Micrographs showing irregular surface features of 0.1 μm polystyrene beads exposed to UV-340 fluorescent lamps in air, freshwater, and seawater environments at 25 °C for one and three months (Courtesy of Mao et al. 2020).

8.8 Conclusions

Weathering of plastic debris in the ocean environment is primarily due to solar UVR-induced oxidation resulting in chain scission and/or crosslinking, which reduces their mechanical integrity, and on extended exposure, causes embrittlement of the material. The rate of photodegradation of land litter occurs orders of magnitude faster compared to that of plastics floating in the ocean at the same location. This is primarily because of diffusion control of oxidation resulting from the lower oxygen solubility in seawater and the shielding of solar UV radiation by surface fouling. Therefore, floating plastic debris directly introduced into the ocean is unlikely to undergo significant fragmentation *via* photodegradation. The debris that is pre-oxidized on beaches and subsequently introduced into the water may, however, further degrade and mechanically fragment in seawater. Along with the macro-fragmentation, a second mode of fragmentation by surface ablation occurs with plastics exposed to UV sources in the laboratory. While this mode of fragmentation produces a large numbers of very small MPs and NPs in laboratory-accelerated weathering studies, if they are also generated in the natural weathering of plastics in seawater under solar UVR, is unclear. Primarily, the thin surface layer that is degraded in diffusion-controlled oxidation undergoes micro-fragmentation to produce these particles. It is unlikely that they can be isolated from environmental samples using standard collection/separation techniques. However, given that very small MPs and NPs have been detected in water, food, and seafood, it is prudent to further study their potential generation *via* abiotic processes in the marine and freshwater environments.

References

Aagaard, T., Hughes, M. G. (2006). Sediment suspension and turbulence in the swash zone of dissipative beaches. *Marine Geology*, 228(1–4): 117–135.

Albertsson, A., Karlsson, S. (1993). Aspects of biodeterioration of inert and degradable polymers. *International Biodeterioration & Biodegradation*, 31(3): 161–170.

Almond, J., Sugumaar, P., Wenzel, M. N., et al. (2020). Determination of the carbonyl index of polyethylene and polypropylene using specified area under band methodology with ATR-FTIR spectroscopy. *e-Polymers* 20(1): 369–381.

Al-Sid-Cheikh, M., Rowland, S. J., Stevenson, K., et al. (2018). Uptake, whole-body distribution, and depuration of nanoplastics by the scallop Pecten maximus at environmentally realistic concentrations. *Environmental Science & Technology*, 52(24): 14480–14486.

Anderson, A., Andrady, A., Hidalgo-Ruz, V., et al. (2015). Sources, fate and effects of microplastics in the marine environment: A global assessment. GESAMP joint group of experts on the scientific aspects of marine environmental protection.

Andrade, J., Fernández-González, V., López-Mahía, P., et al. (2019). A low-cost system to simulate environmental microplastic weathering. *Marine Pollution Bulletin*, 149: 110663.

Andrady, A. L. (1987). Plastics in the marine environment. In *Proceedings of the Symposium on Degradable Plastics*. Society of Plastics Industry, Washington, p. 29.

Andrady, A. L. (1990). Weathering of polyethylene (LDPE) and enhanced photodegradable polyethylene in the marine environment. *Journal of Applied Polymer Science*, 39(2): 363–370.

Andrady, A. L. (2010). Using flow cytometry to detect micro- and nano-scale polymer particles on Proceedings of the Second Research Workshop on Microplastic Marine Debris. NOAA Technical Memorandum, 54.

Andrady A. L. (2011). Microplastics in the marine environment. *Marine Pollution Bulletin*, 62(8): 1596–1605.

Andrady, A. L. (2015). Persistence of plastic litter in the oceans. In Bergmann M., Gutow L., Klages M. (Eds.), *Marine Anthropogenic Litter*. Springer, Cham, pp. 57–72.

Andrady, A.L. (2017a). Solar radiation induced degradation of common plastics under marine exposure cnditions. In Baztan, J., Jorgensten, B., Thompson, R.C., Vanderlinden, J. (Eds.), *Micro 2016. Fate and Impact of Microplastics in Marine Ecosystems*. Elsevier. ISBN 978-0-12-812271-6.

Andrady, A. L. (2017b). The plastic in the microplastic: a review. *Marine Pollution Bulletin*, 119(1): 12–22.

Andrady, A. L., Fueki, K., Torikai, A. (1991). Spectral sensitivity of polycarbonate to light-induced yellowing. *Journal of Applied Polymer Science*, 42(7): 2105–2107.

Andrady, A. L., Pegram, J. E. (1991). Weathering of polystyrene foam on exposure in air and in seawater. *Journal of Applied Polymer Science*, 42(6): 1589–1596.

Andrady, A. L., Pegram, J. E., Searle, N. D. (1996). Wavelength sensitivity of enhanced photodegradable polyethylenes, ECO, and LDPE/MX. *Applied Science*, 62(9): 1457–1463.

Andrady, A. L., Pegram, J. E., Song, Y. (1993). Studies on enhanced degradable plastics. II. Weathering of enhanced photodegradable polyethylenes under marine and freshwater floating exposure. *Journal of Environmental Polymer Degradation*, 1(2): 117–126.

Andrady, A. L., Pegram, J. E., Tropsha, Y. (1993). Changes in carbonyl index and average molecular weight on embrittlement of enhanced-photodegradable polyethylenes. *Journal of Environmental Polymer Degradation*, 1(3): 171–179.

Andrady, A.L. and Pegram, J.E (1989). Outdoor weathering of selected polymeric materials under marine exposure conditions. *Polymer Degradation and Stability*, 26(4): 333–345.

Andrady, A.L., Law, K.L., Donohue, J., Koongolla, B. (2022). Accelerated degradation of low-density polyethylene in air and in sea water. *Science of The Total Environment*, 811: 151368.

Arhant, M., Le Gall, M., Le Gac, P., et al. (2019). Impact of hydrolytic degradation on mechanical properties of PET - Towards an understanding of microplastics formation. *Polymer Degradation and Stability*, 161: 175–182.

Arias-Villamizar, C. A., Vázquez-Morillas, A. (2018). Degradation of conventional and oxodegradable high density polyethylene in tropical aqueous and outdoor environments. *Revista Internacional de Contaminación Ambiental*, 34(1): 137–147.

Allen, N. S., Chirinos-Padron, A., Henman, T.J. (1985). Photoinitiated oxidation of polypropylene: a review. *Progress in Organic Coatings*. 13(2): 97–122.

Bandow, N., Will, V., Wachtendorf, V., et al. (2017). Contaminant release from aged microplastic. *Environmental Chemistry*, 14(6): 394–405.

Barret, J., Chase, Z., Zhang, J., Holl, M.M.B., Willis, K., Williams, A., Hardesty, B.D., Wilcox, C. (2020). Microplastic Pollution in Deep-Sea Sediments From the Great Australian Bight. *Front. Mar. Sci.*, 7:576170.

Barnes, D. K. A., Milner, P. (2004). Drifting plastic and its consequences for sessile organism dispersal in the Atlantic Ocean. *Marine Biology*, 146(4): 815–825.

Beltran-Sanahuja, A., Casado-Coy, N., Simó-Cabrera, L., et al. (2020). Monitoring polymer degradation under different conditions in the marine environment. *Environmental Pollution*, 259: 113836.

Benítez, A., Sánchez, J. J., Arnal, M. L., et al. (2013). Monitoring abiotic degradation of branched polyethylenes formulated with pro-oxidants through different mechanical tests. *Polymer Degradation and Stability*, 98(9): 1705–1716.

Biber, N. F. A., Foggo, A., Thompson, R. C. (2019). Characterising the deterioration of different plastics in air and seawater. *Marine Pollution Bulletin*, 141: 595–602.

Bigger, S. W., Scheirs, J., Delatycki, O. (1992). Effect of light intensity on the photooxidation kinetics of high-density polyethylene. *Journal of Polymer Science: Polymer Chemistry Edition*, 30(10): 2277–2280.

Billingham, N. C. (1989). Localization of oxidation in polypropylene. *Makromolekulare Chemie. Macromolecular Symposia*, 28(1): 145–163.

Billingham, N. C., Hoad, O. J., Chenard, F., et al. (1997). Stabiliser partitioning and oxidative degradation in rubber-toughened polypropylene. *Macromolecular Symposia*, 115(1): 203–214.

Botterell, Z. L. R., Beaumont, N., Dorrington, T., et al. (2019). Bioavailability and effects of microplastics on marine zooplankton: a review. *Environmental Pollution*, 245: 98–110.

Brandon, J., Goldstein, M., Ohman, M. D. (2016). Long-term aging and degradation of microplastic particles: comparing in situ oceanic and experimental weathering patterns. *Marine Pollution Bulletin*, 110(1): 299–308.

Bråte, I. L. N., Blázquez, M., Brooks, S., et al. (2018). Weathering impacts the uptake of polyethylene microparticles from toothpaste in Mediterranean mussels (M. galloprovincialis). *Science of The Total Environment*, 626: 1310–1318.

Cai, L., Wang, J., Peng, J., et al. (2018). Observation of the degradation of three types of plastic pellets exposed to UV irradiation in three different environments. *Science of The Total Environment*, 628–629: 740–747.

Carneiro, J. R., Almeida, P. J., Lopes, M. (2018). Laboratory evaluation of interactions in the degradation of a polypropylene geotextile in marine environments. *Advances in Materials Science and Engineering*, 2018: 1–10.

Carneiro, J. R., Morais, M., Lopes, M. (2018). Degradation of polypropylene geotextiles with different chemical stabilisations in marine environments. *Construction and Building Materials*, 165: 877–886.

Carrasco, F., Surina, J., Colom, X. (1996). FTIR and DSC study of HDPE structural changes and mechanical properties variation when exposed to weathering aging during Canadian winter. *Journal of Applied Polymer Science*, 60: 153–159.

Carvalho, M. E. S., Cruz-Pinto, J. J. C. (1992). The kinetics of photo-oxidation of low-density polyethylene films. *Polymer Engineering and Science*, 32(8): 567–572.

Chabira, S. F., Sebaa, M., G'sell, C. (2008). Influence of climatic ageing on the mechanical properties and the microstructure of low-density polyethylene films. *Journal of Applied Polymer Science*, 110(4): 2516–2524.

Chae, Y., Kim, D., Kim, S. W., et al. (2018). Trophic transfer and individual impact of nano-sized polystyrene in a four-species freshwater food chain. *Scientific Report*, 8: 284.

Chen, C., Chen, L., Yao, Y., et al. (2019). Organotin release from polyvinyl chloride microplastics and concurrent photodegradation in water: Impacts from salinity, dissolved organic matter, and light exposure. *Environmental Science & Technology*, 53(18): 10741–10752.

Chin, J., Nguyen, T., Byrd, E., et al. (2005). Validation of the reciprocity law for coating photodegradation. *Journal of Coatings Technology and Research*, 2(7): 499–508.

Chubarenko, I., Efimova, I., Bagaeva, M., et al. (2020). On mechanical fragmentation of single-use plastics in the sea swash zone with different types of bottom sediments: insights from laboratory experiments. *Marine Pollution Bulletin*, 150: 110726.

Çit, İ., Sınağ, A., Yumak, T., et al. (2009). Comparative pyrolysis of polyolefins (PP and LDPE) and PET. *Polymer Bulletin*, 64(8): 817–834.

Clark, J. R., Cole, M., Lindeque, P. K., et al. (2016). Marine microplastic debris: a targeted plan for understanding and quantifying interactions with marine life. *Frontiers in Ecology and the Environment*, 14(6): 317–324.

Copinet, A., Bertrand, C., Govindin, S., et al. (2004). Effects of ultraviolet light (315 nm), temperature and relative humidity on the degradation of polylactic acid plastic films. *Chemosphere*, 55(5): 763–773.

Corcoran, P. L., Biesinger, M. C., Grifi, M. (2009). Plastics and beaches: a degrading relationship. *Marine Pollution Bulletin*, 58(1): 80–84.

Cordova, M. R., Wahyudi, A.(2016). Microplastic in the deep-sea sediment of southwestern Sumatran waters. *Marine Research in Indonesia*, 41(1): 27–36.

Craig, I. H., White, J. R. (2006). Mechanical properties of photo-degraded recycled photo-degraded polyolefins. *Journal of Materials Science*, 41(3): 993–1006.

Cunliffe, A. V., Davis, A. (1982). Photo-oxidation of thick polymer samples—Part II: he influence of oxygen diffusion on the natural and artificial weathering of polyolefins. *Polymer Degradation and Stability*, 4(1): 17–37.

Da Costa, J. P., Nunes, A. R., Santos, P. S. M., et al. (2018). Degradation of polyethylene microplastics in seawater: insights into the environmental degradation of polymers. *Journal of Environmental Science and Health, Part A*, 53(9): 866–875.

Davies, P., Evrard, G. (2007). Accelerated ageing of polyurethanes for marine applications. *Polymer Degradation and Stability*, 92(8): 1455–1464.

Dawson, A. L., Kawaguchi, S., King, C. K., et al. (2018). Turning microplastics into nanoplastics through digestive fragmentation by Antarctic krill. *Nature Communications*, 9(1): 1001.

Decker, C., Mayo, F. R., Richardson, H. (1973). Aging and degradation of polyolefins. III. Polyethylene and ethylene–propylene copolymers. *Journal of Polymer Science: Polymer Chemistry Edition*, 11(11): 2879–2898.

Dilara, P. A., Briassoulis, D. (1998). Standard testing methods for mechanical properties and degradation of low density polyethylene (LDPE) films used as greenhouse covering materials: a critical evaluation. *Polymer Testing*, 17(8): 549–585.

Ding, J., Zhang, S., Razanajatovo, R. M., et al. (2018). Accumulation, tissue distribution, and biochemical effects of polystyrene microplastics in the freshwater fish red tilapia (Oreochromis niloticus). *Environmental Pollution*, 238: 1–9.

Dulog, L., David, K. (1971). Zur Autoxydation von Polystyrol. *Die Makromolekulare Chemie*, 145(1): 67–84.

Dunne, R. P., Brown, B. E. (1996). Penetration of solar UVB radiation in shallow tropical waters and its potential biological effects on coral reefs; results from the central Indian Ocean and Andaman Sea. *Marine Ecology Progress Series*, 144(1/3): 109–118.

Duvall, D. (2014). Oxidation resistance of Polypropylene random copolymer pipe to chlorinated water. *Journal of Failure Analysis and Prevention*, 14(3): 336–342.

Eerkes-Medrano, D., Thompson, R. C., Aldridge, D. C. (2015). Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Research*, 75: 63–82.

Efimova, I., Bagaeva, M., Bagaev, A., et al. (2018). Secondary microplastics generation in the sea swash zone with coarse bottom sediments: laboratory experiments. *Frontiers in Marine Science*, 5. https://doi.org/10.3389/fmars.2018.00313

Eich, A., Mildenberger T., Laforsch, C., et al. (2015). Biofilm and diatom succession on polyethylene (PE) and biodegradable plastic bags in two marine habitats: early signs of degradation in the pelagic and benthic zone? *PloS One*, 10(9): e0137201.

Elvidge, C. D., Keith, D. M., Tuttle, B. T., et al. (2010). Spectral identification of lighting type and character. *Sensors*, 10(4): 3961–3988.

Erni-Cassola, G., Zadjelovic, V., Gibson, M. I., et al. (2019). Distribution of plastic polymer types in the marine environment; a meta-analysis. *Journal of Hazardous Materials*, 369: 691–698.

Fairbrother, A. W., Hsueh, H. C., Kim, J. H., e al. (2019). Temperature and light intensity effects on photodegradation of high-density polyethylene. *Polymer Degradation and Stability*, 165: 153–160.

Fayolle, B., Colin, X., Audouin, L., et al. (2007). Mechanism of degradation induced embrittlement in polyethylene. *Polymer Degradation and Stability*, 92(2): 231–238.

Fayolle, B., Richaud, E., Colin, X., et al. (2008). Review: degradation-induced embrittlement in semi-crystalline polymers having their amorphous phase in rubbery state. *Journal of Materials Science*, 43(22): 6999–7012.

Feldman, D. (2002). Polymer weathering: photo-oxidation. *Journal of Polymers and the Environment*, 10(4): 163–173.

Fernández-González, V., Andrade-Garda, J. M., López-Mahía, P., et al. (2020). Impact of weathering on the chemical identification of microplastics from usual packaging polymers in the marine environment. *Analytica Chimica Acta*, 1142: 179–188.

Fok, L., Cheung, P. K., Tang, G., et al. (2017). Size distribution of stranded small plastic debris on the coast of Guangdong, South China. *Environmental Pollution, Part A*, 220: 407–412.

François-Heude, A., Richaud, E., Desnoux, E., et al. (2015). A general kinetic model for the photothermal oxidation of polypropylene. *Journal of Photochemistry and Photobiology A: Chemistry*, 296: 48–65.

Fujita, H. (1988). Some unsolved problems on dilute polymer solutions. *Macromolecules*, 21(1): 179–185.

Furneaux, G. C., Ledbury, K. J., Davis, A. (1981). Photo-oxidation of thick polymer samples—Part I: the variation of photo-oxidation with depth in naturally and artificially weathered low density polyethylene. *Polymer Degradation and Stability*, 3(6): 431–442.

Gallo, R., Severini, F. (2013). Course of the changes in thick and thin isotactic polypropylene samples subjected to natural aging. *Polymer Degradation and Stability*, 98(6): 1144–1149.

Gallo, R., Brambilla, L., Castiglioni, C., et al. (2006). Characterization of naturally weathered Polypropylene plates. *Journal of Macromolecular Science, Part A*, 43(3): 535–554.

Gardette, M., Perthue, A., Gardette, J., et al. (2013). Photo- and thermal-oxidation of polyethylene: comparison of mechanisms and influence of unsaturation content. *Polymer Degradation and Stability*, 98(11): 2383–2390.

Garton, A., Carlsson, D. J, Wiles, D. M. (1980). Polymer oxidation and secondary cage combination of peroxyl radicals. *Makromolekulare Chemie*, 181(9): 1841–1846.

Garvey, J. G., Imeror-Clerc, M., Rouzier, S., et al. (2020). Molecular-scale understanding of the embrittlement in polyethylene ocean debris. *Environmental Science & Technology*, 2020, 54: 11173−11181.

Gerritse, J., Leslie, H., de Tender, C. A., et al. (2020). Fragmentation of plastic objects in a laboratory seawater microcosm. *Scientific Reports*, 10(1): 10945.

Gewert, B., Plassmann, M., Sandblom, O., et al. (2018). Identification of chain scission products released to water by plastic exposed to ultraviolet light. *Environmental Science and Technology Letters*, 5(5): 272–276.

Gewert, B., Plassmann, M. M., MacLeod, M. (2015). Pathways for degradation of plastic polymers floating in the marine environment. *Environmental Science: Processes & Impacts*, 17(9): 1513–1521.

Gigault, J., Pedrono, B., Maxit, B., et al. (2016). Marine plastic litter: the unanalyzed nano-fraction. *Environmental Science: Nano*, 3(2): 346–350.

Gijsman, P. (2008). Review on the thermo-oxidative degradation of polymers during processing and in service. *e-Polymers*, 8(1): 1–34.

Gijsman, P. (2017). A review on the mechanism of action and applicability of Hindered Amine Stabilizers. *Polymer Degradation and Stability*, 145: 2–10.

Gok, A., Gordon, D. A., Burns, D. M., et al. (2019). Reciprocity and spectral effects of the degradation of poly(ethylene-terephthalate) under accelerated weathering exposures. *Journal of Applied Polymer Science*, 136(22): 47589.

Grause, G., Chien, M., Inoue, C. (2020). Changes during the weathering of polyolefins. *Polymer Degradation and Stability*, 181: 109364.

Grossetete, T., Gonon, L., Verney, V. (2002). Submicrometric characterization of the heterogeneous photooxidation of polypropylene by microthermal analysis. *Polymer Degradation and Stability*, 78(2): 203–210.

Gryn'ova, G., Hodgson, J. L., Coote, M. L. (2011). Revising the mechanism of polymer autooxidation. *Organic & Biomolecular Chemistry*, 9(2): 480–490.

Gugumus, F. (1990). Photooxidation of polyethylene films, 2. Mechanisms and kinetics of functional group formation. *Angewandte Makromolekulare Chemie*, 182(1): 111–134.

Gugumus, F. (2000). Aspects of the impact of stabilizer mass on performance in polymers. *Polymer Degradation and Stability*, 69(1): 93–104.

Gulmine, J. V., Janissek, P. R., Heise, H. M., et al. (2003). Degradation profile of polyethylene after artificial accelerated weathering. *Polymer Degradation and Stability*, 79(3): 385–397.

Hakkarainen, M., Albertsson, A. (2004). Environmental degradation of polyethylene. *Advances in Polymer Science*, 169: 177–199.

Hartley, G. H. and Guillet, J. E. (1968). Photochemistry of Ketone Polymers. II. Studies of Model Compounds. *Macromolecules* 1(5): 413–417.

Hess, N. A., Ribic, C. A., Vining, I. (1999). Benthic marine debris, with an emphasis on fishery-related items, surrounding Kodiak Island, Alaska, 1994–1996. *Marine Pollution Bulletin*, 38(10): 885–890.

Hiejima, Y., Kida, T., Takeda, K., et al. (2018). Microscopic structural changes during photodegradation of low-density polyethylene detected by Raman spectroscopy. *Polymer Degradation and Stability*, 150: 67–72.

Hodgson, D. J., Bréchon, A. L., Thompson, R. C. (2018). Ingestion and fragmentation of plastic carrier bags by the amphipod Orchestia gammarellus: effects of plastic type and fouling load. *Marine Pollution Bulletin*, 127: 154–159.

Hsieh, C., Wang, J., Chiu, Y. (2016). The degradation behavior of geotextiles in ocean environments. *Geosynthetics International*, 13(5): 210–217.

Hsu, Y., Weir, M. P., Truss, R. W., et al. (2012). A fundamental study on photo-oxidative degradation of linear low density polyethylene films at embrittlement. *Polymer*, 53(12): 2385–2393.

Hsueh, H., Kim, J. H., Orski, S., et al. (2020). Micro and macroscopic mechanical behaviors of high-density polyethylene under UV irradiation and temperature. *Polymer Degradation and Stability*, 174: 109098.

Iñiguez, M. E, Conesa, J. A., Fullana, A. (2018). Recyclability of four types of plastics exposed to UV irradiation in a marine environment. *Waste Management*, 79: 339–345.

Jabarin, S. A., Lofgren, E. A. (1994). Photooxidative effects on properties and structure of high-density polyethylene. *Journal of Applied Polymer Science*, 53(4): 411–423.

James, S. L., Robinson, A. J., Arnold, J. C., et al. (2013). The effects of humidity on photodegradation of poly(vinyl chloride) and polyethylene as measured by the CO2 evolution rate. *Polymer Degradation and Stability*, 98(2): 508–513.

Jang, M., Shim, W. J., Han, G. M., et al. (2018). Formation of microplastics by polychaetes (Marphysa sanguinea) inhabiting expanded polystyrene marine debris. *Marine Pollution Bulletin, Part A*, 131: 365–369.

Julienne, F., Delorme, N., Lagarde, F. (2019). From macroplastics to microplastics: role of water in the fragmentation of polyethylene. *Chemosphere*, 236: 124409.

Julienne, F., Delorme, N., Chassanieux, C., et al. (2018). Influence of environment and polymer morphology on fragmentation and production of micro/nanoplastics. *Proceedings of the MICRO 2018, Fate and Impact of Microplastics: Knowledge, Actions and Solutions*. Lanzarote, 19–23 November 2018, 62.

Kalogerakis, N., Karkanorachaki, K., Kalogerakis, G. C., et al. (2017). Microplastics generation: Onset of fragmentation of polyethylene films in marine environment mesocosms. *Frontiers in Marine Science*, 4: 1–15.

Karlsson, T. M., Hassellöv, M., Jakubowicz, I. (2018). Influence of thermooxidative degradation on the in situ fate of polyethylene in temperate coastal waters. *Marine Pollution Bulletin*, 135: 187–194.

Khaled, A., Rivaton, A., Richard, C., et al. (2018). Phototransformation of plastic containing brominated flame retardants: Enhanced fragmentation and release of photoproducts to water and air. *Environmental Science & Technology*, 52(19): 11123–11131.

Khoironi, A., Hadiyanto, H., Anggoro, S., et al. (2020). Evaluation of polypropylene plastic degradation and microplastic identification in sediments at Tambak Lorok coastal area, Semarang, *Indonesia. Marine Pollution Bulletin*, 151: 110868.

Klemchuk, P. P. (1990). Degradable plastics: A critical review. *Polymer Degradation and Stability*, 27(2): 183–202.

Kollmann, T. M., Wood, D. G. M. (1980). The effect of variations in light intensity on the photo-oxidation of polypropylene. *Polymer Engineering and Science*, 20(10): 684–687.

Kooi, M., Reisser, J., Slat, B., et al. (2016). The effect of particle properties on the depth profile of buoyant plastics in the ocean. *Scientific Reports*, 6(1): 33882.

Kühn, S., van Franeker, J. A. (2020). Quantitative overview of marine debris ingested by marine megafauna. *Marine Pollution Bulletin*, 151: 110858.

Kuzina, S., Mikhailov, A. (1998). Photocatalytic degradation of polystyrene plastic under fluorescent light. *European Polymer Journal*, 34: 291–320.

Kvale, K., Prowe, A. E. F., Chien, C.-T., et al. (2020). The global biological microplastic particle sink. *Scientific Reports*, 10(1): 16670.

Lambert, S., Wagner, M. (2016). Formation of microscopic particles during the degradation of different polymers. *Chemosphere*, 161: 510–517.

Lebreton, L. C. M., van der Zwet, J., Damsteeg, J.-W., et al. (2017). River plastic emissions to the world's oceans. *Nature Communications*, 8(1): 15611.

Leonas, K., Gordan, R. (1993). An accelerated laboratory study evaluating the disintegration rates of plastic films in simulated environments. *Journal of Environmental Polymer Degradation*, 1(1): 45–51.

Long, M., Moriceau, B., Gallinari, M., et al. (2015). Interactions between microplastics and phytoplankton aggregates: impact on their respective fates. *Marine Chemistry*, 175: 39–46.

Lucas, N., Bienaime, C., Belloy, C., et al. (2008). Polymer biodegradation: mechanisms and estimation techniques – a review. *Chemosphere*, 73(4): 429–442.

Mao, R., Lang, M., Yu, X., et al. (2020). Aging mechanism of microplastics with UV irradiation and its effects on the adsorption of heavy metals. *Journal of Hazardous Materials*, 393: 122515.

Martin, J., Chin, J., Nguyen, T. (2003). Reciprocity law experiments in polymeric photodegradation: a critical review. *Progress in Organic Coatings*, 47(3–4): 292–311.

Mattsson, K., Johnson, E. V., Malmendal, A., et al. (2017). Brain damage and behavioural disorders in fish induced by plastic nanoparticles delivered through the food chain. *Scientific Reports*, 7: 11452.

Mayo, F. R. (1978). Relative reactivities in oxidations of polypropylene and polypropylene models. *Macromolecules*, 11(5): 942–946.

Meides, N., Menzel, T., Poetzschner, B. et al. (2021). Reconstructing the environmental degradation of polystyrene by accelerated weathering. *Environmental Science and Technology* 55(12): 7930–7938.

Mendes, L. C., Rufino, E. S., de Paula, F. O. C., et al. (2003). Mechanical, thermal and microstructure evaluation of HDPE after weathering in Rio de Janeiro City. *Polymer Degradation and Stability*, 79(3): 371–383.

Napper, I. E., Thompson, R. C. (2019). Environmental deterioration of biodegradable, oxo-biodegradable, compostable, and conventional plastic carrier bags in the sea, soil, and open-air over a 3-year period. *Environmental Science & Technology*, *53*(9): 4775–4783.

Ni, K., Zhu, J., Liao, X., et al. (2015). Microstructure studies of isotactic polypropylene under natural weathering by positron annihilation lifetime spectroscopy. *Journal of Polymer Research*, 22(6): 1–15.

Niki, E., Decker, C., Mayo, F. R. (1973). Aging and degradation of polyolefins. I. Peroxide-initiated oxidations of atactic polypropylene. *Journal of Polymer Science: Polymer Chemistry Edition*, 11(11): 2813–2845.

O'Brine, T., Thompson, R. C. (2010). Degradation of plastic carrier bags in the marine environment. *Marine Pollution Bulletin*, 60(12): 2279–2283.

Oelschlägel, K., Pfeiffer, J., Potthoff, A. (2017). Imitating the weathering of microplastics in the marine environment. In: Cocca M., Di Pace E., Errico M., et al. (Eds.), *Proceedings of the International Conference on Microplastic Pollution in the Mediterranean Sea*. Springer Water. Springer, Cham, pp. 171–179.

Ojeda, T., Freitas, A., Birck, K., et al. (2011). Degradability of linear polyolefins under natural weathering. *Polymer Degradation and Stability*, 96(4): 703–707.

Pabiot, J., Verdu, J. (1981). The change in mechanical behavior of linear polymers during photochemical aging. *Polymer Engineering and Science*, 21(1): 32–38.

Paluselli, A., Fauvelle, V., Galgani, F., et al. (2019). Phthalate release from plastic fragments and degradation in seawater. *Environmental Science & Technology*, 53(1): 166–175.

Pegram, J. E., Andrady, A. L. (1989). Outdoor weathering of selected polymeric materials under marine exposure conditions. *Polymer Degradation and Stability*, 26(4): 333–345.

Pegram, J. E., Andrady, A. L. (1992). *Outdoor Weathering of Polystyrene Foam*. VCH Publishers, New York, pp. 287–298.

Petukhova, E. S., Fedorov, A. L. (2019). Investigation of the climate resistance of stabilized polyethylene composite materials. *Procedia Structural Integrity*, 20: 75–80.

Pickett, J. E. (2020). Introduction to polymer weathering, stabilization, and testing. In: White, C., Nichols, M., Pickett, J. (Eds.), *Service Life Prediction of Polymers and Coatings*. William Andrew Publishing, Kidlington, pp. 1–8.

Pickett, J. E., Gibson, D. A., Gardner, M. M. (2008). Effects of irradiation conditions on the weathering of engineering thermoplastics. *Polymer Degradation and Stability*, 93(8): 1597–1606.

Pickett, J. E., Kuvshinnikova, O., Sung, L.-P., et al. (2019). Accelerated weathering parameters for some aromatic engineering thermoplastics. *Polymer Degradation and Stability*, 166: 135–144.

Pilař, J., Šlouf, M., Michálková, D., et al. (2017). Pro-oxidant activity of α-tocopherol during photooxidative degradation of polyolefins. ESRI and IR microspectroscopy studies. *Polymer Degradation and Stability*, 138: 55–71.

Pitt, J. A., Kozal, J. S., Jayasundara, N., et al. (2018). Uptake, tissue distribution, and toxicity of polystyrene nanoparticles in developing zebrafish (Danio rerio). *Aquatic Toxicology*, 194: 185–194.

Pospíšil, J., Pilař, J., Billingham, N. C., et al. (2004). Impact of weathering on chemical and morphological changes in stabilized polymers. In: Thomas, Reichart (Ed), *Natural and Artificial Ageing of Polymers*. GUS, Germany, pp. 411–422.

Rabek, J. F. (1987). *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers-Theory and Applications*. John Wiley & Sons, New York, p. 756.

Rabello, M. S., White, J. R. (1997). Crystallization and melting behaviour of photodegraded polypropylene — I. *Chemi-crystallization. Polymer*, 38(26): 6379–6387.

Rajakumar, K., Sarasvathy, V., Thamarai Chelvan, A., et al. (2009). Natural weathering studies of Polypropylene. *Journal of Polymers and the Environment*, 17(3): 191–202.

Rånby, B. (1989). Photodegradation and photo-oxidation of synthetic polymers. *Journal of Analytical and Applied Pyrolysis*, 15: 237–247.

Rani, M., Shim, W. J., Han, G. M., et al. (2017). Benzotriazole-type ultraviolet stabilizers and antioxidants in plastic marine debris and their new products. *Science of The Total Environment*, 579: 745–754.

Ranjan, V. P., Goel, S. (2019). Degradation of low-density polyethylene film exposed to UV radiation in four Environments. *Journal of Hazardous, Toxic, and Radioactive Waste*, 23(4): 04019015.

Reich, L., Stivala, S. (1971). Kinetics and mechanism of oxidative degradation of polymers. In: Reich, L., Stivala, S. (Ed.), *Elements of Polymer Degradation*. McGraw-Hill Book Company, New York, pp. 229–293.

Ren, S.-Y., Sun, Q., Ni, H.-G., et al. (2020). A minimalist approach to quantify emission factor of microplastic by mechanical abrasion. *Chemosphere*, 245: 125630.

Resmeriță, A., Coroaba, A., Darie, R., et al. (2018). Erosion as a possible mechanism for the decrease of size of plastic pieces floating in oceans. *Marine Pollution Bulletin*, 127: 387–395.

Richters, P. (1970). Initiation process in the oxidation of polypropylene. *Macromolecules*, 3(2): 262–264.

Rodriguez, A., Mansoor, B., Ayoub, G., Colin, X. and Benzerga, A., (2020). Effect of UV-aging on the mechanical and fracture behavior of low density polyethylene. *Polymer Degradation & Stability*, 180:109185.

Rowenczyk, L., Dazzi, A., Deniset-Besseau, A., et al. (2020). Microstructure characterization of oceanic polyethylene debris. *Environmental Science & Technology*, 54(7): 4102–4109.

Russell, G. (1957). Deuterium-isotope effects in the autoxidation of Aralkyl hydrocarbons. Mechanism of the interaction of PEroxy radicals. *Journal of the American Chemical Society*, 79(14): 3871–3877.

Selonke, M., Moreira, T., Schafranski, L., et al. (2012). Influence of reprocessing in the formation of functional groups during low density polyethylene aging. *Polímeros*, 22(5): 491–496.

Shah, S. S., Ahmad, I., Ishaq, M. (2017). Degradation study of used polystyrene with UV irradiation. *Advanced Material Science*, 2(3): 1–6.

Shimizu, K., Tokuta, Y., Oishi, A., et al. (2016). Weatherability of polypropylene by accelerated weathering tests and outdoor exposure tests in Japan. *Journal of Polymers*, 2016: 1–14.

Singh, B., Sharma, N. (2008). Mechanistic implications of plastic degradation. *Polymer Degradation and Stability*, 93(3): 561–584.

Skrypnyk, I., Spoormaker, J. (1999). Modeling of surface microcracking caused by ultraviolet degradation in high-density polyethylene. *Materials Science*, 35(4): 527–534.

Song, Y., Hong, S., Eo, S., et al. (2020). Rapid production of micro- and nanoplastics by fragmentation of expanded polystyrene exposed to sunlight. *Environmental Science & Technology*, 54(18): 11191–11200.

Song, Y., Hong, S., Jang, M., et al. (2017). Combined effects of UV exposure duration and mechanical abrasion on microplastic fragmentation by polymer type. *Environmental Science & Technology*, 51(8): 4368–4376.

Stivala, S. S., Kimura, J., and Gabbay, S. M. (1983). Thermal degradation and oxidative processes. In: Allen, N.S. (ed.) *Degradation and Stabilisation of Polyolefins*. London: Elsevier Applied Science, p. 63.

Sudhakar, M., Doble, M., Murthy, P., et al. (2008). Marine microbe-mediated biodegradation of low- and high-density polyethylenes. *International Biodeterioration & Biodegradation*, 61(3): 203–213.

Sumner, P., Hedding, D., Meiklejohn, K. (2007). Rock surface temperatures in southern Namibia and implications for thermally-driven physical weathering. *Zeitschrift für Geomorphologie, Supplementary Issues*, 51(1): 133–147.

Svendin, J. (2020). *Photodegradation of macroplastics to microplastics: a laboratory study on common litter found in urban areas*. M. Thesis Department of Natural Resource Engineering, Luleå University of Technology, Sweden.

Tang, C., Chen, H., Brimblecombe, P., et al. (2018). Textural, surface and chemical properties of polyvinyl chloride particles degraded in a simulated environment. *Marine Pollution Bulletin*, 133: 392–401.

Tang, C., Chen, H., Brimblecombe, P., et al. (2019). Morphology and chemical properties of polypropylene pellets degraded in simulated terrestrial and marine environments. *Marine Pollution Bulletin*, 149: 110626.

ter Halle, A., Ladirat, L., Gendre, X., et al. (2016). Understanding the fragmentation pattern of marine plastic Debris. *Environmental Science & Technology*, 50(11): 5668–5675.

ter Halle, A., Ladirat, L., Martignac, M., et al. (2017). To what extent are microplastics from the open ocean weathered. *Environmental Pollution*, 227: 167–174.

Therias, S., Rapp, G., Masson, C., et al. (2020). Limits of UV-light acceleration on the photooxidation of low-density polyethylene. *Polymer Degradation and Stability*, 183: 109443.

Tidjani, A. (1997). Photooxidation of polypropylene under natural and accelerated weathering conditions. *Journal of Applied Polymer Science*, 64(13): 2497–2503.

Tosin, M., Weber, M., Siotto, M., et al. (2012). Laboratory test methods to determine the degradation of plastics in marine environmental conditions. *Frontiers in Microbiology*, 3: 225.

Turner, A., Arnold, R., Williams, T. (2020). Weathering and persistence of plastic in the marine environment: lessons from LEGO. *Environmental Pollution*, 262: 114299.

Turton, T., White, J. (2001). Effect of stabilizer and pigment on photo-degradation depth profiles in polypropylene. *Polymer Degradation and Stability*, 74(3): 559–568.

Weir, N. (1978). New aspect of photodegradation and photooxidation of polystyrene. *European Polymer Journal*, 14: 9–14.

Weinstein, J. E., Crocker, B. K., Gray, A. D. (2016). From macroplastic to microplastic: Degradation of high-density polyethylene, polypropylene, and polystyrene in a salt marsh habitat. *Environmental Toxicology and Chemistry*, 35: 1632–1640.

Welden, N., Cowie, P. (2017). Degradation of common polymer ropes in a sublittoral marine environment. *Marine Pollution Bulletin*, 118(1–2): 248–253.

White, J. R. (2006). Polymer ageing: physics, chemistry or engineering? *Time to Reflect, Comptes Rendus Chimie*, 9(11–12): 1396–1408.

White, J., Turnbull, A. (1994). Weathering of polymers: mechanisms of degradation and stabilization, testing strategies and modelling. *Journal of Materials Science*, 29(3): 584–613.

White, K., Fischer, R., Ketola, W. (2009). An analysis of the effect of irradiance on the weathering of polymeric materials. In: Martin, J. W., Ryntz, R. A., Chin, J., et al. (Eds.), *Service Life Prediction of Polymeric Materials*. Springer, Boston, pp. 71–82.

Wilcox, C., Hardesty, B. D., Lavender-Law, K. (2020). Abundance of floating plastic particles is increasing in the western North Atlantic Ocean. *Environmental Science & Technology*, 54(2): 790–796.

Winkler, A., Santo, N., Ortenzi, M., et al. (2019). Does mechanical stress cause microplastic release from plastic water bottles? *Water Research*, 166: 115082.

Wu, X., Liu, P., Shi, H., et al. (2020). Photo aging and fragmentation of polypropylene food packaging materials in artificial seawater. *Water Research*, 188: 116456.

Wypych, G. (2015). *Handbook of UV Degradation and Stabilization*, second ed. Chem Tec Publishing, Toronto, p. 430.

Wypych, G. (2020). *Handbook of UV Degradation and Stabilization*, third ed. ChemTec Publishing, Toronto, p. 518.

Xingzhou, H. (1997). Wavelength sensitivity of photo-oxidation of polyethylene. *Polymer Degradation and Stability*, 55(2): 131–134.

Yagoubi, W., Abdelhafidi, A., Sebaa, M., Chabira, S. (2015). Identification of carbonyl species of weathered LDPEfilms by curve fitting and derivative analysis of IR spectra, *Polym. Test.*, 44:37–48.

Yanai, G., Ram, A., Miltz, J. (1995). Accelerated weathering-induced degradation of unprotected multilayer polyethylene slabs. *I. Journal of Applied Polymer Science*, 57(3): 303–310.

Yang, X. (2017). Study on slamming pressure calculation formula of plunging breaking wave on sloping sea dike. *International Journal of Naval Architecture and Ocean Engineering*, 9(4): 439–445.

Ye, S., Andrady, A. L. (1991). Fouling of floating plastic debris under Biscayne Bay exposure conditions. *Marine Pollution Bulletin*, 22(12): 608–613.

Yousif, E., Haddad, R. (2013). Photodegradation and photostabilization of polymers, especially polystyrene: review. *SpringerPlus*, 2(1): 398.

Zhang, D., Liu, X., Huang, W., e al. (2020). Microplastic pollution in deep-sea sediments and organisms of the Western Pacific Ocean. *Environmental Pollution*, 259: 113948.

Zhu, K., Jia, H., Sun, Y., et al. (2020). Long-term photo-transformation of microplastics under simulated sunlight irradiation in aquatic environments: roles of reactive oxygen species. *Water Research*, 173: 115564.

9

Pollutants Sorbed Onto Microplastics

Jianlong Wang and Xuan Guo

Laboratory of Environmental Technology, INET, Tsinghua University, Beijing, P.R. China

9.1 Introduction

Microplastics (MPs; (<5 mm in size) are ubiquitous and pose a potential threat to the marine environment and human health (Andrady 2011, 2017). Moreover, they can concentrate pollutants through sorption and are of a size range that can be ingested by a wide range of marine biota. MPs have aroused global concern in recent years because of their wide distribution, high abundance, and potential risks to the ecosystem (Guo and Wang 2019a, 2019b, 2019c; Huang et al. 2021; Puckowski et al. 2021; Razanajatovo et al. 2018). They can have an adverse effect on the health and well-being of organisms that ingest them, such as fish (Cordova et al. 2020; Koongolla et al. 2018), sea cucumber (Mohsen et al. 2019), copepod (Procter et al. 2019), mussels (Pedersen et al. 2020), and sea birds (Carlin et al. 2020). Once ingested, MPs can have a 'direct effect' of causing blockage of the digestive tract of the ingesting organisms, possibly leading to death (Carbery et al. 2018; Guo and Wang 2019b).

MPs also pose an 'indirect' adverse impact on the organisms from sorbed pollutants. They sorb and concentrate pollutants from surrounding water rapidly because of their hydrophobicity, the small size, and large surface-to-volume ratio (Guo and Wang 2019b). MPs may, therefore, act as important sorbents in polluted bodies of water (Wang et al. 2017). Organic pollutants, such as antibiotics (Lin et al. 2020; Xu et al. 2018a, 2018b), polycyclic aromatic hydrocarbons (PAHs; Yu et al. 2020), polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), flame retardants (Cheng et al. 2020; Jiang et al. 2017; Liu et al. 2018), fuel aromatics (Müller et al. 2018; Wang et al. 2015), and metal ions (Holmes et al. 2012, 2014), are well known to be sorbed by MPs (Guo et al. 2018; Llorca et al. 2018; Zhang et al. 2018). The partition of pollutants between the water phase and the solid plastic is the mechanism underlying sorption. The sorption of pollutants on MPs can be quantified by the partition coefficient K, defined as the ratio of the concentration of pollutants in plastic to that in the liquid phase (in this case, seawater). The MPs carrying sorbed pollutants can potentially deliver these to different aquatic environments and to organisms, affecting their distribution in the environments, through the adsorption–migration–desorption behaviors described in the literature (Fries and Zarfl 2012; León et al. 2018). A particular concern is that once ingested, the contaminated MPs may transfer pollutants to organisms (Desforges et al. 2015) and even accumulate them in the food web as well (Batel et al. 2016; Zhang et al. 2019).

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

In this chapter, the reported research on sorption of organic pollutants and metals ions onto MPs is summarized. In Section 9.2, the sorption capacity of different types of pollutants onto MPs is reviewed. In Section 9.3, the factors that influence the interactions between pollutants and MPs, such as the type of polymer, the degree of weathering, pH, and ionic strength, are reviewed. In Section 9.4, the sorption kinetics and isotherms of pollutants onto MPs are summarized. In Section 9.5, the sorption mechanisms are discussed.

9.2 Pollutants Sorbed by MPs

9.2.1 Organic Pollutants

Efforts have been made to investigate interaction of plastics and MPs with organic pollutants, including antibiotics, PAHs, PCBs, HCHs, DDTs, flame retardants, fuel aromatics, and other types of organic pollutants (Bao et al. 2020; Chen et al. 2019; Gao et al. 2019; Godoy et al. 2019; Guo and Wang 2019a; Guo et al. 2018, 2019a, 2019b, 2020a; Hodson et al. 2017; Holmes et al. 2012, 2014; Hüffer and Hofman 2016; Hu et al. 2017; Jiang et al. 2020; Lin et al. 2020; Liu et al. 2018; Llorca et al. 2018; Razanajatovo et al. 2018; Shan et al. 2020; Wang and Wang 2018a; Wang et al. 2015, 2018a, 2018b, 2020a; Xu et al. 2018a, 2018b; Yang et al. 2019; Yu et al. 2020; Zhang et al. 2018; Zou et al. 2020), as summarized and depicted in Figure 9.1. In the following sections, the sorption of organic pollutants onto MPs is discussed in detail.

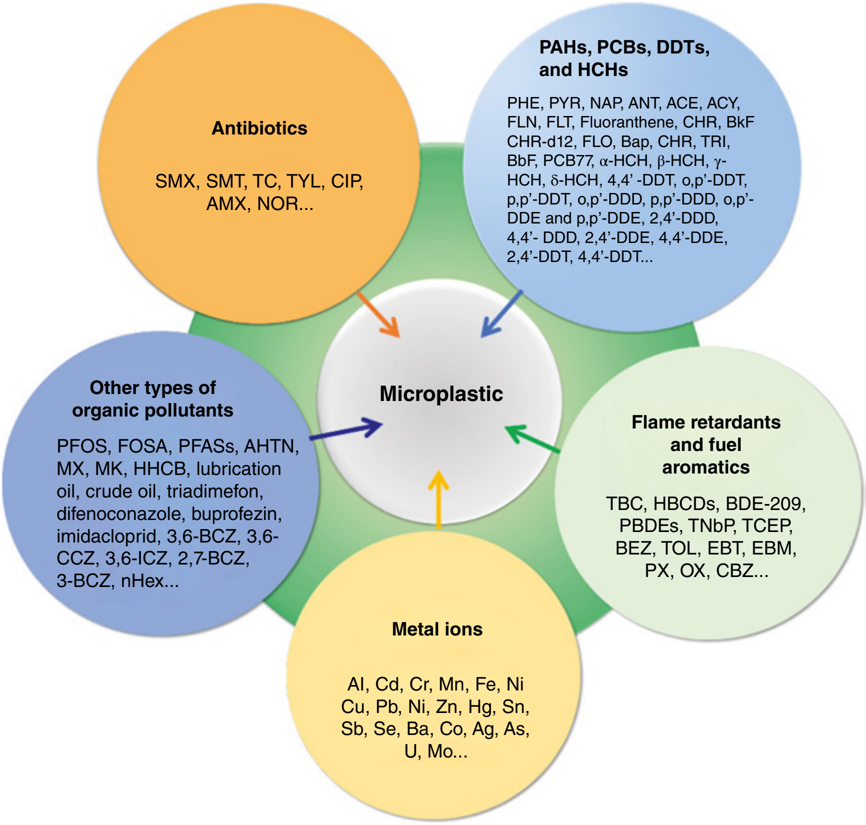


Figure 9.1 Summary of organic pollutants and metal ions reported to be sorbed onto MPs.

9.2.1.1 Antibiotics

Antibiotics are widely used in medicine, agriculture, and animal husbandry, and are frequently detected in global aquatic environments (Wang et al. 2019c), sometimes reaching concentrations as high as several mg/g (Le and Munekage 2004; Wang et al. 2020d). They may inhibit the growth of aquatic organisms or even kill them. Various methods have been investigated for the removal of antibiotics from water and wastewater (Liu et al. 2020; Tang and Wang 2018; Wang and Chu 2016; Wang and Wang 2016, 2019; Wang and Zhuan 2020; Wang and Zhuang 2019; Wang et al. 2020d). The interaction between antibiotics and MPs is receiving increasing attention because of their concentration by MPs that increases their potential bioavailability to ingesting organisms.

Recent studies on the sorption of antibiotics onto MPs are summarized in Table 9.1. A majority of these had investigated the interactions between antibiotics and MPs in laboratory environments with only a few studies conducted in the field. Sulfamethoxazole, tetracycline (TC), and ciprofloxacin (CIP) are three of the most frequently studied antibiotics (Atugoda et al. 2020; Guo and Wang 2019a; Guo et al. 2019a; Huang et al. 2021; Li et al. 2018, 2020; Lin et al. 2020; Puckowski et al. 2021; Shen et al. 2018; Xu et al. 2018a, 2018b). Sulfamethazine, amoxicillin (AMX), tylosin (TYL), and norfloxacin (NOR) can also be sorbed on MPs (Guo et al. 2018, 2019b; Li et al. 2018; Puckowski et al. 2021). The sorption capacity of the antibiotics varies from several μg/g to mg/g and is closely related to the initial concentration C_0 of the compound in water and the molecular characteristics of the specific antibiotics. Xu et al. (2018b) studied the sorption of TC on virgin polyethylene (PE), polypropylene (PP), and polystyrene (PS), at values of C_0 ranging from 0.2 to 5 mg/L, and found the sorption capacity to be relatively low (10–167 μg/g). Li et al. (2018) studied the uptake of five antibiotics on virgin PE, PS, PP, poly(vinyl chloride) (PVC), and PA and reported their distribution coefficient (K_d) to correlate well with octanol/water partition coefficient, K_{ow}, for the compounds. The general sorption capacities of the plastics for antibiotics ranked as follows: CIP > AMX > trimethoprim > sulfadiazine > TC. As expected, MPs had higher affinities to the hydrophobic antibiotics as evidenced by the higher values of log K_{ow} (Li et al. 2018; Razanajatovo et al. 2018). Guo et al. (2018) reported for the sorption of TYL in PE, PP, PS, and PVC to be 1667–3333 μg/g, at values of C_0 in the range of 1–30 mg/L. Atugoda et al. (2020) studied the sorption of CIP (C_0 = 30–500 mg/L) onto MPs of PE and concluded that the maximum sorption capacity predicted by the Hill isotherm was 5.852 mg/g. Antibiotics with multiple polar functional groups can especially facilitate their sorption by MPs (Shen et al. 2018). Based on the above studies, the sorption capacity of antibiotics on MPs appears to be dominated by the concentrations of antibiotics in solution, octanol/water partition coefficients (log K_{ow}), and the polarity of antibiotic molecule.

9.2.1.2 PAHs, PCBs, HCHs, and DDTs

The persistent organic pollutants (POPs) are well known to be sorbed by MPs, with the first research investigations on topic by Endo et al. (2005), Teuten et al. (2007), and Tanaka et al. (2013). In aquatic environments, PAHs originate from two sources: natural sources (such as from sediment deposits) and anthropogenic sources such as refuse incineration and oil leaks (Wang et al. 2018b). The sources of PAHs, PCBs, HCHs, and DDTs in environments are exclusively of anthropogenic origin. Some of these POPs are highly toxic and carcinogenic to humans. Intake of PCBs could affect the reproductive, nervous, and immune system (Wang et al. 2018b).

Various field and laboratory studies that have investigated the sorption of this group of pollutants into MPs are summarized in Table 9.1. The most frequently studied PAHs appear to be phenanthrene (PHE), pyrene (PYR), and naphthalene (NAP; Bakir et al. 2012, 2014a; Bao et al. 2020; Hüffer and Hofmann 2016; Hüffer et al. 2018; Jin et al. 2020; Lee et al. 2014; Mai et al. 2018; Rochman et al. 2013a; Shi et al. 2020; Sørensen et al. 2020; Tan et al. 2019; Wang and Wang 2018a, 2018b; Wang et al. 2019a; Yu et al. 2020; Zhao et al. 2020). In field experiments, the

Table 9.1 Sorption of antibiotics by MPs.

Pollutants	MPs	Environmental conditions	Sorption capacity[a]	Reference
Sulfamethoxazole (SMX)	Virgin PE (46–48 μm)	$C_0 = 1–100$ μg/L, 24 °C, 96 h, pH = 6.85	86.78 μg/g	Razanajatovo et al. (2018)
	Virgin PE (150 μm)	$C_0 = 0.2–5$ mg/L, pH = 2–12, 72 h, 200 rpm, 25 °C	25–700 μg/g	Xu et al. (2018a)
	Aged PE (0.1–0.2 mm) and PS (0.5–1 mm)	$C_0 = 0–10$ mg/L, 24 h, 160 rpm, 25 °C	0–310 μg/g	Guo and Wang (2019a)
	Virgin and aged PS (5 μm)	24 h, 150 rpm, 25 °C	—	Huang et al. (2021)
	Virgin PA, PE, PS, PP, PVC, and PET (100–150 μm)	$C_0 = 0–12$ mg/L, 24 h, 160 rpm, 25 °C	0–2.36 mg/g	Guo et al. (2019a)
Sulfamethazine (SMT)	Virgin PA, PE, PS, PP, PVC, and PET (100–150 μm)	$C_0 = 0–12$ mg/L, 24 h, 160 rpm, 25 °C	0–0.39 mg/g	Guo et al. (2019b)
	Aged PE (0.1–0.2 mm) and PS (0.5–1 mm)	$C_0 = 0–10$ mg/L, 24 h, 160 rpm, 25 °C	0–305 μg/g	Guo and Wang (2019a)
Amoxicillin (AMX)	PE, PS, PP, PVC, and PA (75–180 μm)	$C_0 = 0.5–15$ mg/L, 4 d, 180 rpm, 25 °C	0–3000 μg/g	Li et al. (2018)
Tetracycline (TC)	Nylon (1, 5, 10 mm)	$C_0 = 3–20$ mg/L, pH = 2–12, 190 rpm, 27 °C, salinity 0.05–3.5 mg/L	58.573 mg/g	Lin et al. (2020)
	MPs (150–250 μm)	$C_0 = 10$ mg/L, 5–30 °C, 180 rpm, 10 d	91.7–120.5 μg/g	Shen et al. (2018)
	PVC	$C_0 = 0–100$ mg/L, 25 °C; pH = 7.5	—	Li et al. (2020)
	Virgin PE, PS, PP, PVC, and PA (75–180 μm)	$C_0 = 0.5–15$ mg/L, 4 d, 180 rpm, 25 °C	0–3840 μg/g	Li et al. (2018)
	Virgin PE, PP, and PS (<280 μm)	$C_0 = 0.2–5$ mg/L, pH = 2–12, salinity 0.5–35, 24 h, 200 rpm, 25 °C	10–167 μg/g	Xu et al. (2018b)
Tylosin (TYL)	PE, PP, PS, and PVC	$C_0 = 1–30$ mg/L, pH = 4–9, 48 h, 150 rpm, 25 °C	1667–3333 μg/g	Guo et al. (2018)
Ciprofloxacin (CIP)	Virgin PE, PS, PP, PVC, and PA, (75–180 μm)	$C_0 = 0.5–15$ mg/L, 4 d, 180 rpm, 25 °C	0–1000 μg/g	Li et al. (2018)
	PP, low-density polyethylene (LDPE), high-density polyethylene (HDPE), and PVC	$C_0 = 1.5$ mg/L, 7 d, 300 rpm, 21 °C	$K = 0.1–1.7$ L/kg[b]	Puckowski et al. (2021)
	PE (~100 μm)	$C_0 = 30–500$ mg/L, 12 h, pH = 4–9, 400 rpm	5.852 mg/g	Atugoda et al. (2020)
Norfloxacin (NOR)	PP, LDPE, HDPE, and PVC	$C_0 = 1.5$ mg/L, 7 d, 300 rpm, 21 °C	$K = 0.4–1.7$ L/kg[b]	Puckowski et al. (2021)

[a] The sorption capacity is either the experimental data estimated based on the figures in the reference or the sorption capacity predicted by the isotherms.

[b] K is the partition coefficient provided by the linear isotherm model.

concentrations of PAHs in MPs ranged from 0 to 119 000 ng/g (Mai et al. 2018; Rochman et al. 2013a). For instance, the concentrations of total PCBs in MPs sampled in Tokyo Bay and Sagami Bay were 0.28–429.32 ng/g (Yeo et al. 2020). For HCHs, the sorption capacity was generally lower than that for PAHs, PCBs, and DDTs. However, the concentrations of HCHs in MPs collected from coastal São Paulo, in southeastern Brazil, and beaches in Hong Kong, were in the same range of 0.24–63.5 ng/g (Lo et al. 2019; Taniguchi et al. 2016). MPs collected from big city environments typically carry relatively higher concentrations of this class of POPs compared to those found in remote areas (Guo and Wang 2019b; Wang et al. 2018c).

Laboratory studies on the sorption capacity of MPs are summarized in Table 9.2. Bakir et al. (2012, 2014a, 2014b) reported the sorption capacity of 4,4′-DDT of MPs to be higher than for other congeners of DDT. Also, MPs have higher affinities to δ-HCH than for γ-HCH, α-HCH, and β-HCH in seawater, consistent with their higher values of K_{ow} (Wang et al. 2018c). The values of log K_{ow} of δ-HCH, γ-HCH, α-HCH, and β-HCH were 4.14, 3.55, 3.80, and 3.81, respectively (Lee et al. 2014). Evidence suggests that the affinity of nonpolar compounds to MPs to be relatively weaker than for the planar molecules of equal hydrophobicity (Velzeboer et al. 2014; Wang et al. 2020b). Also, the sorption capacity of PAHs, PCBs, and DDTs in MPs appears to be higher than that of HCHs, suggesting that hydrophobicity of pollutants is a particularly important property in determining their interaction with MPs. The log K_{ow} values of pollutants follow the order; HCHs < PCBs < DDTs < PAHs. The affinities of PAHs, PCBs, HCHs, and DDTs to MPs are positively correlated with the values of log K_{ow} (Hartmann et al. 2017; Wang et al. 2018c).

9.2.1.3 Flame Retardants and Fuel Aromatics

Flame retardants are chemical additives in plastics (see Chapter 2) and include the polybrominated diphenylene ethers (PBDEs) popularly used some years back (by now phased out for the most part). But, residual brominated flame retardants are frequently detected in aquatic environments at concentrations that can reach up to 1000 ng/L at some locations (Bollmann et al. 2012). On the one hand, flame retardants compounded into plastics can be released into water from marine plastic debris, and, on the other hand, plastics can also sorb flame retardants from seawater to serve as carriers of the chemical (Cheng et al. 2020; Jiang et al. 2017; Liu et al. 2018). Table 9.3 shows typical concentrations of flame retardants in MPs, based on recent studies. Field data show hexabromocyclododecanes (HBCDs) in MPs collected from South Korea and other Asia-Pacific coastal regions. The levels of PBDEs in MPs from Tokyo Bay and Sagami Bay, for instance, were 0.17 ± 0.08–3350 ± 5860 μg/g and 0–1785.56 ng/g, respectively. Laboratory studies agree that the sorption capacity of flame retardants can range from ng/g to μg/g. Organophophates are increasingly used as alternative flame retardants, partly because of the phase out of PBDEs. Again, hydrophobicity appears to primarily influence sorption. Shen et al. (2018), for instance, found tri-n-butyl phosphate with higher value of log K_{ow} of 4 had higher affinity to hydrophobic MPs of PE than tris(2-chloroethyl) phosphate (log $K_{ow} = 1.44$).

Recent studies on the sorption of fuel aromatics on MPs are summarized in Table 9.3. Benzene (BEZ) and toluene (TOL) are the most frequently studied fuel aromatics, followed by ethyl benzoate (EBT), ethyl benzene (EBM), *p*-xylene (PX), *o*-xylene (OX), and chlorobenzene (CBZ). The sorption capacity of BEZ and TOL by MPs varies within a wide range from 0.1 to 10^4 μg/g (Hüffer and Hofmann 2016; Hüffer et al. 2018; Müller et al. 2018) with the values of the coefficient log $K_{P/W}$ ranging from 1.43 to 2.34 and 1.56 to 2.29 for pristine and weathered PP, respectively (Müller et al. 2018). The hydrophobicity of fuel aromatics is also positively correlated with their affinities toward MPs (Müller et al. 2018). Similarly, the nonpolar fuel aromatics (such as BEZ, TOL, CBZ, and EBT) show a relatively higher affinity toward nonpolar polymers (Hüffer and Hofmann 2016; Hüffer et al. 2018).

Table 9.2 Sorption of PAHs, PCBs, HCHs, and DDTs by MPs.

Types	Pollutants	MPs	Experimental conditions	Sorption capacity^a	Reference
PAHs	PHE	PVC and PE (200–250 μm)	$C_0 = 0.8–3.1$ μg/L, filtered seawater, 24 h, 220 rpm, 20 °C	1.15–15.5 μg/g	Bakir et al. (2012)
		MPs (333 μm–5 mm)	Field experiment in Bohai and Huanghai Seas	400–119,000 ng/g	Mai et al. (2018)
		PE, PS, and PVC (100–150 μm)	$C_0 = 10–200$ μg/L, artificial freshwater (AFW), 120 h, 200 rpm, 20 °C	303.03–714.29 μg/g	Wang and Wang (2018b)
		PE (≤ 300 μm) and PS (≤ 250 μm)	—	—	Wang et al. (2019a)
		PE and nylon (0.2–2 mm)	$C_0 = 100–1000$ μg/L and 0.2–10 mg/L, synthetic seawater, salinity 25‰, 48 h, 150 rpm, 25.0 °C	270–310 μg/g^a	Wang et al. (2018a)
		PP (52.31%) and PE (27.39%)	Field experiment in Beijiang River	25.6–45.6 ng/g	Tan et al. (2019)
		PVC and PE (200–250 μm)	$C_0 = 0.6–6.1$ μg/L, seawater, salinity 0–25‰, 24 h, 220 rpm, 18 °C	2–4 μg/g	Bakir et al. (2014a)
		PVC (140 μm)	$C_0 = 0.2–2.5$ mg/L, 150 rpm, 25 °C, 60 h, pH = 3–11	—	Bao et al., 2020
		PE, PP, and PS (<250 μm)	Artificial seawater, 150 rpm, 25 °C	—	Lee et al. (2014)
		PS (10 μm) and PE (3–221 μm)	0–14 d, 10 ± 2 °C or 20 ± 1 °C	$K_d = 5 \times 10^{-4}–7 \times 10^{-4}$ L/mg	Sørensen et al. (2020)
		PS pellets (3 mm × 2 mm)	Field experiment in San Diego Harbor Excursions and Shelter Island, 1, 3, 6, 9, and 12 mo field measurement	0.063–0.208 μg/g	Rochman et al. (2013a)
	PYR	PBS, PCL, PU, and PS (150–200 μm)	$C_0 = 20–200$ μg/L, 180 rpm, 25 °C, 5 d	—	Zhao et al. (2020)
		PE, PS, and PVC (100–150 μm)	$C_0 = 0–100$ μg/L, AFW 120 h, 200 rpm, 25 °C	78.7–333 μg/g	Wang and Wang (2018a)
		MPs 15–20 mm (1.0–17.8%), 5–15 mm (13.9–57.9%), and 1.19–5 mm (24.3–85.1%)	Field experiment, MPs collected from Shantou Bay between June and July 2014	∑PAH = 11.2–7710 ng/g	Shi et al. (2020)

	Biofilm developed PE fiber	In situ experiment in Xiangshan Bay, ambient seawater, 1, 2, 3, 4, and 8	—	Jin et al. (2020)
	PE, PP, and PS (<250 µm)	— Artificial seawater, 150 rpm, 25 °C	—	Lee et al. (2014)
	PET pellets (3 mm × 2 mm)	— Five locations throughout San Diego Bay 12-mon field measurement	0.0136–0.203 µg/g	Rochman et al. (2013a)
NAP	PS (10 µm)	C_0 = 0.5–10 mg/L, 150 rpm, 0–122 h, 25 °C	K_d = 11.965 L/g	Yu et al. (2020)
	Aged PS (125–250 µm)	7 d, 125 rpm, 25 ± 2 °C	Within 10^{-2}–10^{4} µg/g	Hüffer et al. (2018)
	MPs 15–20 mm (1.0–17.8%), 5–15 mm (13.9–57.9%), and 1.19–5 mm (24.3–85.1%)	Field experiment, MPs collected from Shantou Bay between June and July 2014	$\sum$PAH = 11.2–7710 ng/g	Shi et al. (2020)
	PE, PA, PS, and PVC (<250 µm)	The values of C_0 range over 3 or 4 orders of magnitude, 17 d (PS), 5 d (PE, PA, PVC), 10 rpm, 25 °C	Within 1–10^{2} µg/g	Hüffer and Hofmann (2016)
ANT	Biofilm developed PE fiber	In situ experiment in Xiangshan Bay, ambient seawater, 1, 2, 3, 4, and 8 wk	—	Jin et al. (2020)
	LDPE (4.2 mm × 4.7 mm × 2.8 mm) and HDPE (4.0 mm × 4.4 mm × 2.0 mm)	C_0 = 1–100 ng/L, 7 d, 300 rpm, 20 ± 1 °C	—	Fries and Zarfl (2012)
	PET pellets (3 mm × 2 mm)	San Diego Harbor Excursions and Shelter Island, 1, 3, 6, 9, and 12 mo field measurement	0–0.126 µg/g	Rochman et al. (2013a)
ACE	Biofilm developed PE fiber	In situ experiment in Xiangshan Bay, ambient seawater, 1, 2, 3, 4, and 8 wk	—	Jin et al. (2020)
	LDPE (4.2 mm × 4.7 mm × 2.8 mm) and HDPE (4.0 mm × 4.4 mm × 2.0 mm)	C_0 = 1–100 ng/L, 7 d, 300 rpm, 20 ± 1 °C	—	Fries and Zarfl (2012)

(*Continued*)

Table 9.2 (Continued)

Types	Pollutants	MPs	Experimental conditions	Sorption capacity[a]	Reference
	ACY, FLT	LDPE (4.2 mm × 4.7 mm × 2.8 mm) and HDPE (4.0 mm × 4.4 mm × 2.0 mm)	$C_0 = 1$–100 ng/L, 7 d, 300 rpm, 20 ± 1 °C	—	Fries and Zarfl (2012)
	Fluoranthene	PS (10 μm) and PE (3–221 μm)	0–14 d 10 ± 2 °C or 20 ± 1 °C	$K_d = 10^{-4}$–2.7×10^{-4} L/mg	Sørensen et al. (2020)
	CHR, BkF CHR-d12, FLO, BaP, CHR, TRI, BbF	PET pellets (3 mm × 2 mm)	San Diego Harbor Excursions and Shelter Island 1, 3, 6, 9, and 12 mo field measurement	0–0.126 μg/g	Rochman et al. (2013a)
PCBs	11 PCBs	PP homo-polymer, PP co-polymer, LDPE and HDPE	$C_0 = 500$ and 5000 ng/g, 50 rpm, 20°C, 24 h	40–4580 ng/g	van der Hal et al. (2020)
	27 PCBs	PET cylindric (3 mm × 2 mm) HDPE, PVC, LDPE, and PP (3 mm)	Five locations throughout San Diego Bay 12-mo field measurement	0.002–0.034 μg/g	Rochman et al. (2013b)
	14 PCBs	Biofilm developed PE fiber	In situ experiment in Xiangshan Bay, ambient seawater, 1, 2, 3, 4, and 8 wk	—	Jin et al. (2020)
	PCB77	PP (0.18–5 mm)	0.05–2.5 mg/L, ultrapure water, simulated seawater, and n-hexane, 24 h, 220 rpm, 25 °C	93.45–344.8 μg/g	Zhan et al. (2016)
	17 PCBs	PE (10–180 μm) and PS (70 nm)	The values of C_0 range in 10^{-5} to 10^{-1} μg/L, fresh and seawater (salinity 34‰), 6 wk, 100 rpm, 20 °C	—	Velzeboer et al. (2014)
	39 PCBs	PE and PP (0.315–5 mm)	Field experiment in Tokyo Bay and Sagami Bay	Total PCBs = 0.28– 429.32 ng/g	Yeo et al. (2020)
HCHs	α-HCH, β-HCH, γ-HCH, δ-HCH	PE, PP, and PS (<250 μm)	100–650 μg/L artificial seawater, 150 rpm, 25 ± 2 °C	—	Lee et al. (2014)

		Plastic pellets	MPs collected from the coast of state of São Paulo, southeastern Brazil	0.24–4.10 ng/g	Taniguchi et al. (2016)
		—	MPs collected from beaches in Hong Kong	5.02–63.5 ng/g	Lo et al. (2019)
DDTs	4,4′-DDT	PVC and PE (200–250 μm)	C_0 = 0.8–3.1 μg/L, filtered seawater, 24 h, 220 rpm, 20 °C	1.32–6.18 μg/g	Bakir et al. (2012)
	o,p′-DDT, p,p′-DDT, o,p′-DDD, p,p′-DDD, o,p′-DDE, and p,p′-DDE	Plastic pellets	MPs collected from the coast of state of São Paulo, southeastern Brazil	< 0.11–840 ng/g	Taniguchi et al. (2016)
	4,4′-DDT	PVC and PE (200–250 μm)	C_0 = 0.6–6.1 and 0.8–3.1 μg/L, seawater, salinity 0–35‰, 24 h, 220 rpm, 18 °C	1.5–10 μg/g	Bakir et al. (2014a)
	4,4′-DDT	PVC and PE (200–250 μm)	C_0 = 0.8–3.1 μg/L, seawater, 24–360 h, 220 rpm, 18 °C	1.2–6.2 μg/g	Bakir et al. (2014b)
	2,4′-DDD, 4,4′-DDD, 2,4′-DDE, 4,4′-DDE, 2,4′-DDT, 4,4′-DDT	0.5–2 mm	MPs collected from beaches in Hong Kong	1.96–626 ng/g	Lo et al. (2019)

---

[a] The sorption capacity is the experimental data estimated based on the figures in the reference or the predicted sorption capacity by the isotherms.

Abbreviations: ANT: anthracene; ACE: acenaphthene; ACY: acenaphthylene; FLT: fluoranthene; CHR: chrysene; BkF: benzo[k]fluoranthene; FLO: fluorene; BaP: benzo[a]pyrene, TRI: triphenylene; BbF: benzo[b]fluoranthene; PBS: polybutylene succinate, PCL: polycaprolactone; PU: polyurethane; PET: polyethylene terephthalate.

Table 9.3 Sorption of flame retardants and fuel aromatics onto MPs.

Types	Pollutants	MPs	Experimental conditions	Sorption capacity[a]	Reference
Flame retardants	TBC HBCDs	PP (0.45–0.85 mm)	C_0 = 10 and 2 μg/L, simulated seawater, salinity 35‰, 24 h, 220 rpm, 18 °C	21.489 μg/g and 1.954–3.34 μg/g	Liu et al. (2018)
	HBCD	EPS (2–3 mm)	MPs were collected from South Korea and other Asia-Pacific coastal regions	0.17 ± 0.08–3350 ± 5860 μg/g	Jiang et al. (2017)
	BDE-209	ABS (0.841–2.000, 0.420–0.595, and 0.149–0.297 mm) and LDPE (2 cm × 3 cm)	—	63.00 ± 1.26 and 910.9 ± 19.5 μg/g	Sun et al. (2019)
	PBDEs	PE and PP (0.315–5 mm)	Field experiment in Tokyo Bay and Sagami Bay	Total PBDEs = 0–1785.56 ng/g	Yeo et al. (2020)
		PET, PP, LDPE, and PS (700–490, 490–49, and 49–4 μm)	Samples were heated at 40 °C to achieve a higher sorption during 2 h and stood for 24 h	—	Singla et al. (2020)
	TnBP and TCEP	PE and PVC (1–5, 0.425–1, 0.125–0.425, and 0.045–0.125 mm)	C_0 = 1–5 mg/L, 220 rpm, 18°C, 36 h	442–1426 ng/g	Chen et al. (2019)
Fuel aromatics	BEZ	Virgin and aged PS (3.5 mm × 2.2 mm) and PP (3–5 mm)	C_0 = 130–190 μg/L, tab water, 2 wk, 10 rpm, 22 °C	—	Müller et al. (2018)
		Aged PS (125–250 μm)	7 d, 125 rpm, 25 ± 2 °C	Within 10^{-2}–10^{4} μg/g	Hüffer et al. (2018)
		PE, PA, PS, and PVC (<250 μm)	The values of C_0 range over 3 or 4 orders of magnitude, artificial seawater, 17 d for PS, 5 d for PE, PA, and PVC, 10 rpm, 25 °C	Within 1–10^{4} μg/g	Hüffer and Hofmann (2016)
	TOL	Virgin and aged PS (3.5 mm × 2.2 mm) and PP (3–5 mm)	C_0 = 130–190 μg/L, tab water, 2 wk, 10 rpm, 22 °C	—	Müller et al. (2018)

	Aged PS (125–250 μm)	7 d, 125 rpm, 25 ± 2 °C	Within 10^{-2}–10^4 μg/g	Hüffer et al. (2018)
	PE, PA, PS, and PVC (<250 μm)	The values of C_0 range over 3 or 4 orders of magnitude, artificial seawater, 17 d for PS, 5 d for PE, PA, and PVC, 10 rpm, 25 °C	Within 0.1–10^3 μg/g	Hüffer and Hofmann (2016)
EBT	PE, PA, PS, and PVC (<250 μm)	The values of C_0 range over 3 or 4 orders of magnitude, artificial seawater, 17 d for PS, 5 d for PE, PA, and PVC, 10 rpm, 25 °C	Within 10–10^4 μg/g	Hüffer and Hofmann (2016)
EBM	Virgin and aged PS (3.5 mm × 2.2 mm), and PP (3–5 mm)	C_0 = 130–190 μg/L, tab water, 2 wk, 10 rpm, 22 °C	—	Müller et al. (2018)
PX			—	
OX			—	
CBZ	PE, PA, PS, and PVC (<250 μm)	The values of C_0 range over 3 or 4 orders of magnitude, artificial seawater, 17 d for PS, 5 d for PE, PA, and PVC, 10 rpm, 25 °C	Within 1–10^4 μg/g	Hüffer and Hofmann (2016)

---

[a] The sorption capacity is the experimental data estimated based on the figures in the reference or the predicted sorption capacity by the isotherms.
Abbreviations: TBC: tris-(2,3-dibromopropyl) isocyanurate; BDE-209: deca-BDE; ABS: crylonitrile butadiene styrene; EPS: expanded polystyrene.

9.2.1.4 Other Types of Pollutants

Other types of pollutants found in MPs include perfluoroalkyl compounds (PFASs); synthetic musk (SM), lubricant oil, crude oil, pesticides, polyhalogenated carbazoles (PHCs), and n-hexane can also be sorbed on MPs (Hüffer and Hofmann 2016; Hu et al. 2017; Jiang et al. 2020; Llorca et al. 2018; Qiu et al. 2019; Shan et al. 2020; Wang et al. 2015; Zhang et al. 2018), and the relevant studies are summarized in Table 9.4.

PFASs are recognized an emerging class of POPs already widely distributed in global aquatic environments. Llorca et al. (2018) investigated the sorption of mixture of PFASs by MPs of HDPE in the size range of 3–16 μm and concluded that the equilibrium concentration of total PFASs in the MPs was 34–210 μg/g. Polar MPs, such as PVC, have a higher affinity to perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonamide (FOSA; Wang et al. 2015). Limited studies have investigated the interaction between SM (made of cyclic ethers, macrocyclic ketones, and indanes) and MPs. The sorption capacity of these compounds ranges from 860 to 1600 ng/g (Dong et al. 2019; Zhang et al. 2018) in PP and PVC MPs. For lubricant oil and crude oil, the sorption capacity in plastics can reach up to mg/g and g/g levels (Hu et al. 2017; Shan et al. 2020) depending on the polymer type. Therefore, MPs may act as important sorbents of oil in contaminated ocean areas. Jiang et al. (2020) and Li et al. (2021) recently studied the sorption of three pesticides onto MPs and concluded that the sorption capacity ranged from 1.892 to 192.8 μg/g. For example, the sorption capacities of PHCs (i.e. 3,6-dibromocarbazole, 3,6-dichlorocarbazole, 3,6-diiodocarbazole, 2,7-dibromocarbazole, and 3-bromocarbazole) on PE, PP, and PVC MPs range from 8.9×10^3 to 3.22×10^5 μg/kg (Qiu et al. 2019).

9.2.2 Metal Ions

The sources of metals pollution in the environment are mainly associated with automobiles, bridges, atmospheric deposition, industrial areas, soil erosion, corroding metal surfaces, and combustion process (Speight 2020; Wang and Chen 2009). Not surprisingly, metals are, therefore, widely detected in the global ocean as well (Arefin et al. 2016; Lao et al. 2019) and interact with MPs in water. Electrostatic and van der Waals interactions are the main mechanism in the adsorption of metal ions by MPs (Guo et al. 2020b; Wang et al. 2020e). Holmes (2012) found the concentrations of metals on MPs exceeded that in the sediment and depended on the degree of weathering of the plastic. They suggest that MPs pick up metals by (i) interactions between bivalent cations (M^{++}) and oxyanions with the charged or polar regions in MPs and (ii) nonspecific interactions between neutral metal–organic complexes and the hydrophobic surfaces of MPs. The formation of biofilms on MPs in aquatic environments can enhance the roughness of MPs and change the surface functional groups and hydrophobicity, increasing its ability to adsorb metals (Wang et al. 2020e).

MPs in aquatic environments can concentrate more than 20 types of metal ions, including Al, Cd, Cr, Mn, Fe, Ni, Cu, Pb, Ni, Zn, Hg, Sn, Sb, Se, Ba, Co, Ag, As, U, and Mo (Figure 9.1), based on the reported laboratory and field studies (Guo and Wang 2019b). The concentrations of metal ions in MPs collected in the field show marked regional differences, with those sampled in inland rivers/lakes in big cities having a higher concentration compared to those collected from bodies of water in remote areas (Guo and Wang 2019b). For example, the concentrations of Zn in MPs sampled in the sediments of Beijiang River in China reach up to 14 815 μg/g (Wang et al. 2017), while the concentration of Zn in MPs collected from two beaches in Malaysia was less than 10 μg/g (Noik et al. 2015). Researchers have conducted laboratory studies to investigate the nature of interactions between MPs and metal ions. The sorption capacity of metals ions, including Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn, on MPs based on these studies is summarized in Table 9.5. As shown in Table 9.5, the

Table 9.4 Sorption of other types of pollutants by MPs.

Types	Pollutants	MPs	Experimental conditions	Sorption amount[a]	Reference
PFASs	PFOS	PE (150 μm), PS (250 μm), and PVC (130 μm)	5–50 μg/L, aqueous solutions, pH 3–7, 7 d, 150 rpm, 25 °C	0–1.4 μg/g	Wang et al. (2015)
	FOSA	PE (150 μm), PS (250 μm), and PVC (130 μm)	C_0 = 5–50 μg/L, aqueous solutions, pH 3–7, 7 d, 150 rpm, 25 °C	1.4–2.4 μg/g	Wang et al. (2015)
	PFASs	HDPE (3–16 μm), PS (10 μm), and PS-COOH (10 μm)	C_0 = 1–20 μg/L, fresh water and seawater, 50 d, 120 rpm, 20 °C	ΣPFAS = 34–210 μg/g	Llorca et al. (2018)
SM	AHTN, MX, MK	PP (0.125–5 mm)	C_0 = 5 μg/L, simulated seawater, salinity 35‰, 24 h, 220 rpm (for 30 min), room temperature	1.3 μg/g 1.8 μg/g 1.2 μg/g	Zhang et al. (2018)
	AHTN, MX, MK, HHCB	PE and PVC	C_0 = 1 mg/L, 0–24 h, 20 °C, simulated seawater	860–1600 ng/g	Dong et al. (2019)
Lubrication oil	Lubrication oil	PE (20–140 μm) and PS (50 μm)	The values of C_0 range over 1 or 2 orders of magnitude, aqueous solution, NaCl 0.001–0.1 mol/L, pH 1–10, 48 h, 293 K	6.8 g/g 5.2 g/g	Hu et al. (2017)
Crude oil	Crude oil	PE (1.7 cm × 0.32 cm)	C_0 = 5–30 mg/L, room temperature bath (25 °C), ice bath (0–4 °C), and boiling water bath (95–100 °C), and pH = 4–7	4.5–20 mg/g	Shan et al. (2020)
Pesticide	Triadimefon and difenoconazole	PBS, PE, and PVC	C_0 = 30–300 μg/L, 0–120 h, 200 rpm, 25 °C	23.9–192.8 μg/g	Jiang et al. (2020)
	Difenoconazole, buprofezin, and Imidacloprid	PE,	C_0 = 10–150 μg/L, 2–30 h, 298 K, pH = 6–10	1.892–2.630 μg/g	Li et al. (2021)
Polyhalogenated carbazoles	3,6-BCZ, 3,6-CCZ, 3,6-ICZ, 2,7-BCZ3-BCZ	PE, PP, PVC (<0.15 mm)	C_0 = 20–100 μg/L, 0–240 h, 5–30 °C, C_{NaCl} = 0.05–3.5%	8.9×10^3–3.22×10^5 μg/kg	Qiu et al. (2019)
n-Hexane	n-Hexane	PE, PA, PS, and PVC (<250 μm)	Range over 3 or 4 orders of magnitude, artificial seawater, 17 d for PS, 5 d for PE, PA, and PVC, 10 rpm, 25 °C	Within 1–10^3 μg/g	Hüffer and Hofmann (2016)

[a] The sorption capacity is the experimental data estimated based on the figures in the reference or the predicted sorption capacity by the isotherms.

Abbreviations: AHTN: tonalide; MX, musk xylene; MK: musk ketone; HHCB: galaxolide; PA: polyamide.

Table 9.5 Sorption of metals ions onto MPs.

Metals	MPs	Experimental conditions	Sorption capacity[a]	Reference
Cd	PE, PET, PP, PVC, and PS (<5 mm)	$C_0 = 0.5–32$ ppm, 5 rpm, 2 wk	0–0.13 mg/g	Godoy et al. (2019)
	Virgin and beached PE resin pellets	$C_0 = 0–20$ μg/L, filtered seawater, salinity 34‰, pH = 7.8 7 d, 150 rpm, 20 ± 1 °C	0.0004–0.010 μg/g	Holmes et al. (2012)
	HDPE (1–2 mm, 0.6–1 mm, and 100–154 μm)	$C_0 = 5$ mg/L, 480 min, 280 rpm, pH = 2–10, 0–100 mg/L Na^+	30.5 μg/g	Wang et al. (2019b)
	Virgin and beached PE pellets (<1 mm)	$C_0 = 0–20$ μg/L, filtered river water and seawater (salinity 33.5‰), pH = 4–10.5, 48 h, 150 rpm	0.000429–0.248 μg/g	Holmes et al. (2014)
	PE, PP, PS, PVC	$C_0 = 1$ ppm, 0–24 h, 25 °C, 150 rpm	36.10–53.48 mg/kg	Guo et al. (2020a)
	Virgin PE and beached pellets (PE>90%)	$C_0 = 0–20$ μg/L, river water, pH = 4–10, 48 h	0.0101–0.248 μg/g	Turner and Holmes (2015)
	PP, PE, PA, PVC (4 mm)	Laboratory experiment ($C_0 = 5$ mg/L, 13 d, 160 rpm, room temperature) and field experiment (along the China coastline)	0–0.023 μg/g	Gao et al. (2019)
	LPE (150–250 μm), HPE (27–45 μm), CPE (150–250 μm), and PVC (0.18–1 μm)	$C_0 = 0.10–50.00$ mg/L, 20 rpm, room temperature, pH = 3–6, $C_{NaCl} =$ 0.01–1 mmol/L	0.01–100 mmol/kg	Zou et al. (2020)
	PS (32–40 μm)	$C_0 = 50$ μg/L, 30 d, 28.0 ± 1.0 °C, pH = 5.6–6.8	—	Wen et al. (2018)
Co	Virgin and beached PE resin pellets	$C_0 = 0–20$ μg/L, filtered seawater, salinity 34‰, pH = 7.8 7 d, 150 rpm, 20 ± 1 °C	0.018–0.038 μg/g	Holmes et al. (2012)
	PE, PET, PP, PVC, and PS (<5 mm)	$C_0 = 0.5–32$ ppm, 5 rpm, 2 wk	0.813 mg/g	Godoy et al. (2019)
	Virgin and beached PE pellets (<1 mm)	$C_0 = 0–20$ μg/L, filtered river water and seawater (salinity 33.5‰), pH = 4–10.5, 48 h, 150 rpm	0.0176–0.0797 μg/g	Holmes et al. (2014)
	PP (1 mm)	100 rpm, 1 wk, 40 °C	0.005–0.014 μg/g	Holmes et al. (2020)

	Virgin PE and beached pellets (PE > 90%)	C_0 = 0–20 μg/L, river water, pH = 4–10, 48 h	0.0692–0.0796 μg/g	Turner and Holmes (2015)
Cr	PE, PET, PP, PVC, and PS (<5 mm)	C_0 = 0.5–32 ppm, 5 rpm, 2 wk	0.473–4.70 mg/g	Godoy et al. (2019)
	Virgin and beached PE resin pellets	C_0 = 0–20 μg/L, filtered seawater, salinity 34‰, pH = 7.8, 7 d, 150 rpm, 20 ± 1 °C	0.297–0.441 μg/g	Holmes et al. (2012)
	PE (200 μm)	C_0 = 0.2, 0.6, and 1.0 μg/mL, artificial seawater	1.7 μg/g	Zon et al. (2018)
	Virgin and beached PE pellets (<1 mm)	C_0 = 0–20 μg/L, filtered river water and seawater (salinity 33.5‰), pH = 4–10.5, 48 h, 150 rpm	0.093–0.441 μg/g	Holmes et al. (2014)
	PE, PP, PVC, and PS (~150 μm)	150 rpm, 22 ± 2 °C, 96 h	2.88–5.07 μg/g	Liao and Yang (2020)
	Virgin PE and beached pellets (PE > 90%)	C_0 = 0–20 μg/L, river water, pH 4–10, 48 h	0.0933 μg/g	Turner and Holmes (2015)
	PP, PE, PA, PVC (4 mm)	Laboratory experiment (C_0 = 5 mg/L, 13 d, 160 rpm, room temperature) and field experiment (along the China coastline)	0–0.084 μg/g	Gao et al. (2019)
Cu	Virgin and beached PE resin pellets	C_0 = 0–20 μg/L, filtered seawater, salinity 34‰, pH = 7.8 7 d, 150 rpm, 20 ± 1 °C	0.261 μg/g	Holmes et al. (2012)
	Virgin and aged PA, PE, PS, PET, PVC	C_0 = 0.05–10 mg/L, 200 rpm, 24 h, 25 °C, pH = 4–8,	<10 μg/g–323.6 μg/g	Yang et al. (2019)
	Virgin and beached PE pellets (<1 mm)	C_0 = 0–20 μg/L, filtered river water and seawater (salinity 33.5‰), pH = 4–10.5, 48 h, 150 rpm	0.101–0.263 μg/g	Holmes et al. (2014)
	Virgin and aged PET (1 mm × 1 mm)	C_0 = 2–10 mg/L, 288–318 K, 150 rpm, 144 h, pH = 3–7	24.6–178.2 μg/g	Wang et al. (2020a)
	Virgin PE and beached pellets (PE > 90%)	C_0 = 0–20 μg/L, river water, pH 4–10, 48 h	0.100 μg/g	Turner and Holmes (2015)
	PE, PET, PP, PVC, and PS (<5 mm)	C_0 = 0.5–32 ppm, 5 rpm, 2 wk	0.259–2.95 mg/g	Godoy et al. (2019)
	Virgin PS beads (0.7–0.9 μm) and aged PVC fragments (1.6–0.8 mm)	Nonfiltered seawater, water or no water exchange, 14 d	0.09–3000 μg/g	Brennecke et al. (2016)

(*Continued*)

Table 9.5 (Continued)

Metals	MPs	Experimental conditions	Sorption capacity[a]	Reference
	PP, PE, PA, PVC (4 mm)	Laboratory experiment ($C_0 = 5$ mg/L, 13 d, 160 rpm, room temperature) and field experiment (along the China coastline)	0.079–0.223 μg/g	Gao et al. (2019)
	LPE (150–250 μm), HPE (27–45 μm), CPE (150–250 μm), and PVC (0.18–1 μm)	$C_0 = 0.10$–50.00 mg/L, 20 rpm, room temperature, pH = 3–6, $C_{\mathrm{NaCl}} =$ 0.01–1 mmol/L	0.1–100 mmol/kg	Zou et al. (2020)
Hg	Virgin PE and beached pellets (PE > 90%)	$C_0 = 0$–20 μg/L, river water, pH = 4–10, 48 h	0.170–2.78 μg/g	Turner and Holmes (2015)
	56.07% MPs had diameter of 0.038–0.5 mm	Field experiment in in the Jinjiang Estuarine Mangrove Reserve	0–0.076 μg/g	Deng et al. (2020)
Ni	Virgin and beached PE resin pellets	$C_0 = 0$–20 μg/L, filtered seawater, salinity 34‰, pH = 7.8, 7 d, 150 rpm, 20 ± 1 °C	0.008–0.070 μg/g	Holmes et al. (2012)
	PE, PET, PP, PVC, and PS (<5 mm)	$C_0 = 0.5$–32 ppm, 5 rpm, 2 wk	0–0.14 mg/g	Godoy et al. (2019)
	Virgin and beached PE pellets (<1 mm)	$C_0 = 0$–20 μg/L, filtered river water and seawater (salinity 33.5‰), pH = 4–10.5, 48 h, 150 rpm	0.00761–0.152 μg/g	Holmes et al. (2014)
	Virgin PE and beached pellets (PE > 90%)	$C_0 = 0$–20 μg/L, river water, pH = 4–10, 48 h	0.0166–0.152 μg/g	Turner and Holmes (2015)
Pb	PE, PET, PP, PVC, and PS (<5 mm)	$C_0 = 0.5$–32 ppm, 5 rpm, 2 wk	1.9–4.93 mg/g	Godoy et al. (2019)
	Virgin and beached PE resin pellets	$C_0 = 0$–20 μg/L, filtered seawater, salinity 34‰, pH = 7.8, 7 d, 150 rpm, 20 ± 1 °C	0.716 μg/g	Holmes et al. (2012)
	Virgin and aged PA	$C_0 = 2$–14 mg/L, pH = 5, 48 h, 185 rpm, 27 °C	0.4637–1.4767 mg/g	Tang et al. (2020)
	Virgin and beached PE pellets (<1 mm)	$C_0 = 0$–20 μg/L, filtered river water and seawater (salinity 33.5‰), pH = 4–10.5, 48 h, 150 rpm	0.191–2.73 μg/g	Holmes et al. (2014)
	PET, PA (0.5–1 mm)	$C_0 = 0.5$–7 ppm, pH = 2–10, 90 min, 25–55.1 °C	—	Oz et al. (2019)
	Virgin PE and beached pellets (PE > 90%)	$C_0 = 0$–20 μg/L, river water, pH = 4–10, 48 h	0.191–2.74 μg/g	Turner and Holmes (2015)

	PP, PE, PA, PVC (4 mm)	Laboratory experiment ($C_0 = 5$ mg/L, 13 d, 160 rpm, room temperature) and field experiment (along the China coastline)	0.107–0.441 μg/g	Gao et al. (2019)
Zn	Virgin PE and beached pellets (PE > 90%)	$C_0 = 2$–20 μg/L, river water, pH = 4–10, 48 h	0.1–0.7 μg/g	Turner and Holmes (2015)
	PE, PET, PP, PVC, and PS (<5 mm)	$C_0 = 0.5$–32 ppm, 5 rpm, 2 wk	0.505–0.634 mg/g	Godoy et al. (2019)
	Virgin and aged PET (1 mm × 1 mm)	$C_0 = 2$–10 mg/L, 288–318 K, 150 rpm, 144 h, pH = 3–7	20.0–32.7 μg/g	Wang et al. (2020a)
	Virgin PS beads (0.7–0.9 μm) and aged PVC fragments (1.6–0.8 mm)	Nonfiltered seawater, water or no water exchange, 14 d	0.18–270 μg/g	Brennecke et al. (2016)
	Plastic bag–derived HDPE (0.92 ± 1.09 mm^2)	$C_0 = 10^2$–10^5 μg/L, background electrolyte (0.1 M $NaNO_3$), 48 h, 220 rpm	236–7171 μg/g	Hodson et al. (2017)

[a] The sorption capacity is the experimental data estimated based on the figures in the reference or the predicted sorption capacity by the isotherms.

sorption capacity of Cd, Co, Cr, and Cu is low (less than 1 μg/g) when the initial concentration of metal ions is 0–20 μg/g (Holmes et al. 2012, 2014; Turner and Holmes 2015). Zon et al. (2018) concluded that the maximum uptake of Cr on PE pellets was 1.7 μg/g, at a value of C_0 of 1 mg/L. That exceeds by far what might be reasonably anticipated in the aquatic environment. The sorption capacity can reach up to several mg/g with high initial concentration of metal ions (0.5–32 ppm; Godoy et al. 2019). The maximum uptakes of Cu and Zn leached from an antifouling paint by MPs were 3000 and 270 μg/g, respectively (Brennecke et al. 2016). Based on these, the initial concentration of metal ions appears to be a major factor that influences their sorption capacity on MPs.

9.3 Influencing Factors

9.3.1 Effect of Polymer Type

Types of polymers constituting the MPs in the ocean environment mainly include PE, PVC, PP, PS, PA, and PET (Guo and Wang 2019b). Published papers that focus on the sorption of pollutants by specific types of MPs in recent years are summarized in Figure 9.2 (Bao et al. 2020; Chen et al. 2019; Gao et al. 2019; Godoy et al. 2019; Guo and Wang 2019a; Guo et al. 2018, 2019a, 2019b, 2020a; Hodson et al. 2017; Holmes et al. 2012, 2014; Hu et al. 2017; Hüffer and Hofman 2016; Jiang et al. 2020; Lin et al. 2020; Liu et al. 2018; Llorca et al. 2018; Razanajatovo et al. 2018; Shan et al. 2020; Wang and Wang 2018a; Wang et al. 2015, 2018a, 2018b, 2020a; Xu et al. 2018a, 2018b; Yang et al. 2019; Yu et al. 2020; Zhang et al. 2018; Zou et al. 2020). Over 90 sets of experiments have been carried out on the sorption behaviors of PE, the most studied plastic.

Different types of MPs have distinct properties, such as the functional groups, polarity, rubbery domains, and the degree of crystallinity (see Chapter 1). The polarity of MPs affects the uptake of polar chemicals (Wang et al. 2015), and specific functional groups, such as amides, often enhancing the sorption of antibiotics by MPs (Li et al. 2018). For instance, the sorption capacity of polar PHCs on the polar MP of PVC is much higher than that on the relatively nonpolar MPs of PP and PE (Qiu et al. 2019). In the sorption of PAHs on polar and nonpolar MPs, it is suggested that hydrogen bonding contributes significantly to their sorption on polar MPs (Li et al. 2018; Zhao et al. 2020) (Figure 9.3). Some of the common plastics are semicrystalline, with fractional crystallinity depending on their

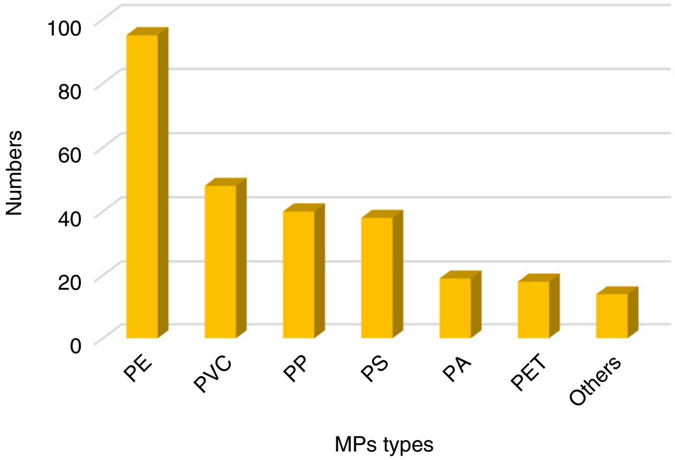


Figure 9.2 MPs studied in literature.

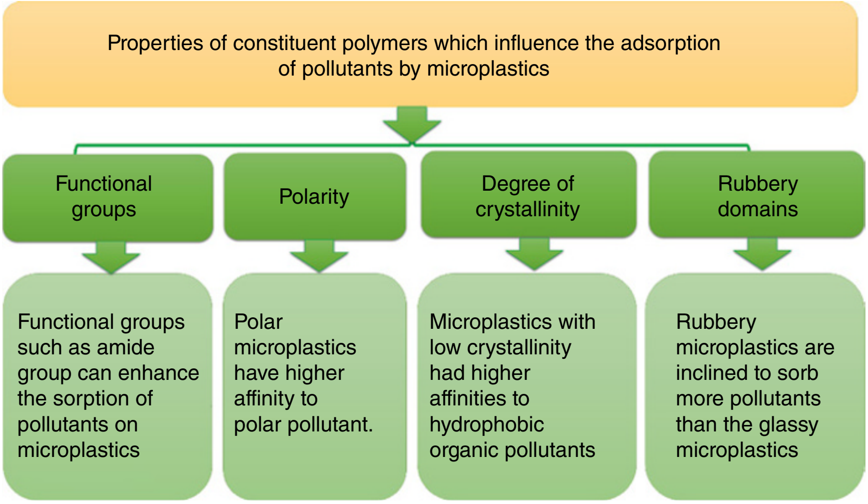


Figure 9.3 Influence of properties of MPs on the sorption of pollutants.

thermal history but generally follow the order of PE > PP > PA > PS (Xu et al. 2019). The sorption of organic pollutants mainly occurs in the amorphous domains, and MPs with low crystallinity (and, therefore, a larger amorphous content) have higher affinities to hydrophobic organic pollutants (Guo et al. 2012). Plastics change from their glassy state to the rubbery state at temperatures higher than the glass transition temperature (T_g) (see also Chapter 1). Rubbery MPs are inclined to sorb more pollutants than glassy MPs (Guo and Wang 2019b). PE with a T_g of −110 °C is a rubbery polymer at ambient temperature (Crawford and Quinn 2017), and MPs of PE have higher affinities to PYR, PHE, lubricating oils, PCBs, PFOS, POSA, and 4,4′-DDT (Bakir et al. 2012; Rochman et al. 2013b; Wang and Wang 2018a, 2018b; Wang et al. 2015).

9.3.2 Effect of the Extent of Weathering

When exposed to solar ultraviolet (UV) radiation, MPs are inclined to undergo oxidative degradation (see Chapter 8). These degradation reactions generally lead to changes in their surface morphology, size, crystallinity, and functional groups (Andrady 2017; Guo and Wang 2019b).

Mechanical forces, such as the hydraulic shear force and sand abrasion, mainly contribute to the surface morphological changes of MPs (Crawford and Quinn 2017). The surface of MPs contains the amorphous as well as the crystal phases. The amorphous phases are degraded relatively easily compared to the crystalline phases. Therefore, cracks and pores can easily form on their surface, as reported for weathered MPs by several researchers (Chen et al. 2018; Hüffer et al. 2018; Liu et al. 2019; Luo et al. 2020). Further degradation of MPs leads to their fragmentation or reduction in size. The BET surface areas of MPs generally increase after weathering (Luo et al. 2020). Higher BET specific surface areas of MPs can provide more sorption sites for pollutants. The sorption of organic pollutants and metals on some types of MPs, therefore, increases as a consequence of weathering (Mao et al. 2020; Müller et al. 2018).

The crystallinity of MPs also generally increases with degradation (Rouillon et al. 2016). On the one hand, the degradation of the amorphous phases in MPs is faster than that of the crystalline domains, increasing the fractional crystallinity of plastics with weathering. On the other hand, the chemi-crystallization in the degradation processes can also increase the crystallinity of MPs (Rouillon et al. 2016; see Chapter 8). In addition, the functional groups of MPs typically change after degradation. Liu et al. (2019) compared the Fourier transform infrared (FTIR) spectrum of virgin and weathered PS and PVC MPs and found that the absorption bands for –OH were found at 3446.17 and 3437.60 cm^{-1} in weathered MPs, but not in the virgin MPs. Increase in the concentration of carbonyl functionalities during weathering also enhances their ability to sorb hydrophilic organic pollutants, such as CIP (Zhou et al. 2020).

9.3.3 Effect of pH and Ionic Strength

Electronegative surface charges by MPs and the speciation of dissolved pollutants are both determined by pH. Li et al. (2018) reported pH at which the net charge on the particle surface reaches zero (the point of zero charge [PZC]) for PE, PS, PVC, PP, and PA polymers to be 6.63, 6.69, 6.65, 6.76, and 6.52, respectively. In acidic solution, the MPs tend to be positively charged, while in alkaline solution, MPs are negatively charged. Therefore, in alkaline solution, the sorption of cationic pollutants (such as Cd, Co, Ni, and Pb) increases (Fu et al. 2020; Guo et al. 2020a; Holmes et al. 2014). Likewise, the sorption capacity of negatively charged pollutants increases in acidic media. MPs of a given polymer often show a clear trend in pollutant-specific sorption capacity with pH. The sorption of PFOS on PE, for instance, decreased with increasing of pH (Wang et al. 2015), and the maximum sorption capacity of ibuprofen by MPs of PE and PP was at pH 2 (Elizalde-Velázquez et al. 2020). The uptakes of CIP by MPs decreased dramatically when the pH values were higher than 7.5 (Atugoda et al. 2020). The combination of these effects generally results in a pronounced pH-dependent of the sorption of pollutants by MPs, and, in laboratory studies, the ocean pH of 8.1 (slightly alkaline) should be taken into consideration.

Ionic strength is another key factor affecting interactions between pollutants and MPs, and can be used as an indicator to distinguish between selective and nonselective sorption processes (Guan et al. 2020). Surface adsorption of charged pollutants to MPs suspended in seawater is best understood in terms of two interactions: (i) the outer sphere or the hydration shell that electrostatically binds ions, and (ii) the inner sphere of the charged surface of the particle. The nonselective physical sorption is an outer-sphere surface complex reaction, and the specific chemical sorption causes complex reaction at the inner-sphere surface (Fedorov and Kornyshev 2014). The ionic strength would influence the outer-sphere surface complex reaction. The presence of Na^+, for instance, decreases the sorption of CIP, AMX, PFASs, α-HCHs, and metals (Fu et al. 2020; Holmes et al. 2014; Li et al. 2018; Llorca et al. 2018; Wang et al. 2018c). It also increases the sorption capacity of lubricant oil by MPs (Hu et al. 2017). Also, the uptake of PCBs on PVC decreases with the increasing levels of Cl^- in solution (Pascall et al. 2005). The above sorption process may be dominated by the outer-sphere surface complex reaction. The competitive sorption between pollutants and other ions in solution may also decrease the overall sorption capacity (Guo et al. 2020a). For other pollutants, ionic strength has limited influence on the sorption capacity of MPs. The sorption of TC and SM by MPs is not significantly affected by the concentration of Na^+ (Xu et al. 2018; Zhang et al. 2018). These sorption processes may be dominated by the inner-sphere surface complex reaction.

9.4 Sorption Kinetics and Isotherms

The linear, Langmuir (1916, 1918), and Freundlich (1906) isotherm models are three of the most frequently used models in the adsorption of organic pollutant and metals ions by MPs. The linear, Langmuir, and Freundlich isotherms can be described by Equations 1–3 as follows:

$$q_e = KC_e \tag{1}$$

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

$$q_e = K_F C_e^{1/n} \tag{3}$$

where q_e (mg/g) and C_e (mg/L) are, respectively, the equilibrium sorption capacity and equilibrium concentrations of adsorbate in solution, K (L/g) is the partition coefficient, K_L (L/mg) is the Langmuir constant that is equal to the ratio of the sorption rate constant to the desorption rate constant, q_m (mg/g), is the maximum adsorption capacity predicted by the Langmuir model, and K_F ($L^{1/n}mg^{1-1/n}/g$) and n are the Freundlich constants.

The reported sorption isotherms of organic pollutants and metals ions by MPs are summarized in Figure 9.4, based on literature (Bao et al. 2020; Chen et al. 2019; Gao et al. 2019; Godoy et al. 2019; Guo and Wang 2019a; Guo et al. 2018, 2019a, 2019b, 2020a; Hodson et al. 2017; Holmes et al. 2012, 2014; Hu et al. 2017; Jiang et al. 2020; Hüffer and Hofman 2016; Lin et al. 2020; Liu et al. 2018; Llorca et al. 2018; Razanajatovo et al. 2018; Shan et al. 2020; Wang and Wang 2018a; Wang et al. 2015, 2018a, 2018b, 2020a; Xu et al. 2018a, 2018b; Yang et al. 2019; Yu et al. 2020; Zhang et al. 2018; Zou et al. 2020).

For antibiotics, the linear isotherm is the most widely used to model sorption equilibrium data (Figure 9.4). The mechanism underlying partition is dominated by hydrophobic and electrostatics interactions (Guo et al. 2019b). The sorption of PAHs, PCBs, DDTs, and HCHs onto MPs is well represented by the Freundlich isotherm that generally describes multilayer physical sorption or the chemical sorption when the occupancy rate of the active sites is about 50% (Wang and Guo 2020a). With flame retardants and fuel aromatics, however, the Langmuir isotherm appears to be a better model for the adsorption process, indicating monolayer chemical adsorption to be the

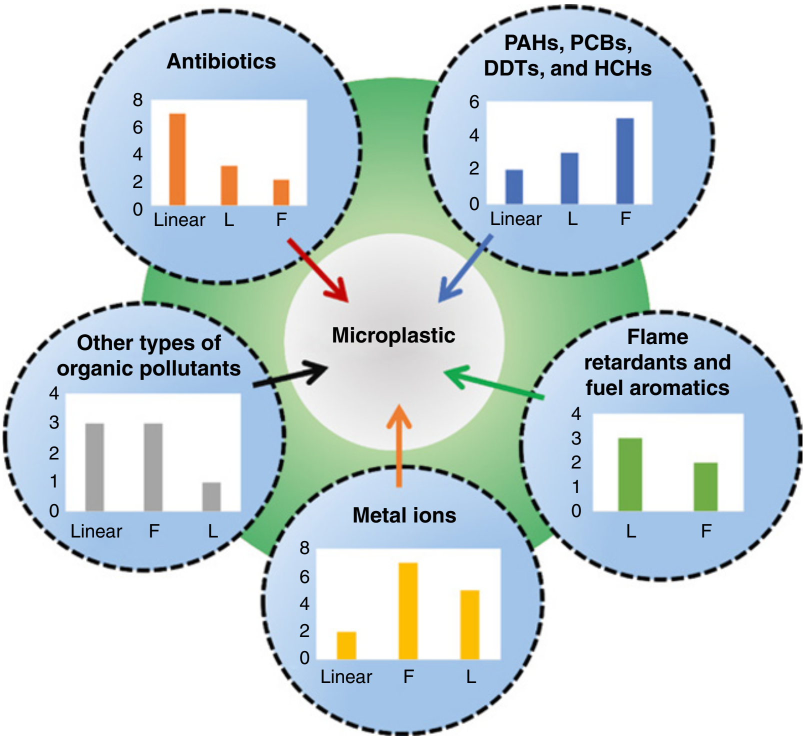


Figure 9.4 Sorption isotherms of pollutants onto MPs based on published literature.

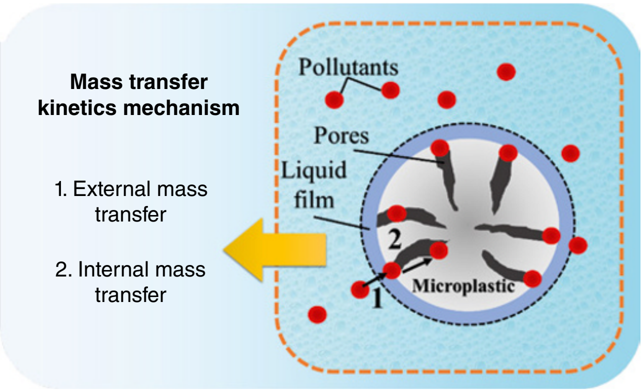


Figure 9.5 Sorption kinetics of pollutants by MPs.

likely main mechanism. The sorption of other types of organic pollutants by MPs is described by both linear and Freundlich models; partition and multilayer sorption dominate the adsorption. The most useful isotherm to model equillibrium sorption data of metals onto MPs appears to be the Freundlich model, followed by the Langmuir model.

Modeling sorption kinetics generally involve three considerations: (i) external mass transfer or the diffusion of the contaminants in the liquid film around MPs, (ii) internal mass transfer or the diffusion of contaminant in the pores inside the MPs, and (iii) sorption of contaminant in active sites. A majority of the recent research reports on sorption kinetics of pollutants on MPs found pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetics models to describe the data (Holmes et al. 2012; Llorca et al. 2018; Xu et al. 2018a, 2018b; Wang and Wang 2018a, 2018b). However, the PFO and PSO models are empirical kinetic models without specific physical interpretations (Wang and Guo 2020b). The mass-transfer kinetic data on sorption cannot be profitably investigated by these empirical models that lack molecular-level interpretations. The phenomenological sorption kinetics models, however, have been applied in the sorption of antibiotics and metals ions by MPs (Guo and Wang 2019c; Guo et al. 2019a, 2020b). The external and internal mass transfer processes have proven to be the rate-limiting steps of pollutants sorption onto MPs (Guo and Wang 2019c; Guo et al. 2019a, 2020b; Figure 9.5).

9.5 Sorption Mechanism

The sorption mechanisms of pollutants by MPs mainly include π–π bonding, H-bonding, van der Waals force, electrostatic force, and hydrophobic interaction (Bao et al. 2020; Chen et al. 2019; Guo et al. 2018, 2020b; Li et al. 2018), as shown in Figure 9.6.

The FTIR and x-ray photoelectron spectroscopy (XPS) of MPs before and after sorption are frequently used to elucidate the sorption mechanism (Lin et al. 2021). The sorption of Pb, Cd, and Sr by MPs is likely physical adsorptions, because FTIR spectra of MPs after sorption display no new absorption bands (Guo and Wang 2019c; Guo et al. 2020a; Lin et al. 2021). The XPS spectra also confirm that physisorption dominates in the sorption of Pb on MPs (Lin et al. 2021). Guo et al. (2018) concluded that the van der Waals force and π–π interaction were the main mechanism in the sorption of TYL. Molecular dynamics (MD) studies, density functional theory (DFT) calculations, and other computational modeling have also been applied to investigate the sorption

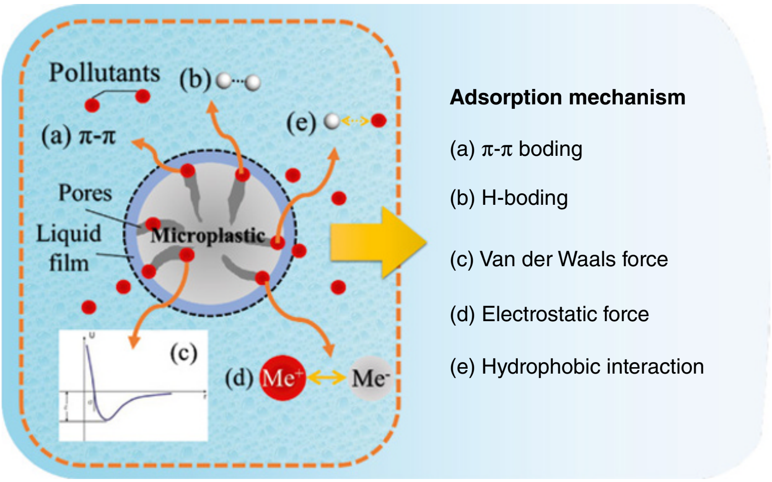


Figure 9.6 Sorption mechanisms of pollutants by MPs.

mechanisms of pollutants by MPs. Li et al. (2021) conducted the MD simulation of the sorption of three pesticides by MPs of PE, and concluded that the pesticides were adhered rapidly to the PE after 200 ps, the main mechanism being a complex interaction between the pesticide molecule with the C and H atoms in PE. Guo et al. (2019b, 2020b) studied MD simulation of antibiotics and metals on MPs and concluded that electrostatic and van der Waals force were the main mechanism involved. Yu et al. (2020), however, using computational modeling of naphthalene on MPs found the strength of the π–π interactions could be affected by some functional groups. Mao et al. (2020) investigated the sorption mechanism of PHE by MPs by DFT calculation and found that the hydrophobic interaction dominated the sorption process.

9.6 Conclusions

MPs sorb a wide range of organic pollutants and metal ions from seawater. Recent research has examined the role of hydrophobicity, salinity, polymer type, and fractional crystallinity of the plastic, on the absorption of pollutants by MPs. Their sorption capacity for pollutants is largely influenced by the initial concentrations of pollutants in water, C_0, and the values of log K_{ow} that is an indication of the affinity of the pollutant for the plastic. The reported values for the capacity ranged from ng/g to mg/g depending on the polymer and sorbent. The type of polymer making up the MPs generally determines the uptake kinetics of pollutants. MPs of PE are the most frequently studied, followed by PVC, PP, and PS. The functional groups, polarity, rubbery domains, and the degree of crystallinity of MPs, all play a major role in the sorption process. Aged MPs characterized by rough surface carrying oxygenated functionalities, are able to sorb higher levels of pollutants relative to virgin MPs. The external and internal diffusion events are the rate-limiting steps in the kinetics of sorption of pollutants by MPs. The linear isotherm model generally describes the sorption of antibiotics successfully, while, Freundlich isotherm fits the kinetic data for sorption of PAHs, PCBs, DDTs, HCHs, and metal ions well. Several types of interactions, including π–π bonding, H-bonding, van der Waals force, electrostatic force, and hydrophobic interactions, serve as the mechanism behind the sorption of pollutants by MPs.

References

Andrady, A.L., 2011. Microplastics in the marine environment. *Marine Pollution Bulletin*, 62, 1596–1605.

Andrady, A.L., 2017. The plastic in microplastics: a review. *Marine Pollution Bulletin*, 119, 12–22.

Arefin, M.T., Rahman, M.M., Wahid-U-Zzaman, M., Kim, J.E., 2016. Heavy metal contamination in surface water used for irrigation: functional assessment of the Turag River in Bangladesh. *Journal of Applied Biological Chemistry*, 59 (1), 83–90.

Atugoda, T., Wijesekara, H., Werellagama, D.R.I.B., Jinadasa, K.B.S.N., Bolan, N.S., Vithanage, M., 2020. Adsorptive interaction of antibiotic ciprofloxacin on polyethylene microplastics: implications for vector transport in water. *Environmental Technology & Innovation*, 19, 100971.

Bakir, A, Rowland, S.J., Thompson, R.C., 2012. Competitive sorption of persistent organic pollutants onto microplastics in the marine environment. *Marine Pollution Bulletin*, 64 (12), 2782–2789.

Bakir, A., Rowland, S.J., Thompson, R.C. 2014a. Transport of persistent organic pollutants by microplastics in estuarine conditions. *Estuarine, Coastal and Shelf Science*, 140, 14–21.

Bakir, A., Rowland, S.J., Thompson, R.C., 2014b. Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions. *Environmental Pollution*, 185, 16–23.

Bao, Z.Z., Chen, Z.F., Zhong, Y., Wang, G.Z., Qi, Z.H., Cai, Z.W., 2020. Adsorption of phenanthrene and its monohydroxy derivatives on polyvinyl chloride microplastics in aqueous solution: model fitting and mechanism analysis. *Science of the Total Environment,* https://doi.org/10.1016/j.scitotenv.2020.142889.

Batel, A., Linti, F., Scherer, M., Erdinger, L., Braunbeck, T., 2016. Transfer of benzo[a]pyrene from microplastics to *Artemia nauplii* and further to zebrafish via a trophic food web experiment: CYP1A induction and visual tracking of persistent organic pollutants. *Environmental Toxicology and Chemistry*, 35, 1656–1666.

Bollmann, U.E., Moller, A., Xie, Z., Ebinghaus, R., Einax, J.W., 2012. Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. *Water Research*, 46, 531–538.

Brennecke, D., Duarte, B., Paiva, F., Caçador, I., Canning-Clode, J., 2016. Microplastics as vector for heavy metal contamination from the marine environment. *Estuarine, Coastal and Shelf Science*, 178, 189–195.

Carbery, M., O'Connor, W., Thavamani, P., 2018. Trophic transfer of microplastics and mixed contaminants in the marine food web and implications for human health. *Environment International*, 115, 400–409.

Carlin, J., Craig, C., Little, S., Donnelly, M., Fox, D., Zhai, L., Walters, L., 2020. Microplastic accumulation in the gastrointestinal tracts in birds of prey in central Florida, USA. *Environmental Pollution*, 264, 114633.

Chen, M., Jin, M., Tao, P., Wang, Z., Xie, W., Yu, X., Wang. K., 2018. Assessment of microplastics derived from mariculture in Xiangshan Bay, China. *Environmental Pollution*, 242, 1146–1156.

Chen, S., Tan, Z., Qi, Y., Ouyang, C., 2019. Sorption of tri-n-butyl phosphate and tris(2-chloroethyl) phosphate on polyethylene and polyvinyl chloride microplastics in seawater. *Marine Pollution Bulletin*, 149, 110490.

Cheng, H., Luo, H., Hu, Y., Tao, S., 2020. Release kinetics as a key linkage between the occurrence of flame retardants in microplastics and their risk to the environment and ecosystem: a critical review. *Water Research*,. 185, 116253.

Cordova, M.R., Riani, E., Shiomoto, A., 2020. Microplastics ingestion by blue panchax fish (*Aplocheilus* sp.) from Ciliwung Estuary, Jakarta, Indonesia. *Marine Pollution Bulletin*, 161, 111763.

Crawford, C.B., Quinn, B., 2017. *Microplastic Pollutants*. Elsevier, Amsterdam, Netherlands.

Deng, J., Guo, P., Zhang, X., Su, H., Zhang, Y., Wu, Y., Li, Y., 2020. Microplastics and accumulated heavy metals in restored mangrove wetland surface sediments at Jinjiang Estuary (Fujian, China). *Marine Pollution Bulletin*, 159, 111482.

Desforges, J.P.W., Galbraith, M., Ross, P.S., 2015. Ingestion of microplastics by zooplankton in the Northeast Pacific Ocean. *Environmental Contamination and Toxicology*, 69 (3), 320–330.

Dong, X., Zheng, M., Qu, L., Shi, L., Wang, L., Zhang, Y., Liu, X., Qu, Y., Zhu, H., 2019. Sorption of tonalide, musk xylene, galaxolide, and musk ketone by microplastics of polyethylene and polyvinyl chloride. *Marine Pollution Bulletin*, 144, 129–133.

Elizalde-Velázquez, A., Subbiah, S., Anderson, T.A., Green, M.J., Zhao, X., Cañas-Carrell, J.E., 2020. Sorption of three common nonsteroidal anti-inflammatory drugs (NSAIDs) to microplastics. *Science of the Total Environment*, 715, 136974.

Endo, S., Takizawa, R., Okuda, K., Takada, H., Chiba, K., Kanehiro, H., Ogi, H., Yamashita, R., Date, T., 2005. Concentration of polychlorinated biphenyls (PCBs) in beached resin pellets: variability among individual particles and regional differences. *Marine Pollution Bulletin*, 50, 1103–1114.

Fedorov, M. V., Kornyshev, A. A., 2014. Ionic liquids at electrified interfaces. *Chemical Reviews*, 114 (5), 2978–3036.

Freundlich, H.M.F., 1906. Über die adsorption in lösungen. *Zeitschrift für Physikalische Chemie*, 57, 385–470.

Fries, E., Zarfl, C., 2012. Sorption of polycyclic aromatic hydrocarbons (PAHs) to low and high density polyethylene (PE). *Environmental Science and Pollution Research*, 19 (4), 1296–1304.

Fu, Q. Tan, X., Ye, S., Ma, L., Gu, Y., Zhang, P., Chen, Q., Yang, Y., Tang, Y., 2020. Mechanism analysis of heavy metal lead captured by natural-aged microplastics. *Chemosphere*. https://doi.org/10.1016/j.chemosphere.2020.128624.

Gao, F., Li, J., Sun, C., Zhang, L., Jiang, F., Cao, W., Zheng, L., 2019. Study on the capability and characteristics of heavy metals enriched on microplastics in marine environment. *Marine Pollution Bulletin*, 144, 61–67.

Godoy, V., Blázquez, G., Calero, M., Quesada, L., Martín-Lara, M.A., 2019. The potential of microplastics as carriers of metals. *Environmental Pollution*, 255, 113363.

Guan, J., Qi, K., Wang, J., Wang, W., Wang, Z., Lu N., Qu, J., 2020. Microplastics as an emerging anthropogenic vector of trace metals in freshwater: significance of biofilms and comparison with natural substrates, *Water Research*,. https://doi.org/10.1016/j.watres.2020.116205.

Guo, X., Chen, C., Wang, J.L., 2019a. Sorption of sulfamethoxazole onto six types of microplastics. *Chemosphere.* 228, 300–308.

Guo, X., Hu, G., Fan, X., Jia, H., 2020a. Sorption properties of cadmium on microplastics: the common practice experiment and a two-dimensional correlation spectroscopic study. *Ecotoxicology and Environmental Safety*, 190, 110118.

Guo, X., Liu, Y., Wang, J.L., 2019b. Sorption of sulfamethazine onto different types of microplastics: a combined experimental and molecular dynamics simulation study. *Marine Pollution Bulletin*, 145, 547–554.

Guo, X., Liu, Y., Wang, J.L., 2020b. Equilibrium, kinetics and molecular dynamic modeling of Sr^{2+} sorption onto microplastics. *Journal of Hazardous Materials*, 400, 123324.

Guo, X., Pang, J., Chen, S., Jia, H., 2018. Sorption properties of tylosin on four different microplastics. *Chemosphere*, 209, 240–245.

Guo, X., Wang, J.L., 2019a. Sorption of antibiotics onto aged microplastics in freshwater and seawater. *Marine Pollution Bulletin*, 149, 110511.

Guo, X., Wang, J.L., 2019b. The chemical behaviors of microplastics in marine environment: a review. *Marine Pollution Bulletin*, 142, 1–14.

Guo, X., Wang, J.L., 2019c. The phenomenological mass transfer kinetics model for Sr^{2+} sorption onto spheroids primary microplastics. *Environmental Pollution*, 250, 737–745.

Hartmann, N.B., Rist, S., Bodin, J., Jensen, L.H.S., Schmidt, S.N., Mayer, P., Baun, A., 2017. Microplastics as vectors for environmental contaminants: exploring sorption, desorption, and transfer to biota. *Integrated Environmental Assessment and Management*, 13 (3), 488–493.

Hodson, M.E., Duffus-Hodson, C.A., Clark, A., Prendergast-Miller, M.T., Thorpe, K.L., 2017. Plastic bag derived-microplastics as a vector for metal exposure in terrestrial invertebrates. *Environmental Science & Technology*, 51, 4714–4721.

Holmes, L.A., Thompson, R.C., Turner, A., 2020. *in vitro* avian bioaccessibility of metals adsorbed to microplastic pellets. *Environmental Pollution*, 261, 114107.

Holmes, L.A., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals to plastic resin pellets in the marine environment. *Environmental Pollution*, 160 (1), 42–48.

Holmes, L.A., Turner, A., Thompson, R.C., 2014. Interactions between trace metals and plastic production pellets under estuarine conditions. *Marine Chemistry*, 167, 25–32.

Hu, J.Q., Yang, S.Z., Guo, L., Xu, X., Yao, T., Xie, F., 2017. Microscopic investigation on the adsorption of lubrication oil on microplastics. *Journal of Molecular Liquids*, 227, 351–355.

Huang, Y., Ding, J., Zhang, G., Liu, S., Zou, H., Wang, Z., Zhu, W., Geng, J., 2021. Interactive effects of microplastics and selected pharmaceuticals on red tilapia: role of microplastic aging. *Science of the Total Environment*, 752, 142256.

Hüffer, T., Hofmann, T., 2016. Sorption of non-polar organic compounds by micro-sized plastic particles in aqueous solution. *Environmental Pollution*, 214, 194–201.

Hüffer, T., Weniger, A.K., Hofmann, T., 2018. Sorption of organic compounds by aged polystyrene microplastic particles. *Environmental Pollution*, 236, 218–225.

Jiang, M., Hu, L., Lu, A., Liang, G., Lin, Z., Zhang, T., Xu, L., Li, B., Gong, W., 2020. Strong sorption of two fungicides onto biodegradable microplastics with emphasis on the negligible role of environmental factors. *Environmental Pollution*, 267, 115496.

Jiang, M., Shim, W.J., Han, G.M., Rani, M., Song, Y.K., Hong, S.H., 2017. Widespread detection of a brominated flame retardant, hexabromocyclododecane, in expanded polystyrene marine debris and microplastics from South Korea and the Asia-Pacific coastal region. *Environmental Pollution*, 231, 785–794.

Jin, M., Yu, X., Yao, Z., Tao, P., Li, G., Yu, X., Zhao, J., Peng, J., 2020. *How biofilms affect the uptake and fate of hydrophobic organic compounds (HOCs) in microplastic: insights from an in situ study of Xiangshan Bay*, China. *Water Research*,. https://doi.org/10.1016/j.watres.2020.116118.

Koongolla, J.B., Andrady, A.L., Kumara, P.B.T.P., Gangabadage, C.S., 2018. Evidence of microplastics pollution in coastal beaches and waters in southern Sri Lanka. *Marine Pollution Bulletin*, 137, 277–284.

Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids. *Journal of the American Chemical Society*, 38 (11), 2221–2295.

Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40 (9), 1361–1403.

Lao, Q., Su, Q., Liu, G., Shen, Y., Chen, F., Lei, X., Qing, S., We, C., Zhang, C., Gao, J., 2019. Spatial distribution of and historical changes in heavy metals in the surface seawater and sediments of the Beibu Gulf, China. *Marine Pollution Bulletin*, 146, 427–434.

Le, T.X., Munekage, Y., 2004. Residues of selected antibiotics in water and mud from shrimp ponds in mangrove areas in Viet Nam. *Marine Pollution Bulletin*, 49, 922–929.

Lee, H., Shim, W.J., Kwon, J.H., 2014. Sorption capacity of plastic debris for hydrophobic organic chemicals. *Science of the Total Environment*, 470, 1545–1552.

León, V.M., García, I., González, E., Samper, R., Fernández-González, V., Muniategui-Lorenzo, S., 2018. Potential transfer of organic pollutants from littoral plastics debris to the marine environment. *Environmental Pollution*, 236, 442–453.

Li, H., Wang, F., Li, J., Deng, F., Zhang, S., 2021. Adsorption of three pesticides on polyethylene microplastics in aqueous solutions: kinetics, isotherms, thermodynamics, and molecular dynamics simulation. *Chemosphere*, 264, 128556.

Li, J., Zhang, K., Zhang, H., 2018. Adsorption of antibiotics on microplastics. *Environmental Pollution*, 237, 460–467.

Li, L., Liu, D., Li, Z., Song, K., He, Y., 2020. Evaluation of microplastic polyvinylchloride and antibiotics tetracycline co-effect on the partial nitrification process. *Marine Pollution Bulletin*, 160, 111671.

Liao, Y. Yang, J., 2020. Microplastic serves as a potential vector for Cr in an in-vitro human digestive model. *Science of the Total Environment*, 703, 134805.

Lin, L., Tang, S., Wang, X., Sun, X., Han, Z., 2020. Accumulation mechanism of tetracycline hydrochloride from aqueous solutions by nylon microplastics. *Environmental Technology & Innovation*, 18, 100750.

Lin, Z., Hu, Y., Yuan, Y., Hu, B., Wang, B., 2021. Comparative analysis of kinetics and mechanisms for Pb(II) sorption onto three kinds of microplastics. *Ecotoxicology and Environmental Safety*, 208, 111451.

Liu, G., Zhu, Z., Yang, Y., Sun, Y., Yu, F., Ma, J., 2019. Sorption behavior and mechanism of hydrophilic organic chemicals to virgin and aged microplastics in freshwater and seawater. *Environmental Pollution*, 246, 26–33.

Liu, X., Zheng M., Wang, L., Ke, R., Lou, Y., Zhang, X., Dong, X., Zhang, Y., 2018. Sorption behaviors of tris-(2,3-dibromopropyl) isocyanurate and hexabromocyclododecanes on polypropylene microplastics. *Marine Pollution Bulletin*, 135, 581–586.

Liu, Y., Guo, J.R., Chen, Y., Tan, N., Wang, J.L., 2020. High-efficient generation of H_2O_2 by aluminum-graphite composite through selective oxygen reduction for degradation of organic contaminants. *Environmental Science & Technology*, 54, 14085–14095.

Llorca, M., Schirinzi, G., Martínez, M., Barceló, D., Farré, M., 2018. Adsorption of perfluoroalkyl substances on microplastics under environmental conditions. *Environmental Pollution*, 235, 680–691.

Lo, H.S., Wong, C.Y., Tam, N.F.Y., Cheung, S.G., 2019. Spatial distribution and source identification of hydrophobic organic compounds (HOCs) on sedimentary microplastic in Hong Kong. *Chemosphere*, 219, 418–426.

Luo, H., Xiang, Y., Zhao, Y., Li, Y., Pan, X., 2020. Nanoscale infrared, thermal and mechanical properties of aged microplastics revealed by an atomic force microscopy coupled with infrared spectroscopy (AFM-IR) technique. *Science of the Total Environment*, 744, 140944.

Mai, L., Bao, L.J., Shi, L., Liu, L.Y., Zeng, E.Y., 2018. Polycyclic aromatic hydrocarbons affiliated with microplastics in surface waters of Bohai and Huanghai Seas, China. *Environmental Pollution*, 241, 834–840.

Mao, R., Lang, M., Yu, X., Wu, R., Yang, X., Guo, X., 2020. Aging mechanism of microplastics with UV irradiation and its effects on the adsorption of heavy metals. *Journal of Hazardous Materials*, 393, 22515.

Mohsen, M., Wang, Q., Zhang, L., Sun, L., Lin, C., Yang, H., 2019. Microplastic ingestion by the farmed sea cucumber *Apostichopus japonicus* in China. *Environmental Pollution*, 245, 1071–1078.

Müller, A., Becker, R., Dorgerloh, U., Simon, F.G., Braun, U., 2018. The effect of polymer aging on the uptake of fuel aromatics and ethers by microplastics. *Environmental Pollution*, 240, 639–646.

Noik, V.J., Tuah, P.M., Seng, L., Sakari, M., 2015. Fingerprinting and quantification of selected heavy metals in meso-and microplastics sampled from Santubong and Trombol beach, Kuching, Sarawak, Malaysia. *2nd International Conference on Agriculture, Environment and Biological Sciences*, Bali, Indonesia, pp. 53–58. http://dx.doi.org/10.17758/IAAST.A0715062.

Oz, N., Kadizade, G., Yurtsever, M., 2019. Investigation of heavy metal adsorption on microplastics. *Applied Ecology and Environmental Research*, 17(4), 7301–7310.

Pascall, M.A., Zabik, M.E., Zabik, M.J., Hernandez, R.J., 2005. Uptake of polychlorinated biphenyls (PCBs) from an aqueous medium by polyethylene, polyvinyl chloride, and polystyrene films. *Journal of Agricultural and Food Chemistry*, 53, 164–169.

Pedersen, A.F., Gopalakrishnan, K., Boegehold, A.G., Peraino, N.J., Westrick, J.A., Kashian, D.R., 2020. Microplastic ingestion by quagga mussels, *Dreissena bugensis*, and its effects on physiological processes. *Environmental Pollution*, 260, 113964.

Procter, J., Hopkins, F.E., Fileman, E.S., Lindeque, P.K., 2019. Smells good enough to eat: dimethyl sulfide (DMS) enhances copepod ingestion of microplastics. *Marine Pollution Bulletin*, 138, 1–6.

Puckowski, A., Cwięk, W., Mioduszewska, K., Stepnowski, P., Białk-Bielińska, A., 2021. Sorption of pharmaceuticals on the surface of microplastics. *Chemosphere*, 263, 127976.

Qiu, Y., Zheng, M., Wang, L., Zhao, Q., Lou, Y., Shi, L., Qu, L., 2019. Sorption of polyhalogenated carbazoles (PHCs) to microplastics. *Marine Pollution Bulletin*, 146, 718–728.

Razanajatovo, R.M., Ding, J., Zhang, S., Jiang, H., Zou, H., 2018. Sorption and desorption of selected pharmaceuticals by polyethylene microplastics. *Marine Pollution Bulletin*, 136, 516–523.

Rochman, C. M., Hoh, E., Hentschel, B. T., Kaye, S. 2013b. Long-term field measurement of sorption of organic contaminants to five types of plastic pellets: implications for plastic marine debris. *Environmental Science & Technology*, 47 (3), 1646–1654.

Rochman, C.M., Manzano, C., Hentschel, B.T., Simonich, S.L.M., Hoh, E., 2013a. Polystyrene plastic: a source and sink for polycyclic aromatic hydrocarbons in the marine environment. *Environmental Science & Technology*, 47 (24), 13976–13984.

Rouillon, C., Bussiere, P.O., Desnoux, E., Collin, S., Vial, C., 2016. Is carbonyl index a quantitative probe to monitor polypropylene photodegradation? *Polymer Degradation and Stability*, 128, 200–208.

Shan, J., Wang, J., Zhan, J., Liu, L., Wu, F., Wang, X., 2020. Sorption behaviors of crude oil on polyethylene microplastics in seawater and digestive tract under simulated real-world conditions. *Chemosphere*, 257, 127225.

Shen, X., Li, D., Sima, X., Cheng, H., Jiang, H., 2018. The effects of environmental conditions on the enrichment of antibiotics on microplastics in simulated natural water column. *Environmental Research*, 166, 377–383.

Shi, J., Sanganyado, E., Wang, L., Li, P., Li, X., Liu, W., 2020. Organic pollutants in sedimentary microplastics from eastern Guangdong: spatial distribution and source identification. *Ecotoxicology and Environmental Safety*, 193, 110356.

Singla, M., Díaz, J., Broto-Puig, F., Borrós, S., 2020. Sorption and release process of polybrominated diphenyl ethers (PBDEs) from different composition microplastics in aqueous medium: solubility parameter approach. *Environmental Pollution*, 262, 114377.

Sørensen, L., Rogers, E., Altin, D., Salaberria, I., Booth, A.M., 2020. Sorption of PAHs to microplastic and their bioavailability and toxicity to marine copepods under co-exposure conditions. *Environmental Pollution*, 258, 113844.

Speight, J.G., 2020. *Sources of Water Pollution. Natural Water Remediation Chemistry and Technology*. Elsevier, Amsterdam, Netherlands, pp. 165–198.

Sun, B., Hu, Y., Cheng, H., Tao, S., 2019. Releases of brominated flame retardants (BFRs) from microplastics in aqueous medium: kinetics and molecular-size dependence of diffusion. *Water Research*,. 15, 215–225.

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M.-A., Watanuki, Y., 2013. Accumulation of plastic-derived chemicals in tissues of seabirds ingesting marine plastics. *Marine Pollution Bulletin*, 69, 219–222.

Tan, X., Yu, X., Cai, L., Wang, J., Peng, J., 2019. Microplastics and associated PAHs in surface water from the Feilaixia reservoir in the Beijiang River, China. *Chemosphere*, 221, 834–840.

Tang, J.T., Wang, J.L., 2018. Metal organic framework with coordinatively unsaturated sites as efficient Fenton-like catalyst for enhanced degradation of sulfamethazine. *Environmental Science & Technology*, 52, 5367–5377.

Tang, S., Lin, L., Wang, X., Feng, A., Yu, A., 2020. Pb (II) uptake onto nylon microplastics: interaction mechanism and adsorption performance. *Journal of Hazardous Materials*, 386, 121960.

Taniguchi, S., Colabuono, F. I., Dias, P. S., Oliveira, R., Fisner, M., Turra, A., Izar, G.M., Abessa, D.M.S., Saha, M., Hosoda, J., Yamashita, R., Takada, H., Lourençoa, R.A., Magalhãesa, C.A., Bícegoa, M.C., Montonea, R.C., 2016. Spatial variability in persistent organic pollutants and polycyclic aromatic hydrocarbons found in beach-stranded pellets along the coast of the state of São Paulo, southeastern Brazil. *Marine Pollution Bulletin*, 106 (1–2), 87–94.

Teuten, E.L., Rowland, S.J., Galloway, T.S., Thompson, R.C., 2007. Potential for plastics to transport hydrophobic contaminants. *Environmental Science & Technology*, 41, 7759–7764.

Turner, A., Holmes, L. A., 2015. Adsorption of trace metals by microplastic pellets in fresh water. *Environ. Chem.* 12, 600–610.

van der Hal, N., Yeruham, E., Shukis, D., Rilov, G., Astrahan, P., Angel, D.L., 2020. Uptake and incorporation of PCBs by eastern Mediterranean rabbitfish that consumed microplastics. *Marine Pollution Bulletin*, 150, 110697.

Velzeboer, I., Kwadijk, C.J.A.F., Koelmans, A.A., 2014. Strong sorption of PCBs to nanoplastics, microplastics, carboon nanotubes, and fullerens. *Environmental Science & Technology*, 48, 4869–4876.

Wang, F., Shih, K.M., Li, X.Y., 2015. The partition behavior of perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonamide (FOSA) on microplastics. *Chemosphere*, 119, 841–847.

Wang, F., Wang, F., Zeng, E.Y., 2018b. *Sorption of Toxic Chemicals on Microplastics. Microplastic Contamination in Aquatic Environments*. Elsevier, Oxford, United Kingdom, pp. 225–247.

Wang, F., Wong, C.S., Chen, D., Lu, X., Wang, F., Zeng, E.Y., 2018c. Interaction of toxic chemicals with microplastics: a critical review. *Water Research*,. 139, 208–219.

Wang, F., Yang, W., Cheng, P., Zhang, S., Zhang, S., Jiao, W., et al., 2019b. Adsorption characteristics of cadmium onto microplastics from aqueous solutions. *Chemosphere*, 235, 1073–1080.

Wang, J., Coffin, S., Sun, C., Schlenk, D., Gan, J., 2019a. Negligible effects of microplastics on animal fitness and HOC bioaccumulation in earthworm *Eisenia fetida* in soil. *Environmental Pollution*, 249, 776–784.

Wang, J., Peng, J., Tan, Z., Gao, Y., Zhan, Z., Chen, Q., Cai, L., 2017. Microplastics in the surface sediments from the Beijiang River littoral zone: composition, abundance, surface textures and interaction with heavy metals. *Chemosphere*, 171, 248–258.

Wang, J.L., Chen, C., 2009. Biosorbents for heavy metals removal and their future. *Biotechnology Advances*, 27, 195–226.

Wang, J.L., Chu, L.B., 2016. Irradiation treatment of pharmaceutical and personal care products (PPCPs) in water and wastewater: an overview. *Radiation Physics and Chemistry*, 125, 6–64.

Wang, J.L., Chu, L.B., Wojnárovits L., Takács, E., 2020d. Occurrence and fate of antibiotics, antibiotic resistant genes (ARGs) and antibiotic resistant bacteria (ARB) in municipal wastewater treatment plant: an overview. *Science of the Total Environment*, 744, 140997.

Wang, Y., Wang, X., Li, Y., Li, J., Wang, F., Xia, X., Zhao, J., 2020e. Biofilm alters tetracycline and copper adsorption behaviors onto polyethylene microplastics. *Chemical Engineering Journal*, 392, 123808.

Wang, J.L., Guo, X., 2020a. Adsorption isotherm models: classification, physical meaning, application and solving method. *Chemosphere*, 258, 127279.

Wang, J.L., Guo, X., 2020b. Adsorption kinetic models: physical meanings, applications, and solving methods. *Journal of Hazardous Materials*, 390, 122156.

Wang, J.L., Wang, S.Z., 2016. Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: a review. *Journal of Environmental Management*, 182, 620–640.

Wang, J.L., Wang, S.Z., 2019. Preparation, modification and environmental application of biochar: a review. *Journal of Cleaner Production*, 227, 1002–1022.

Wang, J.L., Zhuan, R., Chu, L.B., 2019c. The occurrence, distribution and degradation of antibiotics by ionizing radiation: an overview. *Science of the Total Environment*, 646, 1385–1397.

Wang, J.L., Zhuan, R., 2020. Degradation of antibiotics by advanced oxidation processes: an overview. *Science of the Total Environment*, 701,135023.

Wang, J.L., Zhuang, S.T., 2019. Covalent organic frameworks (COFs) for environmental applications. *Coordination Chemistry Reviews*, 400, 213046.

Wang, Q., Zhang, Y., Wangjin, X., Wang, Y., Meng, G., Chen, Y., 2020a. The adsorption behavior of metals in aqueous solution by microplastics effected by UV radiation. *Journal of Environmental Sciences*, 87, 272–280.

Wang, S.Z., Liu, Y., Wang, J.L. 2020c. Peroxymonosulfate activation by Fe-Co-O co-doped graphite carbon nitride for degradation of sulfamethoxazole. *Environmental Science & Technology*, 54, 10361–10369.

Wang, T., Wang, L., Chen, Q., Kalogerakis, N., Ji, R., Ma, Y., 2020b. Interactions between microplastics and organic pollutants: effects on toxicity, bioaccumulation, degradation, and transport. *Science of the Total Environment*, 748, 142427.

Wang, W.F., Wang J., 2018a. Comparative evaluation of sorption kinetics and isotherm of pyrene onto microplastics. *Chemosphere*, 193, 567–573.

Wang, W.F., Wang J., 2018b. Different partition of polycyclic aromatic hydrocarbon on environmental particulates in freshwater: microplastics in comparison to natural sediment. *Ecotoxicology and Environmental Safety*, 147, 648–655.

Wang, Z., Chen, M., Zhang, L., Wang, K., Yu, X., Zheng, Z., Zheng, R., 2018a. Sorption behaviors of phenanthrene on the microplastics identified in a mariculture farm in Xiangshan Bay, southeastern China. *Science of the Total Environment*, 628–629, 1617–1626.

Wen, B., Jin, S.R., Chen, Z.Z., Gao, J.Z., Liu, Y.N., Feng, X.S., 2018. Single and combined effects of microplastics and cadmium on the cadmium accumulation, antioxidant defence and innate immunity of the discus fish (*Symphysodon aequifasciatus*). *Environmental Pollution*, 243, 462–471.

Xu, B., Liu, F., Brookes, P.C., Xu, J., 2018b. Microplastics play a minor role in tetracycline sorption in the presence of dissolved organic matter. *Environmental Pollution*, 240, 87–94.

Xu, B., Liu, F., Brookes, P.C., Xu, J.M., 2018a. The sorption kinetics and isotherms of sulfamethoxazole with polyethylene microplastics. *Marine Pollution Bulletin*, 131, 191–196.

Xu, P., Ge, W., Chai, C., Zhang, Y., Jiang, T., Xia, B., 2019. Sorption of polybrominated diphenyl ethers by microplastics. *Marine Pollution Bulletin*, 145, 260–269.

Yang, J., Cang, L., Sun, Q., Dong, G., Ata-Ul-Karim, S.T., Zhou, D., 2019. Effects of soil environmental factors and UV aging on Cu^{2+} adsorption on microplastics. *Environmental Science and Pollution Research*, 26, 23027–23036.

Yeo, B.G., Takada, H., Yamashita, R., Okazaki, Y., Uchida, K., Tokai, T., Tanaka, K., Trenholm, N., 2020. PCBs and PBDEs in microplastic particles and zooplankton in open water in the Pacific Ocean and around the coast of Japan. *Marine Pollution Bulletin*, 151, 110806.

Yu, H., Yang, B., Waigi, M.G., Peng, F., Li, Z., Hu, X., 2020. The effects of functional groups on the sorption of naphthalene on microplastics. *Chemosphere*, 261, 127592.

Zhan, Z.W., Wang, J.D., Peng, J.P., Xie, Q.L., Huang, Y., Gao, Y.F., 2016. Sorption of 3,3',4,4'-tetrachlorobiphenyl by microplastics: a case study of polypropylene. *Marine Pollution Bulletin*, 110 (1), 559–563.

Zhang, X., Zheng, M., Wang, L., Lou, Y., Shi, L., Jiang S., 2018. Sorption of three synthetic musks by microplastics. *Marine Pollution Bulletin*, 126, 606–609.

Zhang, S., Ding, J., Razanajatovo, R.M. Jiang, H., Zou, H., Zhu, W., 2019. Interactive effects of polystyrene microplastics and roxithromycin on bioaccumulation and biochemical status in the freshwater fish red tilapia (*Oreochromis niloticus*). *Science of the Total Environment*, 648, 1431–1439.

Zhao, L., Rong, L., Xu, J., Lian, J., Wang, L., Sun, H., 2020. Sorption of five organic compounds by polar and nonpolar microplastics. *Chemosphere*, 257, 127206.

Zhou, L., Wang, T., Qu, G., Jia, H., Zhu L., 2020. Probing the aging processes and mechanisms of microplastic under simulated multiple actions generated by discharge plasma. *Journal of Hazardous Materials*, 398, 122956.

Zon, N.F., Iskendar, A., Azman, S., Sarijan, S., Ismail, R., 2018. Sorptive behaviour of chromium on polyethylene microbeads in artificial seawater. *MATEC Web of Conferences*, 250, 06001.

Zou, J., Liu, X., Zhang, D., Yuan, X., 2020. Adsorption of three bivalent metals by four chemical distinct microplastics. *Chemosphere*, 248, 126064.

10

Colonization of Plastic Marine Debris

The Known, the Unknown, and the Unknowable

Linda A. Amaral-Zettler[1,2]

[1] *NIOZ – Royal Netherlands Institute for Sea Research, Den Burg, The Netherlands*
[2] *Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, Amsterdam, The Netherlands*

10.1 Introduction

The call for research concerning microbial interactions with marine microplastics (MPs; Harrison et al. 2011) has reached a decadal milestone, leaving us with not only novel insights into this field of investigation but also many unanswered questions. This chapter reflects on this decade of discovery with respect to the "Plastisphere" that refers to the thin layer of life that colonizes the outside of plastic debris, with a focus on the microscopic life that colonizes plastics in marine systems.

The search for life on plastic marine debris (PMD) was largely influenced by the International Census of Marine Microbes (ICoMM; Amaral-Zettler et al. 2010) that sought to characterize the genetic diversity and relative abundance of microbial life in the world ocean using massively parallel sequencing of Bacteria (Sogin et al. 2006), Archaea (Huber et al. 2007), and microbial Eukarya (Amaral-Zettler et al. 2009). One of the unifying themes of the Census of Marine Life (www.coml.org) was the concept of understanding what was **Known** about (microbial) diversity in the ocean, what was **Unknown** and still to be discovered, and what may remain a mystery – the so-called **Unknowable**. Some of the open questions that followed the census included *Why are there so many different kinds of microbes? Is there such a thing as microbial endemicity? How many microbial niches exist?* and *What is the role of the rare biosphere?* The ICoMM focused primarily on microbes that live in the water column or in sediments with an occasional study that considered particle-attached taxa but largely ignored "microbiomes" including those occurring on biotic and abiotic substrates such as plastic debris. We learned from large-scale analyses that water-column and sediment communities are very distinct (Zinger et al. 2011) and that their distributions were largely shaped by the surrounding physicochemical environment. We also learned that the microbial community structure in the marine environment is largely dominated by a few taxa, followed by a long-tail distribution of rare taxa. Several of the questions framed by the first Census of Marine Life can also be asked of the Plastisphere. This chapter revisits the state of knowledge regarding the Plastisphere in the context of the Known, Unknown, and Unknowable.

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

10.2 Preamble

Carpenter and Smith (1972) were the first to document microbes on plastics collected in the open ocean. Shortly after this, Sieburth (1975) published his book *Microbial Seascapes*, with beautiful scanning electron microscopy (SEM) images of microbial biofilms on a variety of surfaces including (macro)plastic from coastal environments. However, research on this novel topic was relatively limited until Harrison et al. (2011) summarized the limited state of then-current knowledge and called on the scientific community to increase investigations of interactions between microorganisms and marine MP and the publication of the first high-throughput sequencing study documenting the diversity of microbes on plastic in the North Atlantic Subtropical Gyre or “Garbage Patch” (Zettler et al. 2013). Since then, the number of publications studying various aspects of microbe–plastic interactions has increased significantly (Onda and Sharief 2021), with a recent flurry of review papers, including at least 12 since 2020. Different reviews emphasize different aspects of microbe–plastic interaction, such as degradation (Yuan et al. 2020), biogeochemistry (Rogers et al. 2020), ecology (Amaral-Zettler et al. 2020; Oberbeckmann and Labrenz 2020; Yang et al. 2020), contaminants and risks (Khalid et al. 2021; Mammo et al. 2020), colonization (Caruso 2020; Onda and Sharief 2021; Wright et al. 2020b), microbiome (Lear et al. 2021), or microalgae (Nava and Leoni 2021). Because of the extensive coverage in previous reviews, including those listed earlier, I have chosen NOT to duplicate those efforts. Instead, in this chapter, I take advantage of recent reviews to outline common themes those authors raised, highlighting some recent advances, and lines of investigation that seem particularly likely to increase our knowledge of how colonization influences the structure and function of the Plastisphere and how these communities may impact marine environments. The timely topic of biodegradation is covered in another chapter of this book (Chapter 11), so it will not be addressed in this chapter.

10.3 The Known

10.3.1 What Do We Know About Who Lives in the Plastisphere – Phylogenetic Diversity?

The understanding that plastics are a new habitat for microbial and microscopic life has been recognized for nearly 50 years since the discovery of PMD itself in the early 1970s with evidence of diatoms, bacteria, and even hydroids being detected on the surface of plastic debris (Carpenter and Smith 1972; Figure 10.1). Despite the long-standing recognition that both bacteria and microbial eukaryotes (e.g. biofilm-forming diatoms) produce extracellular polymeric substances that form the foundation of biofilms on plastic, there is still a tendency in the literature to assume that bacteria are always the initial colonizers. However, it has been known for several decades that diatoms can colonize surfaces such as glass within hours (Cooksey et al. 1984), as well as plastic debris (unpublished results). Within a week, diatoms can completely dominate surfaces in coastal waters (Figure 10.2). Consequently, it is not only the plastic surface characteristics and leachates influencing the composition of early colonizing bacterial communities such as obligate hydrocarbon-degrading bacteria (OHDB; Erni-Cassola et al. 2020) but also the dissolved organic matter being produced by diatoms and other Plastisphere denizens. Dudek et al. (2020) acknowledged the possible role of the diatoms in shaping bacterial community structure in the Plastisphere but misidentify attachment fibers of diatoms as hyphomonad bacteria known to metabolize polycyclic aromatic hydrocarbons. Hyphomonads do exist in the Plastisphere, but Figure 10.3 points out the differences between these

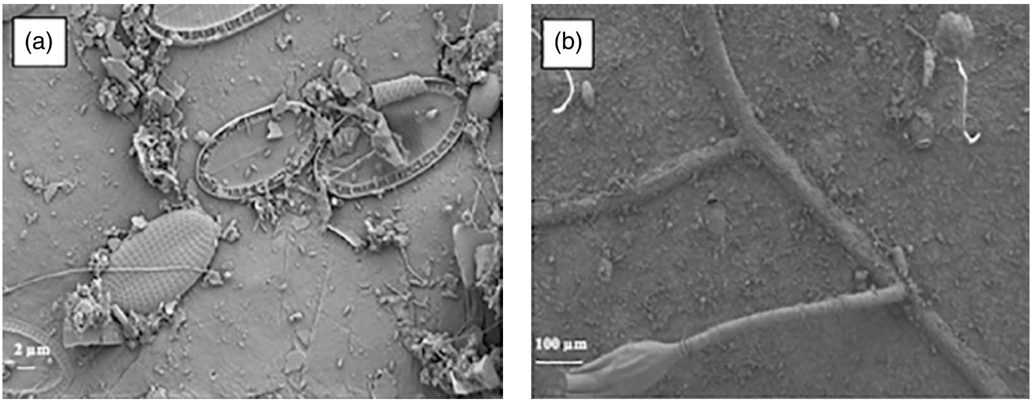
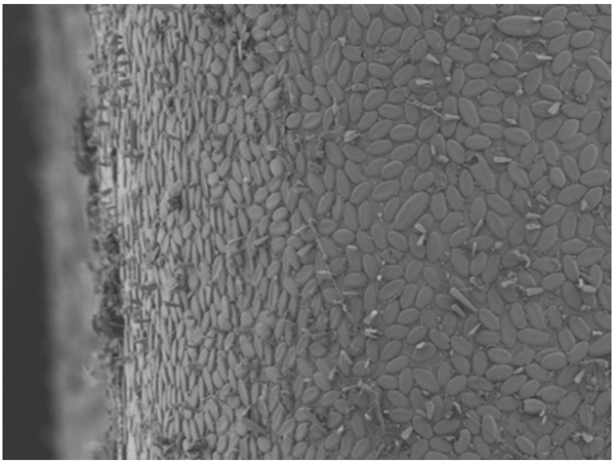


Figure 10.1 Consistency in the Plastisphere: (a) bacteria, diatoms, and (b) hydroids that Carpenter and Smith (1972) reported are still commonly seen on most plastic collected from surface waters in marine systems.

Figure 10.2 Diatom biofilm covering the surface of glass submerged in the marine environment after one week.



and the diatom fibers. All the same, the importance of examining the Plastisphere community as a whole is slowly catching hold in the research community.

The question of whether the Plastisphere selects for microorganisms like the rhizosphere or phycosphere (Wright et al. 2020b) has been argued against on grounds that existing studies do not show a consistent trend for plastic-specific taxa (Wright et al. 2020b). However, this was never the intended definition of the Plastisphere; because the Plastisphere organisms have to come from somewhere, it is unlikely that *any* of them will be found only on plastic. However, most studies show differences between the communities on plastic and other substrates, at least during early colonization. There is also a difference between targeted selection and differential selection that is important to acknowledge when it comes to understanding the community composition of the Plastisphere. A big gap in our understanding of Plastisphere community assembly may also be an artifact of experimental designs that intentionally exclude larger “fouling” organisms (e.g. multicellular community members) that are integral community members even on MPs (plastic 1–5 mm) that are large enough to be colonized by them. While we have always known that

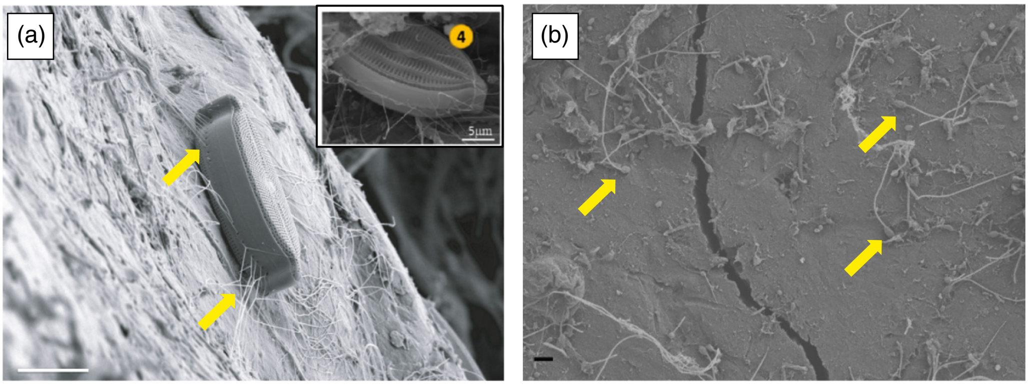


Figure 10.3 (a) A single diatom attached to the surface of a piece of plastic marine debris (PMD) with chitan (chitin-poly-*N*-acetylglucosamine) fibers extruded from the cell (scale bar 10 μm). Inset image extracted from Figure 10.5a (D4) *Mastogloia corsicana*, from Dudek 2020, p 07, Figure 05A(D4) / With permission from JOHN WILEY & SONS, INC. / https://aslopubs.onlinelibrary.wiley.com/doi/epdf/10.1002/lol2.10141 showing similar chitinous fibers. (b) Contrast with putative hyphomonad-like stalked bacteria attached to the surface of PMD (scale bar 2 μm).

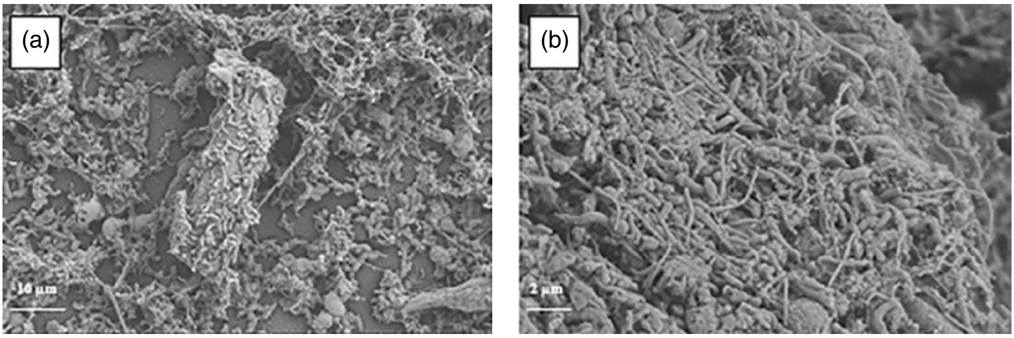


Figure 10.4 Scanning electron microscopy images showing associations between different bacteria and diatoms within Plastisphere biofilms. (a) Pennate diatom covered with a variety of bacteria on a piece of high-density polyethylene. (b) Thick, multi-species mat of bacteria on a piece of polyhydroxybutyrate placed at the sediment surface.

biofouling organisms colonize marine debris of any composition, we are now also keenly aware of the associated microbiomes that all multicellular life carries with it, as well as microbial eukaryotic life. In this respect, the "phycosphere" really does meet the Plastisphere in that both unicellular and multicellular algae, and their associated phycospheres, are consistent members of the Plastisphere (diatom with bacteria, bacterial associations within biofilm; Figure 10.4a,b).

What remains striking about the community structure observed in the Plastisphere in samples collected directly from the environment (not part of incubation experiments, laboratory, or otherwise) are the differences in relative abundances (evenness) seen across the communities when compared to the surrounding seawater (Figure 10.5). Seawater samples tend to be dominated by relatively few highly abundant taxa, whereas plastic samples are not. Differences between attached and planktonic microbial communities are to be expected, but results from nonplastic surfaces in environmental samples are rare; more are needed to determine whether this pattern is unique to plastic and whether the microbiomes of eukaryotes attached to plastic help explain some of the patterns.

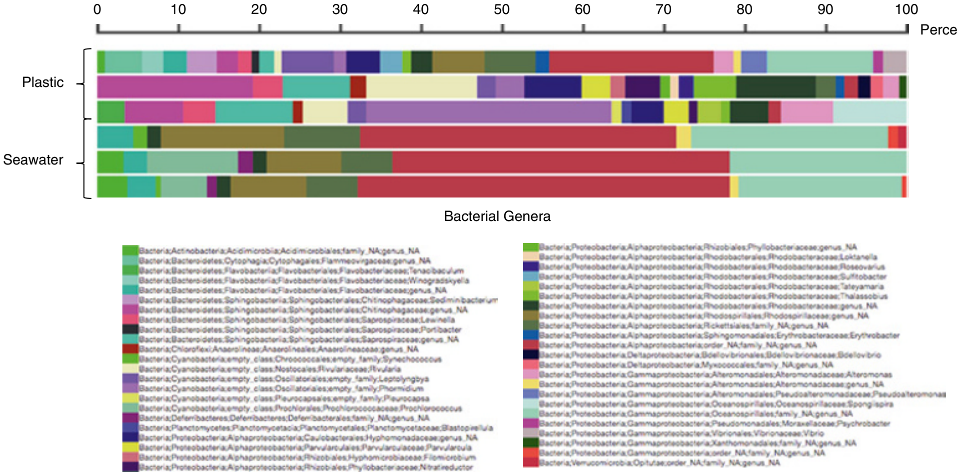


Figure 10.5 Bacterial community structure on plastic marine debris (polyethylene from the North Atlantic Subtropical Gyre) versus seawater communities showing distinct patterns in dominance and also evenness.

Some insight can also be gained from time series experiments to examine the differences in community structure over time and how they diverge or remain the same. For example, De Tender et al. (2017a) compared communities that developed on experimental plastic incubations in onshore and off-shore environments with randomly sampled pieces of plastic debris in the surrounding North Sea. They found the pieces collected from the environment to be most similar to early-phase biofilms observed on plastics sampled in the harbor. This suggested that microbial communities found on plastics in the open environment are likely very dynamic and prone to resetting after disturbance. Disturbance in the marine setting might also explain the often-encountered increased evenness we observe in Plastisphere communities characterized from ocean gyres.

It is generally agreed that during initial colonization events, the substrate can select for different groups of microbes (Muthukrishnan et al. 2018; Ogonowski et al. 2018), but as the biofilm covers the surface and matures, the communities on different substrates converge (Dang et al. 2008; Wright et al. 2021b). The inherent bias that prefiltration of water in laboratory-based studies (Ogonowski et al. 2018) or grazer exclusion via netting in in situ field incubations (Zhang et al. 2021) brings to our understanding of general patterns is yet to be quantified. Perhaps understanding the divergent nature of Plastisphere community structure is in the realm of the unknowable despite efforts to systematically study this question.

Despite challenges forming general conclusions about the nature of Plastisphere community structures, meta-analyses of amplicon data sets have started to shed light on broadscale patterns or “core” taxa associated with the marine Plastisphere (De Tender et al. 2017b; Oberbeckmann and Labrenz 2020; Wright et al. 2021b), including the presence of Rhodobacteraceae as consistent (often dominant) members (De Tender et al. 2017b; Oberbeckmann and Labrenz 2020) and also the shared presence of Sphingomonadaceae (e.g. *Erythrobacter*; Wright et al. 2021b) across many plastic data sets. Another significant find was that members of the Oceanospirillales tended to be more frequently encountered on aliphatic plastics, while the Alteromonadales were more abundant on other types of plastic (Wright et al. 2021b). The later perhaps being a product of the dominance of data sets looking at time series incubations wherein members of these hydrocarbonoclastic orders are more abundant at early time points, but become part of the “rare biosphere” at later stages (Pedrós-Alió 2012). Several additional insights and questions emerged from these collective efforts and the reader is referred to these studies for more detailed observations.

10.4 The Unknown, but Knowable

10.4.1 What Can We Know About the Functional Diversity of the Plastisphere?

There has been one study using BioLog plates that measure substrate utilization in freshwater (Arias-Andres et al. 2018a), but very few studies in the literature have attempted to characterize the functional diversity of the marine Plastisphere. Some studies have used methods that provide proxies by inferring metabolic potential based on taxonomic affiliation of relatives with sequenced genomes (Debroas et al. 2017; Zhang et al. 2021) using bioinformatics programs including PICRUSt (Langille et al. 2013) or Bugbase (Ward et al. 2017), the latter an online platform that makes use of the former. While this application may be relevant for coastal studies wherein a majority of known genomes have been isolated, it is unknown how well our knowledge of the metabolism of open-ocean organisms is reflected in present genome archives, particularly for biofilm-associated communities (Zhang et al. 2019) such as the Plastisphere.

Metagenomic investigations remain relatively rare, particularly for samples collected directly from the environment (Bryant et al. 2016), but metagenomic or genomic studies that involve incubation experiments are increasing (Meyer-Cifuentes et al. 2020; Pinnell and Turner 2019; Wright et al. 2021a). Among the challenges associated with generating metagenomic data from field collected samples are the inherently low biomass and thus genomic DNA present on individual pieces of plastic – especially those less than 1 mm in dimension, but also the possible presence of large eukaryotic genomes that can dominate a given sample. This creates a challenge for obtaining good coverage for metagenome-assembled genomes of Plastisphere representatives and often necessitates deep sequencing coverage since it is difficult to determine a priori the relative contributions of different domains of life present on a piece of MP. To get around these hurdles, many groups have resorted to pooling samples to obtain sufficient biomass (at the cost of obliterating genomic signatures on individual MPs) or in the case of incubation experiments, excluding eukaryotes (and their genomic signatures) via prefiltration or size-fractionation strategies taken with global marine genomic sampling campaigns like the Global Ocean Survey, Tara Oceans, and Malaspina expeditions. Many studies state that they actively excluded sequences belonging to eukaryotes. This simplifies analysis, but clearly we need to include all domains if we truly want to understand the functional diversity of the Plastisphere.

Yet another window into Plastisphere functional diversity is a more traditional cultivation-based approach to interrogate the physiology of Plastisphere members in a laboratory setting (de Vogel et al. 2021; Wright et al. 2020a), but our success in cultivating representative Plastisphere members remains to be determined. Greater efforts to study the function of uncultivable Plastisphere members depend on new methodologies that are giving us access to combined cell-sorting and labeling approaches recently reviewed in Thrash (2021). Given that plastics are a relatively new substrate, communities that inhabit them have had a finite amount of time to adapt to the particular characteristics of this habitat, so we do not really know if and whether the genomes of Plastisphere members reflect conditions characteristic of environments where plastic accumulates, including the open-ocean gyres. Therefore, the isolation of Plastisphere members that may possess novel functional genes with respect to degradation and biodegradation of conventional and biodegradable and compostable plastics remains an active area of research into the foreseeable future.

10.4.2 What Role Does the Plastisphere Play in Vertical Transport of MPs?

Biofouling of plastic leading to sinking is often mentioned as one of the mechanisms removing buoyant plastic from surface waters. This was originally suggested by Holmstrom (1975) to explain sheets of low-density polyethylene (PE) coated with calcareous algae and bryozoans dredged from the sea bottom by Swedish fishermen and documented in an experiment by Ye and Andrady (1991) who showed that a variety of plastic items moored in coastal waters of Florida sank due to biofouling after six weeks. More recently, there have been field (Ryan 2015), experimental (Fazey and Ryan 2016; Kaiser et al. 2017), and theoretical (Chubarenko et al. 2016; Kooi et al. 2017) studies supporting the idea that fouling causes buoyant plastic to sink. Most of the experimental studies report whether plastic floats or sinks, but we need more quantitative measurements of the actual density of fouled particles, as well as biofilm thickness and density. These values, as well as additional measurements of the size and shape of plastic in the environment, are required for accurate modeling and prediction of the movement of plastic and where it ends up in the ocean. In addition to the microbial contributions to changes in MP density, we do not know how the Plastisphere changes as a particle sinks – such a question might be addressed using mesocosms in the laboratory or preferably in the field. The extent to which one can extrapolate from the laboratory to the field and the effect of time, seasonality, and physicochemical environmental influences, however, will likely remain unknown for some time.

Because current inventories of surface plastic account for only a small fraction of the plastic we believe has entered the ocean (van Sebille et al. 2015), it is thought that much of the "missing" plastic has either fragmented into pieces too small for us to accurately sample or it is now below the surface or in the sediments. Many polymers, including polystyrene (PS), polyvinyl chloride, Polyethylene terephthalate (PET), nylon, and most of the newer compostable plastics, are denser than seawater, so they will sink unless they have trapped air as for sealed beverage containers. As mentioned previously, there is also evidence that buoyant plastics such as PE, polypropylene, and expanded PS also sink once they become biofouled. If there is a slow, continuous "rain" of plastic particles through the water column, we would expect it to show up in sediment traps, but there are remarkably few reports of this. Separation of plastic from sediments is labor intensive, but recent studies show that plastic particles, including buoyant polymers, are abundant in marine sediments (Bergmann et al. 2017; Gomiero et al. 2019). We would expect the Plastisphere communities to change as particles sink below the surface and settle on/into the sediments, but we have no information about the microbes associated with plastic in the water column, and very little from the sediments (De Tender et al. 2015, 2017a; Woodall et al. 2018; Wu et al. 2020). Collecting pieces of plastic without disturbing the biofilm from either location is challenging, but this should be a research priority if we believe the sediments are the ultimate sink for most marine plastic.

10.4.3 What Roles Do Eukaryotes, Microbial Consortia, and Interactions Play in the Plastisphere?

Early studies concentrated on bacterial members of the Plastisphere, but recently, there is greater recognition that eukaryotes are important members of this ecosystem and increasing numbers of studies are including them (Amaral-Zettler et al. 2021; Bryant et al. 2016; Debroas et al. 2017; Dudek et al. 2020; Kettner et al. 2017, 2019; Lacerda et al. 2020). Microbial consortia, as well as symbiotic, parasitic, and predator–prey relationships, undoubtedly play a role in shaping Plastisphere community structure and function, but we still know very little about interactions between members of this community. There have been a few studies using co-occurrence and network analyses to investigate associations within the Plastisphere based on operational taxonomic units (OTUs) (Amaral-Zettler et al. 2021; Debroas et al. 2017; Jiang et al. 2018; Kettner et al. 2019; Zettler et al. 2013), and SEM images show us something of the structure of the biofilm on plastics so we know that different kinds of cells are often closely associated (Figure 10.4a,b). There has been some progress in identifying the spatial arrangement of different taxa in the Plastisphere biofilm based on fluorescence in situ hybridization (FISH) techniques (Harrison et al. 2014; Schlundt et al. 2020), but we need to learn more about *what* they are doing: What is the physiology of the Plastisphere and What role does it play in the biogeochemical cycling of greenhouse gases (Cornejo-D'Ottone et al. 2020; Royer et al. 2018) sulfur (Pinnell and Turner 2019) and carbon (Zhao et al. 2020) in the marine environment? What about nitrogen fixation in the oligotrophic gyres by the cyanobacteria that are common residents of the Plastisphere? Is the net effect of the Plastisphere to increase production by phototrophic (Bryant et al. 2016) and heterotrophic (Dussud et al. 2018; Romera-Castillo et al. 2018) microbes, or is there a net negative effect due to leachates from the plastic (Tetu et al. 2020)? Are the diverse members of this community exchanging metabolites, signaling molecules, or genes in a synergistic manner?

10.4.4 What Is the Impact of Weathering on Plastic Colonization?

Most studies to date have investigated microbial community succession on plastic using virgin (un-weathered) polymers or un-weathered post-consumer plastic materials tethered in the environment or in laboratory aquaria. Therefore, it is largely unknown whether or not weathered plastics differentially enrich for certain community members over others. A commonly accepted notion is that virgin plastics release short-chain carbon molecules leftover from the manufacturing process that leach into the environment and serve as a carbon source for OHDB. One study that ventured into this uncharted area compared communities on three-month-old thermo-oxidized PE versus virgin PE film and found differences in early colonizing bacteria (notably *Roseobacter*-, *Oleiphilus*-, and *Aestuariibacter*-like taxa) after two days of incubation, but after nine days, these differences were no longer detectable with the OHDBs becoming members of the "rare biosphere" (Erni-Cassola et al. 2020). It is important to note that this study and that by Dussud et al. (2018) were incubation experiments that both used thermo-weathered plastics, not plastics weathered directly in the environment where the extent and form of weathering is unknown. It may be possible to replicate these experiments using "uncontrolled" weathering conditions that might better reflect what is happening in the natural environment, for example after a biofilm has "reset" after a disturbance.

10.4.5 Is the Plastisphere a Hotspot for Horizontal Gene Transfer Regarding Antibiotic Resistance, Persistent Organic Pollutant Degradation, Metal Tolerance, and Pathogenicity?

An area of increased interest regarding plastic colonization is the extent to which PMD might enrich for microbes that are capable of degrading not only short-chain carbon molecules associated with plastic leachates but also whether Plastisphere members are capable of degrading plasticizers have increased metal resistance genes (MRGs), or carry genes involved in pathogenicity. Laboratory experiments employed a genetically modified *Escherichia coli* with a fluorescently labeled plasmid to demonstrate increased frequency of plasmid transfer in MP-associated treatments versus water and natural aggregate controls (Arias-Andres et al. 2018b). This led to other studies that identified antibiotic resistance genes (ARGs) in open-ocean metagenomic surveys of environmentally collected macroplastic and MP (Bryant et al. 2016; Yang et al. 2018) and also metagenomes derived from coastal incubation experiments (Pinnell and Turner 2019; Sun et al. 2020) of both biodegradable (polyhydroxyalkanoate [PHA]) and PET, with PET Plastispheres showing higher abundances of multidrug resistance genes than PHA. The study that mined the open-ocean metagenomes found no differences between ARGs in MPs versus macroplastics but reported a higher relative abundance of ARGs in the Plastisphere versus the surrounding seawater. The study further concluded that PMD serves as a reservoir for both ARGs and MRGs but that open-ocean PMD was less enriched in these genes than microbial communities found in more polluted environments such as sewage sludge or landfill leachate. Because ARGs and MRGs tend to co-occur and ARGs tend to occur on larger plasmids (Wein et al. 2020), it is unknown what the selective pressure of maintaining these large plasmids might be in open-ocean Plastisphere communities. Since weathered MPs appear to have a reduced capacity to absorb antibiotics (Guo and Wang 2019), it may be the case that retention of plasmids that carry ARGs and MRGs may not be subjected to purifying selection that might otherwise eliminate them from a population (Wein et al. 2019). These authors hypothesized that environmental conditions might be involved in plasmid maintenance and this could be systematically explored in Plastisphere communities.

Figure 10.6 "Plastic tides" of biobeads from sewage treatment overflow in the UK washing ashore in Maasvlakte, The Netherlands. *Source:* © Stellata Koop.

In addition to interrogating metagenomes for evidence of ARGs and MRGs, other studies have used a culture-based approach to identify Plastisphere isolates that (i) degrade plasticizers (Wright et al. 2020a), (ii) represent potential human pathogenetic vibrios (Laverty et al. 2020), and (iii) represent potential fish and opportunistic human pathogens (Radisic et al. 2020). Studies with isolates are a good start, but understanding how these behave within their multispecies biofilm communities is an important next step to see how big an impact they might have in the environment. As with identifying instances of species invasions associated with PMD introductions, confirming that PMD is responsible for spreading disease is equally challenging. Confirming that isolates are capable of infection would be the first step to doing so.

10.4.6 How Do Plastisphere Communities Change During Transport and What Is the Community Turnover?

Most PMD originates from land, and only on rare occasions do we know the source or timing of arrival (Figure 10.6). We, therefore, typically do not know what the turnover rate in the Plastisphere community is as it moves from rivers to estuaries to open waters. The fate of a given piece of plastic debris can be influenced by many different abiotic and biotic factors. Studies consistently support the idea that the geographic location is one of the main determinants of Plastisphere community structure, and this has been suggested as evidence that turnover is rapid and few microbes are transported between environments on plastic. However, this overlooks the existence of resistant resting/dormant stages that some microbes enter when conditions are unfavorable. These resting stages and other rare members of the community could persist and bloom when conditions again become favorable. We also know that multicellular organisms attached to plastic persist for long periods and can be transported long distances (Faria and Kitahara 2020; Hansen et al. 2019; Rech et al. 2018), and each of these larger organisms carries with it a diverse microbiome, each of which contributes to the metabolic capability of the Plastisphere community. Nevertheless, the role of plastics in the transport of nonindigenous species, harmful algal blooms, and actual pathogens as opposed to the often reported "potential pathogens" remains unclear and provides an important topic for future research.

10.4.7 Can the Plastisphere Serve as a Platform for Applying Ecological Theory?

Several of the unanswered questions regarding Plastisphere colonization might be well served by incorporating more ecological theory, or even testing hypotheses based on macroecological theory. Some existing studies applied tested latitudinal gradients in diversity of Plastisphere communities, for example (Amaral-Zettler et al. 2015). Other obvious areas where ecological theory might be applied include examining priority effects and assessing the nature of community assembly in Plastisphere communities (e.g. neutral theory). Incorporation of experimental practices borrowed from vegetation ecology includes common garden (or transplant) experiments (Clausen et al. 1940), an approach taken recently to compare Plastisphere communities on environmentally collected plastics to those from an in situ incubation experiment with known polymers (Zhang et al. 2021). These experiments could be performed in more open marine waters to test the rate of recruitment in open oligotrophic environments as opposed to eutrophic ones to see if similar patterns hold. Whether disturbance drives evenness patterns seen in some Plastisphere communities, particular open-ocean ones, as well as aspects of invasion ecology, community coalescence, fragmentation, and knockout are all ripe for testing using experimental approaches (Bell 2019).

10.5 The Unknowable

Some interesting questions about plastic and microbes in the environment will probably remain unknown for the foreseeable future, at least pending the development of novel insights and analytical techniques. For example, what is the source and age of plastic collected in marine systems? Occasionally, larger pieces of plastic such as bottles have labels or recognizable shapes allowing us to determine the source and approximate age. However, most pieces collected from the surface, intermediate depths, or the sediment are small and/or unlabeled, so we do not know the source, when they were manufactured, or how long they have been in that particular environment. Both the extent of chemical oxidation and the composition/successional stage of the Plastisphere have been suggested as tools for aging marine plastic, and both can provide valuable information about relative ages. Distinguishing a piece of plastic that entered the ocean a week ago from one that has been there for a year is probably feasible with either of these methods, but finer scale determinations are difficult. The oxidation state will be affected by location, depth, and the degree of coverage due to biofouling, and the composition of the biofilm can be "reset" if the piece has been grazed or ingested, resulting in partial or total removal of the microbial community. Theoretically, it should be possible to learn something about the origin of a polymer by analyzing the physicochemical "fingerprint," particularly with regard to additives. However, these probably change with age as additives leach out differentially, and in addition, most plastic formulations are closely guarded proprietary secrets.

In addition to uncertainty about the age of a particular piece of plastic in the ocean, another question that will be very difficult to answer accurately is how long plastic lasts in the ocean before being completely degraded. Plastic has been in production for a relatively short time relative to its predicted longevity of decades to centuries. Estimates can be made based on analysis of environmental plastic and experimental results, but extrapolating these estimates to predict how long the plastic in our oceans will last is tenuous at best given the variety of polymers with differing cocktails of additives, ending up in marine environments ranging from oligotrophic, warm, well-lit surface waters to eutrophic, cold, dark sediments. Related to uncertainty about the longevity of plastic in the ocean is the question of whether microbial consortia will adapt to increasing stocks of plastics by increasing the ability to break down long-chain polymers, speeding up the very slow rates that have been estimated so far. It has been pointed out that until other more easily incorporated sources of carbon are exhausted, it remains energetically expensive to use plastic as a carbon source (Oberbeckmann and Labrenz 2020). With increasing amounts of plastic in the ocean, and particularly in those areas where plastic is concentrated and other sources of carbon may be limited or become exhausted (e.g. below the sediment surface), selection for the ability to use plastic as a carbon source may increase.

10.6 Conclusion

As it is clear from the papers cited in this chapter, as well as in the recent reviews mentioned previously, we have learned a lot about microbial interactions with marine MPs in the past decade. Nevertheless, there is still a lot of work to do, interesting questions to answer, and society-relevant issues of health and food safety to consider. I expect the most progress will come from collaborative projects that take advantage of a variety of -omic, visualization, culturing, and experimental work to investigate microbe–plastic and microbe–microbe interactions in the Plastisphere from a variety of viewpoints. Let us roll up our sleeves and get to work!

References

Amaral-Zettler, L., Artigas, L. F., Baross, J., Bharathi, L., Boetius, A., Chandramohan, D., Herndl, G., Kogure, K., Neal, P., Pedros-Alio, C., Ramette, A., Schouten, S., Stal, L. J., Thessen, A., De Leeuw, J., Sogin, M. 2010. A global census of marine microbes. *In:* Mcintyre, A. (ed.) *Life in the World's Oceans: Diversity, Distribution and Abundance*. Oxford: Blackwell Publishing Ltd.

Amaral-Zettler, L., Zettler, E., Mincer, T. 2020. Ecology of the Plastisphere. *Nature Reviews Microbiology*, 18, 139–151.

Amaral-Zettler, L.A., Ballerini, T., Zettler, E.R., Asbun, A. A., Adame, A., Casotti, R., Dumontet, B., Donnarumma, V., Engelmann, J. C., Frère, L., Mansui, J. 2021. Diversity and predicted inter-and intra-domain interactions in the Mediterranean Plastisphere. *Environmental Pollution*, 117439. doi:10.1016/j.envpol.2021.117439.

Amaral-Zettler, L. A., Mccliment, E. A., Ducklow, H. W., Huse, S. M. 2009. A method for studying Protistan diversity using massively parallel sequencing of V9 hypervariable regions of small-subunit ribosomal RNA genes. *PLoS One*, 4, e6372–e6372.

Amaral-Zettler, L. A., Zettler, E. R., Slikas, B., Boyd, G. D., Melvin, D. W., Morrall, C. E., Proskurowski, G., Mincer, T. J. 2015. The biogeography of the Plastisphere: implications for policy. *Frontiers in Ecology and the Environment*, 13, 541–546.

Arias-Andres, M., Kettner, M. T., Miki, T., Grossart, H. P. 2018a. Microplastics: new substrates for heterotrophic activity contribute to altering organic matter cycles in aquatic ecosystems. *Science of the Total Environment*, 635, 1152–1159.

Arias-Andres, M., Klumper, U., Rojas-Jimenez, K., Grossart, H. P. 2018b. Microplastic pollution increases gene exchange in aquatic ecosystems. *Environmental Pollution*, 237, 253–261.

Bell, T. 2019. Next-generation experiments linking community structure and ecosystem functioning. *Environmental Microbiology Reports*, 11, 20–22.

Bergmann, M., Wirzberger, V., Krumpen, T., Lorenz, C., Primpke, S., Tekman, M. B., Gerdts, G. 2017. High quantities of microplastic in Arctic deep-sea sediments from the HAUSGARTEN Observatory. *Environmental Science & Technology*, 51, 11000–11010.

Bryant, J. A., Clemente, T. M., Viviani, D. A., Fong, A. A., Thomas, K. A., Kemp, P., Karl, D. M., White, A. E., Delong, E. F. 2016. Diversity and activity of communities inhabiting plastic debris in the North Pacific Gyre. *mSystems,* 1–19.

Carpenter, E. J., Smith, K. L. 1972. Plastics on the Sargasso sea surface. *Science*, 175, 1240–1241.

Caruso, G. 2020. Microbial colonization in marine environments: overview of current knowledge and emerging research topics. *Journal of Marine Science and Engineering*, 8, 1–23.

Chubarenko, I., Bagaev, A., Zobkov, M., Esiukova, E. 2016. On some physical and dynamical properties of microplastic particles in marine environment. *Marine Pollution Bulletin*, 108, 105–112.

Clausen, J., Keck, D. D., Hiersey, W. M. 1940. Experimental studies on the nature of plant species. *I. Effect of Varied Environment on Western North American Plants*. Washington D.C.: Carnegie Institution of Washington Publication.

Cooksey, B., Cooksey, K. E., Miller, C. A., Paul, J. P., Webster, D., Rubin, R. 1984. The attachment of microfouling diatoms. *In:* Costlow, J. D., Tipper, R. C. (eds.) *Marine Biodeterioration: An Interdisciplinary Study*. Annapolis: US Naval Institute Press.

Cornejo-D’ottone, M., Molina, V., Pavez, J., Silva, N. 2020. Greenhouse gas cycling by the plastisphere: the sleeper issue of plastic pollution. *Chemosphere*, 246, 125709.

Dang, H., Li, T., Chen, M., Huang, G. 2008. Cross-ocean distribution of Rhodobacterales bacteria as primary surface colonizers in temperate coastal marine waters. *Applied and Environmental Microbiology*, 74, 52–60.

De Tender, C., Devriese, L. I., Haegeman, A., Maes, S., Vangeyte, J., Cattrijsse, A., Dawyndt, P., Ruttink, T. 2017a. Temporal dynamics of bacterial and fungal colonization on plastic debris in the North Sea. *Environmental Science & Technology*, 51, 7350–7360.

De Tender, C., Schlundt, C., Devriese, L. I., Mincer, T. J., Zettler, E. R., Amaral-Zettler, L. A. 2017b. A review of microscopy and comparative molecular-based methods to characterize “Plastisphere” communities. *Analytical Methods*, 9, 2132–2143.

De Tender, C. A., Devriese, L. I., Haegeman, A., Maes, S., Ruttink, T., Dawyndt, P. 2015. Bacterial community profiling of plastic litter in the Belgian part of the North Sea. *Environmental Science & Technology*, 49, 9629–9638.

De Vogel, F. A., Schlundt, C., Stote, R. E., Ratto, J. A., Amaral-Zettler, L. A. 2021. Comparative genomics of marine bacteria from a historically defined plastic biodegradation consortium with the capacity to biodegrade polyhydroxyalkanoates. *Microorganisms*, 9, 1–26.

Debroas, D., Mone, A., Ter Halle, A. 2017. Plastics in the North Atlantic garbage patch: a boat–microbe for hitchhikers and plastic degraders. *Environmental Science & Technology*, 599–600, 1222–1232.

Dudek, K. L., Cruz, B. N., Polidoro, B., Neuer, S. 2020. Microbial colonization of microplastics in the Caribbean Sea. *Limnology and Oceanography Letters*, 5, 5–17.

Dussud, C., Hudec, C., George, M., Fabre, P., Higgs, P., Bruzaud, S., Delort, A. M., Eyheraguibel, B., Meistertzheim, A. L., Jacquin, J., Cheng, J., Callac, N., Odobel, C., Rabouille, S., Ghiglione, J. F. 2018. Colonization of non-biodegradable and biodegradable plastics by marine microorganisms. *Frontiers in Microbiology*, 9, 1571.

Erni-Cassola, G., Wright, R. J., Gibson, M. I., Christie-Oleza, J. A. 2020. Early colonization of weathered polyethylene by distinct bacteria in marine coastal seawater. *Microbial Ecology*, 79, 517–526.

Faria, L. C., Kitahara, M. V. 2020. Invasive corals hitchhiking in the Southwestern Atlantic. *The Scientific Naturalist*, 101, e03066.

Fazey, F. M., Ryan, P. G. 2016. Biofouling on buoyant marine plastics: an experimental study into the effect of size on surface longevity. *Environmental Pollution*, 210, 354–360.

Gomiero, A., Oysaed, K. B., Agustsson, T., Van Hoytema, N., Van Thiel, T., Grati, F. 2019. First record of characterization, concentration and distribution of microplastics in coastal sediments of an urban fjord in south west Norway using a thermal degradation method. *Chemosphere*, 227, 705–714.

Guo, X., Wang, J. 2019. Sorption of antibiotics onto aged microplastics in freshwater and seawater. *Marine Pollution Bulletin*, 149, 110511.

Hansen, G. I., Hanyuda, T., Kawai, H. 2019. Invasion threat of benthic marine algae arriving on Japanese tsunami marine debris in Oregon and Washington, USA. *Phycologia*, 57, 641–658.

Harrison, J. P., Sapp, M., Schratzberger, M., Osborn, A. M. 2011. Interactions between microorganisms and marine microplastics: a call for research. *Marine Technology Society Journal*, 45, 12–20.

Harrison, J. P., Schratzberger, M., Sapp, M., Osborn, A. M. 2014. Rapid bacterial colonization of low-density polyethylene microplastics in coastal sediment microcosms. *BMC Microbiology*, 14, 232–247.

Holmström, A. 1975. Plastic films on the bottom of the Skagerack. *Nature*, 255, 622–623.

Huber, J. A., Mark Welch, D. B., Morrison, H. G., Huse, S. M., Neal, P. R., Butterfield, D. A., Sogin, M. L. 2007. Microbial population structures in the deep marine biosphere. *Science*, 318, 97–100.

Jiang, P., Zhao, S., Zhu, L., Li, D. 2018. Microplastic-associated bacterial assemblages in the intertidal zone of the Yangtze Estuary. *Science of the Total Environment*, 624, 48–54.

Kaiser, D., Kowalski, N., Waniek, J. J. 2017. Effects of biofouling on the sinking behavior of microplastics. *Environmental Research Letters*, 12, 124003.

Kettner, M. T., Oberbeckmann, S., Labrenz, M., Grossart, H. P. 2019. The eukaryotic life on microplastics in brackish ecosystems. *Frontiers in Microbiology*, 10, 538.

Kettner, M. T., Rojas-Jimenez, K., Oberbeckmann, S., Labrenz, M., Grossart, H. P. 2017. Microplastics alter composition of fungal communities in aquatic ecosystems. *Environmental Microbiology*, 19, 4447–4459.

Khalid, N., Aqeel, M., Noman, A., Hashem, M., Mostafa, Y. S., Alhaithloul, H. A. S., Alghanem, S. M. 2021. Linking effects of microplastics to ecological impacts in marine environments. *Chemosphere*, 264, 128541.

Kooi, M., Nes, E. H. V., Scheffer, M., Koelmans, A. A. 2017. Ups and downs in the ocean: effects of biofouling on vertical transport of microplastics. *Environmental Science & Technology*, 51, 7963–7971.

Lacerda, A., Proietti, M. C., Secchi, E. R., Taylor, J. D. 2020. Diverse groups of fungi are associated with plastics in the surface waters of the Western South Atlantic and the Antarctic Peninsula. *Molecular Ecology*, 29, 1903–1918.

Langille, M. G. I., Zaneveld, J., Caporaso, J. G., Mcdonald, D., Knights, D., Reyes, J. A., Clemente, J. C., Burkepile, D. E., Thurber, R. L. V., Knight, R., Beiko, R. G., Huttenhower, C. 2013. Predictive functional profiling of microbial communities using 16S rRNA marker gene sequences. *Nature Biotechnology*, 31, 814–821.

Laverty, A. L., Primpke, S., Lorenz, C., Gerdts, G., Dobbs, F. C. 2020. Bacterial biofilms colonizing plastics in estuarine waters, with an emphasis on *Vibrio* spp. and their antibacterial resistance. *PLoS One*, 15, e0237704.

Lear, G., Kingsbury, J. M., Franchini, S., Gambarini, V., Maday, S. D. M., Wallbank, J. A., Weaver, L., Pantos, O. 2021. Plastics and the microbiome: impacts and solutions. *Environmental Microbiome*, 16, 1–19.

Mammo, F. K., Amoah, I. D., Gani, K. M., Pillay, L., Ratha, S. K., Bux, F., Kumari, S. 2020. Microplastics in the environment: interactions with microbes and chemical contaminants. *Science of the Total Environment*, 743, 140518.

Meyer-Cifuentes, I. E., Werner, J., Jehmlich, N., WILL, S. E., Neumann-Schaal, M., Ozturk, B. 2020. Synergistic biodegradation of aromatic-aliphatic copolyester plastic by a marine microbial consortium. *Nature Communications*, 11, 5790.

Muthukrishnan, T., Al Khaburi, M., Abed, R. M. M. 2018. Fouling microbial communities on plastics compared with wood and steel: are they substrate- or location-specific? *Microbial Ecology*, 78(2), 361–374.

Nava, V., Leoni, B. 2021. A critical review of interactions between microplastics, microalgae and aquatic ecosystem function. *Water Research*, 188, 116476.

Oberbeckmann, S., Labrenz, M. 2020. Marine microbial assemblages on microplastics: diversity, adaptation, and role in degradation. *Annual Review of Marine Science*, 12, 209–232.

Ogonowski, M., Motiei, A., Ininbergs, K., Hell, E., Gerdes, Z., Udekwu, K. I., Bacsik, Z., Gorokhova, E. 2018. Evidence for selective bacterial community structuring on microplastics. *Environmental Microbiology*, 20, 2796–2808.

Onda, D. F. L., Sharief, K. M. 2021. Identification of microorganisms related to microplastics. *Handbook of Microplastics in the Environment*. Springer Reference Chemistry & Mat. Science Reference Module Physical and Materials Science.

Pedrós-Alió, C. 2012. The rare bacterial biosphere. *Annual Review of Marine Science*, 4, 449–466.

Pinnell, L. J., Turner, J. W. 2019. Shotgun metagenomics reveals the benthic microbial community response to plastic and bioplastic in a coastal marine environment. *Frontiers in Microbiology*, 10, 1252.

Radisic, V., Nimje, P. S., Bienfait, A. M., Marathe, N. P. 2020. Marine plastics from Norwegian West Coast carry potentially virulent fish pathogens and opportunistic human pathogens harboring new variants of antibiotic resistance genes. *Microorganisms*, 8, 1–13.

Rech, S., Thiel, M., Borrell Pichs, Y. J., Garcia-Vazquez, E. 2018. Travelling light: fouling biota on macroplastics arriving on beaches of remote Rapa Nui (Easter Island) in the South Pacific Subtropical Gyre. *Marine Pollution Bulletin*, 137, 119–128.

Rogers, K. L., Carreres-Calabuig, J. A., Gorokhova, E., Posth, N. R. 2020. Micro-by-micro interactions: how microorganisms influence the fate of marine microplastics. *Limnology and Oceanography Letters*, 5, 18–36.

Romera-Castillo, C., Pinto, M., Langer, T. M., Alvarez-Salgado, X. A., Herndl, G. J. 2018. Dissolved organic carbon leaching from plastics stimulates microbial activity in the ocean. *Nature Communications*, 9, 1430.

Royer, S. J., Ferron, S., Wilson, S. T., Karl, D. M. 2018. Production of methane and ethylene from plastic in the environment. *PLoS One*, 13, e0200574.

Ryan, P. G. 2015. Does size and buoyancy affect the long-distance transport of floating debris? *Environmental Research Letters*, 10, 1–6.

Schlundt, C., Welch, J. L. M., Knochel, A. M., Zettler, E. R., Amaral-Zettler, L. A. 2020. Spatial structure in the "Plastisphere": molecular resources for imaging microscopic communities on plastic marine debris. *Molecular Ecology Resources*, 20, 620–634.

Sieburth, J. M. 1975. *Microbial Seascapes: A Pictorial Essay on Marine Microorganisms and Their Environments*. Baltimore, MD: University Park Press.

Sogin, M. L., Morrison, H. G., Huber, J. A., Welch, D. M., Huse, S. M., Neal, P. R., Arrieta, J. M., Herndl, G. J. 2006. Microbial diversity in the deep sea and the underexplored "Rare Biosphere". *Proceedings of the National Academy of Sciences of the United States of America*, 103, 12115–12120.

Sun, Y., Cao, N., Duan, C., Wang, Q., Ding, C., Wang, J. 2020. Selection of antibiotic resistance genes on biodegradable and non-biodegradable microplastics. *Journal of Hazardous Materials*, 409, 124979.

Tetu, S. G., Sarker, I., Moore, L. R. 2020. How will marine plastic pollution affect bacterial primary producers? *Communications Biology*, 3, 55.

Thrash, J. C. 2021. Towards culturing the microbe of your choice. *Environmental Microbiology Reports*, 13, 36–41.

Van Sebille, E., Wilcox, C., Lebreton, L., Maximenko, N., Hardesty, B. D., Van Franeker, J. A., Eriksen, M., Siegel, D., Galgani, F., Law, K. L. 2015. A global inventory of small floating plastic debris. *Environmental Research Letters*, 10, 124006.

Ward, T., Larson, J., Meulemans, J., Hillmann, B., Lynch, J., Sidiropoulos, D., Spear, J. R., Caporaso, G., Blekhman, R., Knight, R., Fink, R., Knights, D. 2017. *BugBase predicts organism-level microbiome phenotypes. bioRxiv*, 1–19.

Wein, T., Hulter, N. F., Mizrahi, I., Dagan, T. 2019. Emergence of plasmid stability under non-selective conditions maintains antibiotic resistance. *Nature Communications*, 10, 2595.

Wein, T., Wang, Y., Hülter, N. F., Hammerschmidt, K., Dagan, T. 2020. Antibiotics interfere with the evolution of plasmid stability. *Current Biology*, 30, 3841–3847.

Woodall, L. C., Jungblut, A. D., Hopkins, K., Hall, A., Robinson, L. F., Gwinnett, C., Paterson, G. L. J. 2018. Deep-sea anthropogenic macrodebris harbours rich and diverse communities of Bacteria and Archaea. *PLoS One*, 13, e0206220.

Wright, R. J., Bosch, R., Gibson, M. I., Christie-Oleza, J. A. 2020a. Plasticizer degradation by marine bacterial isolates: a proteogenomic and metabolomic characterization. *Environmental Science & Technology*, 54, 2244–2256.

Wright, R. J., Erni-Cassola, G., Zadjelovic, V., Latva, M., Christie-Oleza, J. A. 2020b. Marine plastic debris: a new surface for microbial colonization. *Environmental Science & Technology*, 54, 11657–11672.

Wright, R. J., Bosch, R., Langille, M. G. I. *et al.* 2021a. Correction to: A multi-OMIC characterisation of biodegradation and microbial community succession within the PET Plastisphere. *Microbiome*, 9, 155. doi:10.1186/s40168-021-01120-y.

Wright, R. J., Langille, M. G. I., Walker, T. R. 2021b. Food or just a free ride? A meta-analysis reveals the global diversity of the Plastisphere. *ISME Journal*, 15, 789–806. doi:10.1038/s41396-020-00814-9.

Wu, N., Zhang, Y., Zhao, Z., He, J., Li, W., Li, J., Xu, W., Ma, Y., Niu, Z. 2020. Colonization characteristics of bacterial communities on microplastics compared with ambient environments (water and sediment) in Haihe Estuary. *Science of the Total Environment*, 708, 134876.

Yang, Y., Liu, G., Song, W., Ye, C., Lin, H., Li, Z., Liu, W. 2018. Plastics in the marine environment are reservoirs for antibiotic and metal resistance genes. *Environment International*, 123, 79–86.

Yang, Y., Liu, W., Zhang, Z., Grossart, H. P., Gadd, G. M. 2020. Microplastics provide new microbial niches in aquatic environments. *Applied Microbiology and Biotechnology*, 104, 6501–6511.

Ye, S., Andrady, A. L. 1991. Fouling of floating plastic debris under Biscayne Bay exposure conditions. *Marine Pollution Bulletin*, 22, 608–613.

Yuan, J., Ma, J., Sun, Y., Zhou, T., Zhao, Y., Yu, F. 2020. Microbial degradation and other environmental aspects of microplastics/plastics. *Science of the Total Environment*, 715, 136968.

Zettler, E. R., Mincer, T. J., Amaral-Zettler, L. A. 2013. Life in the “plastisphere”: microbial communities on plastic marine debris. *Environmental Science & Technology*, 47, 7137–7146.

Zhang, W., Ding, W., Li, Y. X., Tam, C., Bougouffa, S., Wang, R., Pei, B., Chiang, H., Leung, P., Lu, Y., Sun, J., Fu, H., Bajic, V. B., Liu, H., Webster, N. S., Qian, P. Y. 2019. Marine biofilms constitute a bank of hidden microbial diversity and functional potential. *Nature Communications*, 10, 517.

Zhang, X., Zhang, Y., Wu, N., Li, W., Song, X., Ma, Y., Niu, Z. 2021. Colonization characteristics of bacterial communities on plastic debris: the localization of immigrant bacterial communities. *Water Research*, 193, 116883.

Zhao, S., Zettler, E., Amaral-Zettler, L. A., Mincer, T. 2021. Microbial carrying capacity and carbon biomass of plastic marine debris. *ISME Journal*, 15, 67–77.

Zinger, L., Amaral-Zettler, L. A., Fuhrman, J. A., Horner-Devine, M. C., Huse, S. M., Welch, D. B., Martiny, J. B., Sogin, M., Boetius, A., Ramette, A. 2011. Global patterns of bacterial beta-diversity in seafloor and seawater ecosystems. *PLoS One*, 6, e24570.

11

Marine Biodegradation of Common Plastics

Anthony L. Andrady

Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC, USA

The ocean that covers over 71% of the Earth's surface carries approximately 332 million cubic miles of seawater[1] rich in phylogenetic and functional diversity. The crucial role of the oceans in contributing to oxygen in the atmosphere and regulating the Earth's climate, is well known. In recent times, the oceans receive a substantial annual increment of plastic debris from land-based sources as well as marine activities, conservatively estimated in 2015 at 4.8–12.7 MMT (Jambek et al. 2015). This annual load of plastics entering the ocean is thought to mostly accumulate in the bottom sediment; however, its fate is poorly understood, underlining the importance of researching the biodegradation potential of this emerging pollutant in the ocean environment. Environmental breakdown of plastics in the ocean is a complex process with several modes of degradation occurring in concert to slowly convert the polymer material into small molecules such as CO_2, CH_4, or water (Andrady 2011). Of these, biodegradation is a particularly slow process, especially relative to photo-degradation of plastic debris. Despite being slow, it is still the sole mechanism of degradation of plastics in deep water or in the bottom sediment. Research on marine biodegradation of plastics often has to rely on laboratory-accelerated test environments (Briassoulis et al. 2020). In laboratory mesocosms with natural microbial consortia, or in bioreactors with enriched monocultures of selected microorganisms, or even mixes of microorganisms not typically found in the field, accelerated biodegradation proceeds at measurable rates. But laboratory conditions generally fall short of what plastics debris is subjected to in the marine environment, and rapid biodegradation of a plastic in the laboratory does not necessarily translate into the same in ocean exposures and *vice versa* (Harrison et al. 2018). This chapter, addresses the question of biodegradation of commodity plastics varieties typically encountered in the ocean environment.

Degradation was already defined in Chapter 8 as a chemical change in which the structure of the polymer[2] is altered, usually with accompanying chain scission, yielding smaller-sized molecules of a lower average molecular weight (Andrady 2017). Biodegradation is defined as any degradation caused by the action of living organisms (Ishigaki et al. 2004), especially microbial organisms, and can be either aerobic or anaerobic processes (Kristensen 1995; Sudhakar et al. 2007) in the

---

[1] U.S. Geological survey estimates the volume of water in oceans to be 321 500 000 $(\text{miles})^3$. That of fresh water in all lakes and rivers combined is minute by comparison amounting to only 22 339 $(\text{miles})^3$.

[2] In this chapter, the terms "plastics" and "polymers" are used interchangeably for convenience. But, as pointed out in Chapter 1, while all plastics are polymers, the latter group also includes non-plastic polymers as well. Plastics are a subset of the larger group of polymers.

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

ocean environment. Any degradation of polymers in the laboratory by enzymes isolated from microorganisms is also classified as a biodegradation. Degradation of the polymer results in the formation of several different products including oligomers and monomers that can biodegrade ultimately into small molecular products such as methane (CH_4) or carbon dioxide (CO_2). The initial breakdown of the polymer molecules into smaller organic molecules by the action of microbial enzymes defines initial stage of biodegradation and obtains changes in physical and mechanical properties of the plastic.

It is convenient to think of the biotic breakdown of a plastic material as occurring in two stages: (i) enzymatic biotransformation of the polymer into intermediate products that typically take place extracellularly; and (ii) the assimilation of these products by microorganisms resulting in their mineralization or conversion into small molecules such as CO_2 and water, that takes place intracellularly. This sequence is illustrated in Figure 11.1.

The term "biodegradation" is confusingly used in the literature to also mean only the first step of the process. (Haider et al. 2019). Though the use of the term in this context is widespread, it is still desirable to use the alternative term "biotransformation" to denote the extracellular enzymatic degradation step as suggested in the Organisation for Economic Co-operation and Development (OECD) guidelines, to avoid confusion in using the term "biodegradation" to mean biomineralization (Lambert and Wagner 2017). The mere biotransformation of a plastic into an unspecified set of products is of little value from an environmental standpoint. These products may even be more toxic compared to the plastic or be equally recalcitrant. It is the mineralization or the complete biodegradation of the polymer, with all its constituent carbon converted into simple products (such as CO_2 or water, or under anoxic conditions into CH_4 and CO_2) or incorporated into biomass, that is environmentally desirable. This end point in the biodegradation of a plastic material is called "complete mineralization."

Mineralization of plastics, the environmentally desirable end point of biodegradation (in the field or laboratory), can only be identified by monitoring the metabolic gases generated by microorganisms utilizing the plastic substrate as a nutrient. Measures such as the weight loss, surface area loss, and reduction in mechanical integrity, for instance, may quantify the depletion of plastics by assessing bio-transformation, but do not produce any information on concurrent biomineralization, the metric of ecological significance. The term "biodegradation" is used in this discussion to mean biotransformation with subsequent biomineralization. Mineralization of polymers can be abiotic as well and it is important to identify that mineralization refers only to the biotic process. Weight-loss measurements may or may not indicate true biodegradations as it is not always clear if any mineralization did take place.

A plastic that is "biomineralizable" in a specific environment should mineralize in that environment in a reasonable time, that is defined by the standards adopted in testing the material.

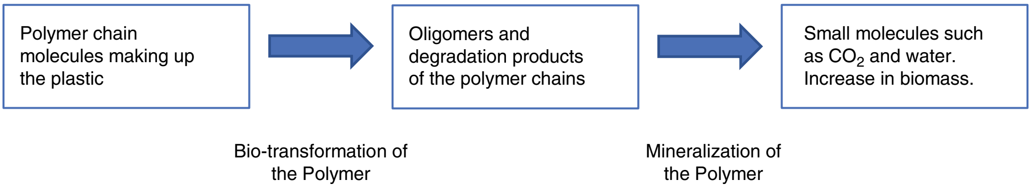


Figure 11.1 Schematic representation of the two-step biodegradation process of organic polymers in the environment.

Although some varieties of plastics are often claimed as being "biodegradable" in the literature, the designation has little meaning; all organic substances are invariably biodegradable and biomineralizable, however long the process may take. A practical "biodegradable" plastic is expected to completely mineralize in a reasonable, measurable period of time, in a specific environment. What is agreed upon as a "reasonable" duration and "complete" conversion, will vary with the biotic environment and is specified in standard test methods used. For instance, a standardized respirometer test that uses seawater or marine sediment inoculum, may specify 60% mineralization within six months at a specified temperature. Biodegradability is not inherent to the plastic, but a system property that is always determined by the combination of the type of plastic and the biotic environment it is placed in. Even the obviously biodegradable food items are very well preserved when stored in abiotic controlled environments, even over millennia; wheat grains and biscuits recovered from the Egyptian pyramids remained un-biodegraded thanks to the dry abiotic conditions they were stored in. Biodegradation of polymers (including plastics) in the marine environment results from the interplay between the morphological/structural features of the material and the biotic features of the environment it is exposed to. Any practical claim of biodegradability must, therefore, always be linked to relevant environmental conditions (Albertsson and Hakkarainen 2017). For example, "PHB is biodegradable in seawater" is a meaningless claim, while "0.1 mm thick films of PHB show 41% ultimate mineralization in 100 days, in an aerobic seawater environment, when tested according to ASTM D 6691" is an informative claim. With many different definitions available to claim "biodegradability," it is not surprising that many of the plastic products labeled as such, do not fully mineralize under natural conditions (Napper and Thompson 2019).

11.1 The Marine Environment

The ocean poses a challenging environment for biodegradation of plastic litter. Although some seasonal and geographic variations are present, the average surface water temperature in the ocean is ~17 °C, dropping to 0–4 °C at a depth of 2000 m. The average salinity of surface water is ~35 PSU%, and its pH is 8.1 ± 0.02, but lower in deep water (Wang et al. 2021). The biotic characteristics in the ocean also varies with depth, with the deep sediment offering a cold, anoxic, high-pressure environment rich in anaerobic microorganisms. Surface waters have an average of 10^6 microbial cells per mL (Nakayama et al. 2019), while that in the sediment the counts are typically three orders

Table 11.1 Characteristics of the different ecological niches in the ocean environment.

	Microbes (mL)	Water	Oxygen (mg/L)	Salt (%)	Temperature (°C)	Pressure (atm)	pH	External force
Offshore	10^1–10^5	+++++	4–9	<30	≈17.4	1–20	8.0–8.7	√
Upper ocean	5×10^5	+++++	4–9	≈35	≈17.4	20–1100	8.0–8.7	√
Below 200 m	5×10^4	+++++	4–9	≈35	0–4	20–1100	8.0–8.7	√
Compost	$>10^9$	+++++	≈310	<0.05	48–65	≈	≤7	√
Soil	10^6–10^9	++	≈20	<0.05	20–40	≈1	≤7	√

Source: Reproduced Courtesy of Wang et al. (2021).
External force: mechanical forces from tides, waves, and other factors in natural seawater.

of magnitude higher (Kuwae and Hospkawa 1999). The dissolved and suspended carbon in deep water and sediment is typically quite old, dating back 12 000 years, as revealed by ^{14}C dating (Hansell et al. 2009). Table 11.1 compares generalized characteristics in the marine water column with soil and compost environments.

11.1.1 Marine Biodegradation Mechanism

The process of biodegradation of plastics in the marine environment (or aqueous environments in general) is conveniently described in terms of three main steps, though these steps often occur simultaneously in nature.

1) Biofilm formation or surface fouling. A plastic material placed in water forms a thin biofilm that recruits marine bacteria within hours of exposure (Zettler et al. 2013). This adhesion of bacterial cells on to solid surfaces is a universal phenomenon with all types of material (Flemming 2016) and is mediated by a "sticky" bacterial exopolymer. Initial microbial settlers in the biofilm are the protobacteria, but within 24–36 hours it recruits a wider range of microorganisms (Lee et al. 2008; Oberbeckmann et al. 2015). The early settlers show a relatively low capacity to biotransform plastics (Lobelle and Cunliffe 2011). The composition of the initial biofilm invariably changes, undergoing succession of the consortium (Urbanek et it al. 2018) into a mature, more diverse, foulant layer, eventually recruiting even macrofoulants such as bivalves (Cao et al. 2011). Plastics that float in seawater may become negatively buoyant as a result of adhering encrustation of biofilm species. The bacterial and fungal composition of the surface biofilm of plastics placed in different oceanic regions, such as the North Pacific gyre (Debroas et al. 2017), has been reported with the diversity of flora studied using rRNA techniques (Hakkarainen and Albertsson 2004; Zettler et al. 2013).

   Fouling of common plastics such as polyethylene (PE) (Harrison et al. 2015; Lobelle and Cunliffe 2011), poly(ethylene terephthalate) (PET); Oberbeckmann et al. 2014, 2015), poly(vinyl chloride) (PVC) (Dag et al. 2008), and polystyrene (PS) (Briand et al. 2012), has been studied. Often, the plastic would have been photo- or thermally degraded prior to entering seawater. Biofilm colony composition on pre-oxidized and presumably, more hydrophilic, PE surfaces is reported to be different from that on virgin PE surfaces (Dussud et al. 2015; Eich et al. 2015; Simoes et al. 2010).
2) Biotransformation. The action of enzymes (such as oxygenases, lipases, esterases, and depolymerases) secreted by microorganisms colonizing the biofilm results in the extracellular breakdown of polymer molecules (Dussud and Ghiglione 2014; Dussud et al. 2018; Haddad et al. 2005; Sivan et al. 2006). Depending on the specific polymer, the enzyme may cleave the chains randomly (be endo-acting) or at chain ends (be exo-acting). It is a surface phenomenon that occurs within the biofilm carrying microorganism and reduces the average molecular weight of the surface layers of the plastic. This partial breakdown of polymer chains is central to the overall biodegradation process. Some of the low-molecular-weight, water-soluble products of degradation can diffuse into microbial cells where they can be metabolized (Gallert and Winter 2005). Diverse microbial species populate a "mature" biofilm due to succession (Oberbeckmann et al. 2015) and several of these can be involved in the degradation process (Syranidou et al. 2018).
3) Uptake and mineralization. The oligomers and other products of biotransformation that are low enough in molecular weight (less than about 600 Da) (Eyheraguibel et al. 2017) permeate into microbial cells residing in the biofilm. Once in the cell, they are metabolized by other

enzymes and used as an energy source *via* the citric acid cycle (Gallert and Winter 2005). The cells not only derive energy but also use some of the carbon from polymer to grow additional biomass. The end point of this process is the complete conversion of the carbon in the polymer into small molecules such as CO_2 and water.

Figure 11.2 is a schematic illustration of aerobic biodegradation in semi- crystalline plastics. To be ecologically relevant the plastic must completely mineralize within a reasonable and measurable time frame. Of these steps, step 1 is the slower rate-determining step as the low-molecular-weight products mineralize readily once taken up by microbial cells. How rapidly a plastic material needs to mineralize completely to qualify as a biodegradable plastic (and to be labeled as such) is decided by the standards agreed upon by national (e.g. ASTM, DIN) and international (e.g. OECD) standards organizations. The active microbial consortia in the foulant layer uses the energy derived from metabolized products, for cell growth and reproduction, resulting in generating new biomass that will also in turn be slowly assimilated over time, producing more CO_2. Aerobic biodegradation can be represented by the following equations:

$$\mathrm{CH_{polymer}} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{C_{biomass}}$$

$$\mathrm{C_{biomass}} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

As the kinetics of the two reactions are different, this results in an initial fast evolution of CO_2 followed by a slow evolution due to mineralization of the new biomass over time. Except for a “lag period” of initial consolidation of microbial flora on the surface, gas evolution is observed throughout the biodegradation process. Respirometry (to be discussed in a later section) is able to conveniently monitor this metabolic gas evolution. The two critical environmentally-relevant metrics measured by respirometriy are, (i) the mineralization rate of the plastic, and (ii) the maximum fraction of the carbon from plastic that is converted to CO_2 in aerobic processes or to gases such as CH_4 in anaerobic processes. When no residual polymer or its degradation products other than CO_2, CH_4 and water in the system, the plastic is said to be fully mineralized.

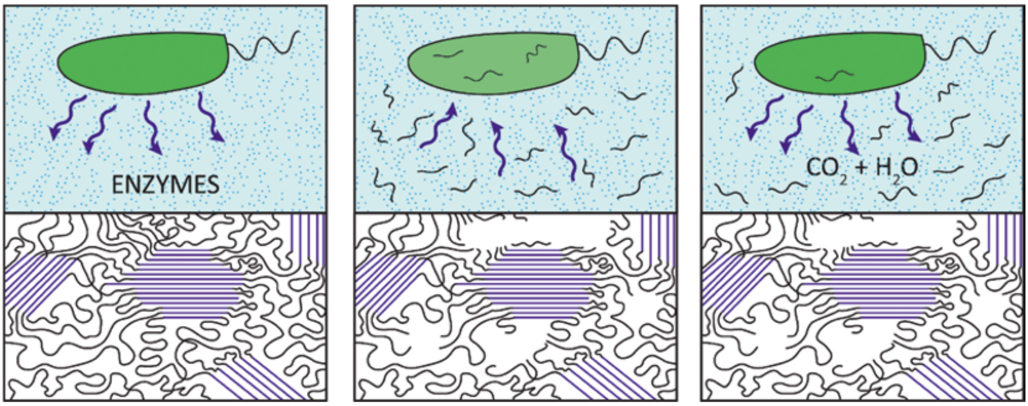


Figure 11.2 An illustration of the biodegradation process of a semi-crystalline polymer. Left: Bacterium in the biofilm secretes enzymes that convert amorphous parts of the plastic into small molecular products. Middle: These products (indicated by wavy lines) permeate into the bacterial cell. Right: Bacterium metabolizes sorbed product molecules aerobically, giving out CO_2 and water into the biofilm. The lower set of figures illustrate preferential biodegradation of amorphous polymer.

11.1.2 Impact of Buoyancy on Biodegradation

PE and PP plastics, the most abundant plastics in marine floating debris, are potentially subject to photodegradation facilitated by solar ultraviolet radiation (UVR). However, with the progress of surface fouling, their direct exposure to solar UVR is gradually reduced, and because of increased density due to the foulant layer, these plastics may sink beyond the photic zone into deep water (Andrady and Ye 1991; Lobelle and Cunliffe 2011). A South African study (Fazey and Ryan 2016) recently estimated sinking to occur in 17–66 days of floating marine exposure. The surface longevity of floating plastic debris controlled by fouling, depends on the size of plastic debris (Fazey and Ryan 2016) as well as it's shape factor (Fazey and Ryan 2016; Porter et al. 2018). The surface area to volume ratio influences the settling rate to the bottom sediment. Given the efficient UV shielding afforded by the layer of surface foulants and the relatively lower oxygen concentration in seawater compared to air, the duration the plastic floats in surface water is far too short to obtain any significant photo-oxidation. Photo-oxidative degradation of plastics in seawater is well known to be much slower relative to that in air (see Chapter 8). However, the plastics debris that has been exposed to UVR on beach environment, or transported by rivers into the ocean, can be significantly photodegraded by the time they enter the water column. The rate of biodegradation of pre-oxidized plastics can be different from that of virgin plastics. The oxidative changes in the surface chemistry of this debris may determine the composition of the consortium of fouling organisms colonizing it (Oberbeckmann et al. 2015; Romera-Castillo et al, 2018), thereby also guiding its biodegradation. The oxidation products, for instance, may encourgae mineralization (Chellini et al. 2003), or inhibit the growth of biofilm species (Zhu et al. 2020).

Other plastics found in marine debris, such as PS, PET, PVC, cellulose acetate (from cigarette filters), and nylon, are all denser than seawater and sink to deep water or the bottom sediment as soon as they enter the ocean. Their biodegradation proceeds entirely in the bottom sediment with the help of anaerobic microorganisms that are adapted to thrive at low temperature and high pressure. Anaerobic processes generally tend to be even slower compared to aerobic biodegradation (Ishigaki et al. 2004; Kristensen et al. 1995), though aerobically biodegradable plastics such as PHBV (Mohee et al. 2008) appear to show rapid weight loss in the marine sediment as well (Beltran-Sanhuja et al. 2020). With poly(lactic acid) (PLA), compared to the very limited weight-loss obtained in seawater, that in the sediment is several times faster (Beltran-Sanhuja et al. 2020).

11.1.3 A Food Source or a Surface to Settle on?

With rapidly biodegradable polymers such as cellulose, laboratory mineralization convincingly demonstrates the material is utilized as a nutrient by the marine consortia in the biofilm or the foulant layer. With these, the question of passive attachment versus active biodegradation by foulants does not arise, as high extent of mineralization confirms metabolic utilization of the base polymer. But, how about plastics that show no signs of mineralization in laboratory exposures, such as PE or PP, that still carry a rich foulant layer? Do fouling microorganisms passively attach themselves to these plastic materials or do they also effect a minimal level of biodegradation with assimilation rates and carbon conversions that are simply too low to reliably measure?

Settlement of marine organisms occurs on all surfaces exposed to seawater including glass or metal (Oberbeckmann et al. 2016). Adhering to a surface often helps attached organisms to survive (Steinberg and Kolodkin-Gal 2015), protecting them from harsh environments (Decho and Gutierrez 2017). Rich fouling colonies are common on bioinert plastics such as PE and PP (Zettler et al. 2020). Fouling is a necessary step to bulid up a high concentration of the enzymes in the biofilm relative to that in seawater. But, biofilm formation and surface fouling of plastics in ocean environment is a necessary, but not a sufficient, condition for significant biodegradation to occur. However, the species diversity in the biofilms on bioinert plastics are generally different from that in surrounding seawater in pelagic environments (Dussud et al. 2018; Ogonowski et al. 2018; Zettler et al. 2013) and also from that of plastics in the sediment (Harrison et al. 2014). Whether this selective colonization by species is driven by their ability to utilize the plastics nutritionally, or is merely related to differences in their surface features such as roughness or surface-free energy (Rummel et al. 2017) preferred by attaching organisms, is not clear.

11.1.4 Biodegradability of Common Plastics in the Ocean

With most common plastics including PE, PP, PS, PVC, cellulose, acetate, or PET that constitute a majority of marine plastic debris, biodegradation is painstakingly slow under aerobic pelagic exposure. This is likely true also of benthic sediment exposure as well, though there are no good estimates of mineralization rates to support the latter expectation. Given that plastics have been in the ocean for only 70 years or so, efficient plastic-assimilating species of bacteria or fungi are yet to evolve. If some species in a biofilm consortium did develop polymer-degrading capability, they will likely form a minor constituent, dominated by other species that can utilize natural carbon sources such as chitin or cellulose abundant in seawater. Based on respirometry in the laboratory, two classes of plastics based on their rate of biodegradability can be identified: the slow biodegraders that do not show measurable mineralization after several months of incubation in enriched marine (water and/or sediment) media; and the rapid biodegraders under same test conditions, such as aliphatic polyesters and polyurethanes. This categorization of plastics based on aerobic environments might change if anaerobic mineralization is also considered.

Plastics that rapidly biodegrade in the ocean are able to do so because they are structurally susceptible to some of the enzymes that are already present in the ocean environment (Dey et al. 2012; Leja et al. 2010; Upreti et al. 2003). These enzymes had evolved not in response to plastics, but to mineralize naturally-occurring polymers, especially bio-polyesters. In laboratory test, plastics that show readily measurable mineralization rates with maximum carbon conversions >60%, include PCL, PLA, poly(butylene succinate) (PBS), and poly(butylene succinate-co-adipate) (PBSA). In general, rapidly biodegradable plastics can be demonstrated to biomineralize completely into simple molecules such as CO_2, H_2O, NH_3, or CH_4 in an observable timescale in the laboratory (Andrady 2011; Mohee et al. 2008; Sing and Sharma 2008). Though often referred to as "biodegradable" plastics in scientific and trade literature (Gu 2003; Kumar et al. 2011), the term "rapidly biodegradable" is a better alternative since all polymers are invariably biodegradable and "biodegradable plastic" is a misnomer. Similarly, the conventional plastics PE or PS described as recalcitrant are referred to as "effectively nonbiodegradable" plastics in the present discussion. In laboratory respirometry using sludge inoculua from a waste water plant, the biopolymers show ~70% mineralization in seawater. The rates of mineralization of textile fibers studied was as follows (Zambrano et al. 2020): microcrystalline cellulose (MCC) > cotton > rayon > polyester/cotton ≫ polyester.

How rapidly a given plastic material mineralizes depends on the composition of the biotic community as well as abiotic factors such as temperature and salinity. Therefore, reference to biodegradability must be relative to that of a known readily-mineralizable substrate exposed to the same test conditions. Mineralization studies typically include positive controls such as cellulose that provide a ceiling for the rate of mineralization in that environment. Predominant plastic debris in the ocean, especially PE, PP, and PS, however, belongs to the "effectively nonbiodegradable" category and cannot be demonstrated to mineralize at all in standard laboratory tests. Aromatic polyester, PET, is an exception as it undergoes measurable mineralization under such conditions.

As a class, biofilms that develop on effectively nonbiodegradable common plastics (PE, PP, PS, and PET) often appear to attract bacterial colonizers belonging to several preferred families (Roager and Sonnenschein 2019), including Flavobacteriaceae, Saprospiraceae, Hyphomonadaceae, Rhodobacteraceae, Erythrobacteraceae, Sphingomonadaceae, Comamonadaceae, Alcanivoracaceae, Pseudoalteromonadaceae, Oceanospirillaceae, and Vibrionaceae. Some of these families are represented in the "plastisphere" communities on plastic debris across geographic locations (Bryant et al. 2016; Didier et al. 2017). Whether these colonizers are attracted to the plastic because they are able to successfully biodegrade the substrate (Pinto et al. 2019) or as a result of chemotaxy due to leachates, or hydrophobic interactions with cell walls, is not entirely clear. Also, the composition of microbial consortia in the plastisphere tends to be not polymer-specific; Zettler (2015) reported the stronger clustering of species by geography, and others, by climatic factors (Muthukrishnan et al. 2019), compared to that by the type of plastic.

Plastics that are effectively nonbiodegradable in natural environments such as PP still undergo weight-loss at easily observable rates when incubated with enriched cultures of microorganisms in the laboratory (Auta et al. 2017), Weight-loss, though taken to be due to biotransformation and possibly mineralization, could also be due to fragmentation into ultra-fine particles. For instance, bacterial and fungal species isolated from coastal waste and mangrove sediment obtain weight loss in PE and PP polyethylene (Auta et al. 2018; Devi et al. 2019). Incubating LDPE with a mix of four marine bacterial strains (*Cobetia* sp., *Halomonas* sp., *Exigobacterium* sp., and *Alcanivorax* sp., identified on the basis of 16S rRNA sequences) resulted in a weight loss of 1.75% in 90 days (Khandare et al. 2021). Auta et al. (2017) found plastics incubated for four weeks with *Bacillus cereus*, enriched from mangrove sediment at room temperature lost 1.6%, 6.6%, and 7.4% of their weight, for PE, PS, and PET, respectively. Surface of these effectively nonbiodegradable plastics show pitting with shapes or impressions corresponding to that of fouling bacterial species (Oberbeckmann et al., 2016; Zettler et al. 2013) suggestive of substrate utilization to some extent. Roager and Sonnenschein (2019) summarized the plastic-degrading marine bacteria presently known, based on weight loss studies of common plastics, as shown in Table 11.2.

Weight loss, though a convenient technique to assess degradation of plastics, is difficult to establish accurately in marine exposures because of errors introduced by adhering surface biomass. Foulants can be cleaned off mechanically but with inevitable removal of some plastic in the process, introducing errors. Digestion (solubilization) or oxidation of adhering biomass leaving the plastic matrix intact can yield better weight-loss information. But, weight or area loss does not indicate mineralization necessarily and is not a proxy for biotransformation either. However, other metrics such as the reduced average molecular weight (Mn g/mol) of the polymer, taken together with weight loss, could be indicative of biotransformation (Rongrong and Chaomin 2021), provided that the effects of photodegradation have been excluded. Pre-photodegraded samples were used for instance, in the biodegradation studies on PS (Syranidou et al. 2017) and PE (Haddad et al. 2005). Photo-degradation alters the surface chemistry of plastics and produces small-molecular degradation products that may biomineralize easily. Even if they were to mineralize marginally, their carbon conversion is not fully bio-mediated.

11.2 Rates of Biodegradation of Common Plastics

How rapidly a polymer biodegrades in a given environment depends on several factors that primarily include (i) it's inherent biodegradability that depends on the polymer chemical structure; (ii) it's fractional crystallinity (Debroas et al. 2017); (ii) its geometric form (Yang et al. 2005),

Table 11.2 Suggested rates of plastic biodegradation in the marine environment based on weight loss for common plastics.

Class	Species	Polymer	Weight loss (%)	Duration (d)	Bacterial origin	Citation
Actinobacteria	*Kocuria palustris*	LDPE	1	30	Seawater, Arabian Sea	Harshvardhan and Jha (2013)
	Rhodococcus sp. 36	PP	6.4	40	Mangrove sediment	Auta et al. (2017)
Bacilli	*Bacillus cereus BF20*	LDPE, HDPE	5.2	365	Indian Ocean	Sudhakar et al. (2008)
	Bacillus cereus	PE, PET, PS	1.6, 6.6, 7.4	40	Mangrove sediment, Malaysia	Auta et al. (2017)
	Bacillus gottheilii	PE, PET, PP, PS	6.2, 3.0, 3.6, 5.8	40	Mangrove sediment, Malaysia	Auta et al. (2017)
	Bacillus pumilus	LDPE	1.5	30	Seawater Arabian sea	Harshvardhan et al. (2013)
	Bacillus sp. 27	PP	4	40	Mangrove sediment, Malaysia	Auta et al. (2017)
	Bacillus sphericus Alt.	LDPE, HDPE	10, 3.5	365	Indian Ocean	Sudakar et al. (2008)
	Bacillus subtilis HI584	LDPE	1.75	30	Seawater Arabian Sea	Harshvardhan et al. (2013)

(with those having higher specific surface area obtaining relatively higher rates of biodegradation); and (iv) the microbial environment the plastic is exposed to. Polymers such as aliphatic polyesters biodegrade readily in most biotic environments because esterases secreted by microorganisms that are adapted to natural substrates such as bacterial polyesters (Leja et al. 2010: Premraj and Doble 2005), can also cleave the ester bonds in synthetic polymers (Sekiguchi et al. 2011; Shimao 2001), and in biomass-derived PLA (Ohkita et al. 2006; Shah et al. 2008). These plastics are inherently biodegradable in aqueous environments. By contrast, plastics such as PE, PP, and PS do not carry any main chain ester bonds readily amenable to lysis by any the available microbial enzyme system in the environment. Unfortunately, it's these recalcitrant plastics that dominate marine plastic debris.

The rates of biodegradation of semi-crystalline plastics is determined by their fractional crystallinity (Pantani and Sorrentino 2013; Wei et al. 2019). Highly drawn fibers or annealed films with a low amorphous content will be slow to biodegrade in any environment. The dependence of the rate of weight loss on the percent crystallinity of the polymer, is illustrated in Figure 11.3: Left (Wei et al. 2019) for enzymatic degradation of PET films (3 x 0.5 cm.) in the laboratory; the linear fit of the data is good, with $r = \sim 0.92$. The change in fractional crystallinity due to annealing at 70 °C is compared to that due to removal of amorphous content by biodegradation at the same temperature (Figure 11.3, Right). Enzymatic process is faster, but available only at the surface of a plastic material and will only be effective within the thin layer defined by their diffusion into the bulk (proteins are large molecules with very low diffusivity in polymers). Geometric forms such as thin laminate and fine particle with a high specific surface area (cm^2/g) therefore obtain higher rates of biodegradation as enzymatic interactions are predominantly surface phenomena. Thickness dependence of biodegradation was shown in a recent study on marine biodegradation of poly(hydroxyalkanoates) (PHA) (Dilkes-Hoffman et al. 2019). If the exopolymer present in the biofilm entraps any microplastics or nanoplastics within it, these particles will undergo fast biodegradation within the biofilm because of their higher specific surface area coupled with the higher concentrations of enzymes (Michels et al. 2018).

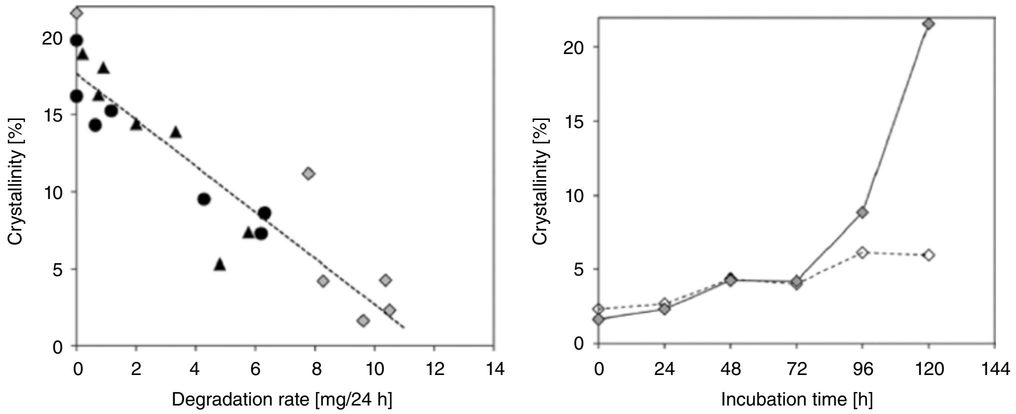


Figure 11.3 Left: Inverse dependence of enzymatic biodegradation rate (mg weight loss per 24 hours) at 70 °C, with fractional crystallinity of the PET films (250 μm) as determined by differential scanning calorimetry [DSC]). Circles and the triangles denote two post-consumer PET film samples, while the diamonds denote an amorphous PET film. Right: Change in fractional crystallinity at 70 °C, due to physical aging (open symbol) and from enzymatic biodegradation (filled symbols). *Source:* Courtesy Wei et al. (2019); reproduced by Creative Commons CC BY license.

Invariably, the biodegradation rates of rapidly biodegradable plastics depend on the microbial cell density of species in the biofilm colony, capable of mineralyzing the polymer. However, some species in the biofilm may undergo considerable adaptations to be able to utilize the polymer substrates they are attached to (Tribedi et al. 2015). Adaptation is an evolutionary change in the microbial community that over several generations in contact with the plastic, yield variants that can biodegrade the substrate (Baptiste et al. 2019). The microbial species may evolve novel catabolic pathways or even novel enzymes in response to the organic substrates (i.e. dissolved carbon from abiotic degradation of plastics) (Kolvenbach et al. 2014; Romera-Castillo et al. 2018). Such adaptations already known to play a crucial role in the biodegradation of organic chemicals (Itrich et al. 2015), may also play a similar role in plastics. That adaptation can occur in a relatively short period of pre-exposure to chemicals (Kim et al. 2017; Saez et al. 2015) makes it a particularly interesting possibility. For instance, Japanese researchers isolated PET-degrading species from a PET recycling waste environment (Taniguchi et al. 2019). Waste water from papermaking operations are rich in cellulose and inocula, and the local microbes will be preadapted to cellulose biodegradation.

11.2.1 Rapidly Biodegradable Plastics

Plastics that biodegrade rapidly in the ocean environment can be found in each of the three classes of plastics classified according to the feedstock used in their manufacture (see Chapter 1 for the classification). Typically their complete mineralization is observed within weeks of exposure to laboratory aerobic consortia. As already pointed out in Chapter 1, (Table 1.3) there is no relationship between the type of feedstock used in a plastic and their environmental biodegradability. Selected examples of rapidly biodegradable plastics in each category are as follows:

1) Biopolymers or polymers produced by living organisms: poly(3-hydroxybutyrate); poly-(3-hydroxyvalerate); and their copolymers, poly(3-hydroxybutyrate-*co*-3-hydroxy valerate), and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate).
2) Polymers from monomers synthesized from biomass feedstock: PLA, PBS, and PBSA.
3) Polymers from conventional fossil fuel feedstock: polycaprolactone (PCL), poly(butylene adipate terephthalate) (PBAT), polyglycolide, PBSA, and poly(vinyl alcohol) (PVA).

Enzymes involved in the biodegradation of polyesters are mainly lipases, esterases, cutinases, proteases, and ureases, secreted by a range of marine bacteria and fungi. Carboxylic ester hydrolases, especially the esterases and lipases, are globally present in the marine environment (Barzkar et al. 2021). These enzymes hydrolyze the ester bond at ambient temperatures yielding acid- and alcohol-terminated chain ends.

The total global production of rapidly biodegradable plastics, however, is very limited (1.17 MMT in 2019) and mainly made up of PLA, PBAT, and PBT (that make up 25%, 24.1%, and 7.7% of the production, respectively). PLA is an especially attractive biodegradable plastic because of its excellent mechanical properties, thermal resistance, and transparency (Auras et al. 2004), even though its high T_g (°C) makes it somewhat brittle. PBAT manufactured from terephthalic acid is also likely to increase in popularity because of its low cost relative to PCL. While PCL is biodegradable in seawater or sediment (Lu et al. 2018), it has limited applications because of its low melting point of 58 °C. Polyesters are the most popular class of biodegradable polymer for seawater applications, and with some types, significant abiotic hydrolysis contribute to their environmental breakdown. Under favorable conditions, abiotic hydrolysis reactions can even be orders of magnitude faster than enzymatic hydrolysis. Though hydrolysis does not contribute to mineralization reaction, it can indirectly impact the rates as biotransformation is the rate-determining step in biodegradation. The biodegradability of PLA in the ocean environment, however, is poor and the plastic degrades faster in freshwater compared to in seawater (Deroine et al. 2014). Interestingly, PLA biodegrades five times faster in the marine bottom sediment compared to in seawater (Beltran-Sanahuja et al. 2020).

Biodegradation of polyesters occurs rapidly enough in the environment, to be monitored by the weight loss of the sample (that measures biotransformation, fragmentation and mineralization). Rates from weight loss and BOD measurements correlate with each other, as seen in the data in Table 11.3, for different polyester films exposed to seawater at 25°C, over a 28-day period in the laboratory (Kasuya et al. 1998). However, the average molecular weights (Mn g/mol) of the polyesters used and their crystallinities, would have been different for these samples, and any ranking in the relative rates of biodegradation will therefore be of little value. The study also found the rates in seawater to be generally slower than for freshwater media.

Reported data on the biodegradation of rapidly biodegradable polymers in seawater, based on their weight loss, reduction in average Mn (g/mol), and decrease in mechanical properties were, recently tabulated by Wang et al. (2021). The data, however, pertain to different durations of exposure ranging from 5 to 52 weeks, using samples of different geometry and thickness (with varying fractional crystallinitiesy as well) and are therefore, difficult to compare. In side-by side evaluations of weight loss in static seawater environments the following order in the rates of their weight loss was reported for selected polyesters: PCL > PHB > PLA (Bagheri et al. 2017). PLA exposed to natural seawater in the field suffered no weight loss and was virtually intact after six months of exposure (Deroine et al. 2014). Under laboratory-accelerated conditions, however, PLA did show signs of biodegradation in seawater, especially in the bottom sediment, based on their increasing fractional crystallinity and spectroscopic determination of degradation products (Beltran-Sanhuja et al. 2020).

While the above discussion was limited to aerobic biodegradation, most plastic debris in the ocean invariably end up in deep water or the bottom sediment. Any biodegradation in the cold, bottom sediment would proceed predominantly *via* anaerobic biodegradation. Products from hydrolysis of polyesters may themselves undergo anaerobic breakdown producing methane, as ionic acceptors such as SO_4^- or NO_3^- are available in the sediment. A prerequisite, however, is the presence of anaerobic microorganisms in the biofilm (Mohee et al. 2008). Anaerobic mineralization of aliphatic polyesters has been demonstrated, but not using any marine microbial species. PCL, for example, anaerobically mineralizes (92%) at 55 °C in 75 days (Yagi et al. 2009); PHB (100%) at 35 °C in 225 days (Gutierrez-Wing

Table 11.3 Aerobic biodegradation of aliphatic polyester films in seawater.

Polyester	Mn × 10^{-3} (g/mol)	Seawater bay (weight loss)	Seawater bay (BOD)	Seawater deep (weight loss)	Seawater deep (BOD)
P(3HB)	350	41±16	27±10	23±13	14±10
P(2HB-*co*-14%3HV)	186	100±0	84±2	100±0	78±5
P(2HB-*co*-10%4HV)	223	70±30	51±27	59±15	43±4
Poly(ϵ-caprolactone)	110	100±0	79±2	67±21	56±9
Poly(ethylene succinate)	30	2±1	1±1	5±2	3±2
Poly(ethylene adipate)	40	100±0	65±13	57±14	46±3
Poly(butylene succinate)	30	2±2	1±1	2±3	2±0
Poly(butylene adipate)	30	34±2	20±2	11±10	10±5

et al. 2020); PLA (99%) at 55 °C in 56 days; and PHBV (90%) at 35 °C in 30 days (Reischwitz et al. 1997). None of these studies used marine sediment microorganisms and were conducted at elevated temperatures relative to that of ambient seawater. In another study, deep seawater from a depth of 321 m was pumped continuously into tanks containing samples of PCL and PHBV monofilament fibers. A 12-month exposure under these conditions resulted in aerobic biotransformation of these polymers with reduction in tensile properties and surface pitting or cracks (Sekiguchi et al. 2011). While deep water marine organisms were used in this study, the degradation was still aerobic and dependent only on the facultative anaerobes in the deep water sample. Also, the degradation was at ambient pressure that do not represent hyperbaric deep water conditions. Yet, the observation that monofilament fibers underwent biotransformation in seawater is significant because fiber geometry was used; microfibers, mostly PET textile fibers, are a well-known class of marine pollutants. Surface waters of all ocean basins show microfibers (a majority of the PET fibers will be in the sediment) making textile fibers an important category of marine pollutants.

Rapidly biodegradable plastics in seawater or in the shallow sediment, may aerobically mineralize in a practical timescale and help reduce the ecological impacts of marine plastic debris in the ocean. However, their anaerobic biodegradation in the sediment needs to be further investigated.

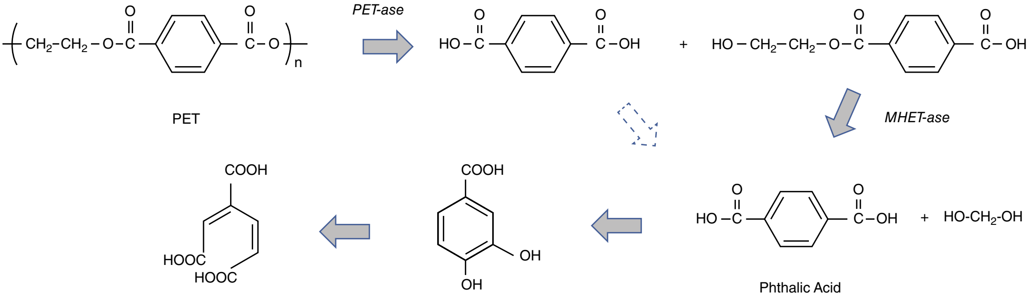
11.2.2 Biodegradation of Poly(ethylene terephthalate)

The thermoplastic aromatic polyester used in plastic bottles as well as in textile fiber is a major contaminant in the marine sediment. While aliphatic polyesters are readily biodegradable in the ocean, aromatic polyesters are generally considered to be effectively nonbiodegradable (Tokiwa et al. 2009). For example, PET beverage bottles are abundantly found in the marine sediment (see Chapter 6) but are susceptible to marine microbial degradation under specialized laboratory conditions. However, some of the naturally occurring enzymes, especially esterases, that hydrolyze aliphatic polyesters, are able to hydrolyze synthetic PET as well, at least in the laboratory. Numerous PET-degrading enzymes, mostly cutinases or serine esterases, have been detected in the environment (these have been recently reviewed by Taniguchi et al. 2019), with biodegradation of PET demonstrated in the laboratory by several of the species including *Thermobifida fusca*, *Saccharomonospora viridis*, *Thermomyces insolens*, and *Candida Antarctica*. However, these organisms act too slowly on PET to be of practical significance in marine debris applications (de Castro et al. 2017; Wei et al. 2017). However, PET-degrading microbes appear to be generally rare in nature. Screening 300 samples of marine sediment (Gao and Sun 2020) yielded only three species of bacteria capable of degrading (biotransforming) both PET and PP under anaerobic conditions, based on marked changes in their molecular weight distribution (MWD) as determined by gel permeation chromatography (GPC) (Rongrong and Chaomin 2021).

PET products encountered as marine plastic debris is not readily biodegradable in the anaerobic ocean environment and tends to accumulate in the sediment; this is especially true of the highly crystalline polyester fibers. Degradation of the plastic under deep water or sediment exposure conditions, however, has not been extensively studied (Müller et al. 2001). Fourier transform infrared spectroscopy (FTIR) on samples of PET bottles recovered from the bottom sediment revealed, that unlike in laboratory studies, hydrolysis was not the exclusive mechanism involved in their degradation (Ioakeimidis et al. 2016). Spectral signatures indicative of oxidation (absorption band at $1715/\text{cm}^{-1}$ in FTIR spectra) were found in bottles exposed to the sediment >15 years, going by the expiration dates on bottles (Ioakeimidis et al. 2016). In common with all studies on recovered ocean debris, it is difficult to ascertain if the oxidative degradation occurred in air prior to the bottle being discarded in the ocean. Also, changes in spectral signatures do not correlate with the mineralization of the polymer.

Recent work by Denaro et al. (2020) reported changes in spectral characteristic of PET incubated for 45 days with aerobic marine consortia rich in hydrocarbon-degrading microbes, in the laboratory. Changes were observed in FTIR spectra of the PET in bands at 1712/cm (carbonyl stretching) as well as at 1240 and 1094 cm^{-1} ($CO{-}O{-}CH_2$ stretching modes), suggesting hydrolysis of the ester bond. The studies suggest that hydrocarbon-degrading bacteria, especially *Alcanivorax* sp. that is known to degrade LDPE, may also be able to biotransform PET under marine conditions.

An especially significant, and the most studied, enzyme in this regard, is a PET-ase isolated from a consortium of microorganisms in the sludge of a PET recycling plant in Japan in 2016, This consortium was found to degrade PET aerobically at the rate of 0.13 $mg/cm^2/day$ to reach a maximum 75% mineralization of the carbon, at 30–37 °C (Yoshida et al. 2016). The gram-negative aerobic bacterium that is particularly efficient in degrading PET, *Ideonella sakaiensis* (201-F6) (Yang et al. 2016; Yoshida et al. 2016) was isolated from this consortium. It was capable of mineralizing PET at a rate that was twice that by the consortium. The PET-ase from this species is the most effective hydrolase known to biodegrade PET. Son et al. (2019) demonstrated that a molecularly engineered variant of this enzyme to enhance its thermostability, also increased its hydrolytic activity 14-fold. However, the function or even the survivabiliy of the organism in the colder anoxic marine bottom sediment has not been studied.



The simplified scheme above shows the main steps in the biodegradation of PET by this bacterial species, *I. sakaiensis*.

The extracellular PET-ase enzyme secreted by *I. sakaiensis* hydrolyzes ester linkages of PET to yield mono(2-hydroxyethyl) terephthalic acid (MHET) as well as phthalic acid. Both these product molecules are small enough to be absorbed by the bacterium and catabolized intracellularly. The MHET is taken up by the bacterium through porosity in its membrane and degraded in the periplasmic space (Taniguchi et al. 2019), being hydrolyzed into phthalic acid and glycol by the bacterial MHET-ase. The terephthalic acid is converted into simple acids that can be metabolized *via* the citric acid cycle in the cell to yield CO_2 and water. A detailed discussion of the mechanism was recently published (Joo et al. 2018).

11.3 Plastics That Are Effectively Nonbiodegradable: Polyethylene, Polypropylene, and Polystyrene

Common plastics used in high volume, such as PE and PP, biodegrade particularly slowly in all natural environments and especially in the ocean environment. This is to be expected as it is their exceptional durability and bio-inertness that resulted in their success in high-volume applications. PE, the thermoplastic produced in highest volume globally, is particularly resistant to biodegradation. While it is also the most-studied plastic in biodegradation research, only about 5% of the studies on PE have used marine microorganisms (Matjašič et al. 2021). Despite the rich flora in the surface biofilm it develops, hydrocarbon biodegraders do not appear to thrive in the consortium.

Published literature on marine biodegradation of common plastics pertain mostly to aerobic biodegradation. In these, the plastics are either (i) exposed to native consortia in natural marine environments such as surface water or the sediment; or (ii) incubated in laboratory reactors with inocula either derived from the ocean or laboratory-grown marine microbial species. The latter studies have also used natural marine consortia augmented with specific microbial species. A critical drawback in field testing plastics for marine biodegradability is that only area-loss and weight-loss data can be conveniently generated but these are not indicative of mineralization. If the plastic were to be converted to microplastics or nanoplastics or biotransformed into recalcitrant products that do not mineralize, these approaches yield misleading results. It is challenging to monitor biodegradation, especially carbon conversion, in a marine sediment setting.

A comprehensive tabulation of plastic-biodegrading microorganisms was recently compiled by Amobonye (2021). Over 20 bacterial genera capable of biodegrading PE, for instance, are reported in the literature (Jacquin et al. 2019), including *Pseudomonas, Ralstonia, Stenotrophomonas, Klebsiella, Acinetobacter*, *Rhodococcus, Staphylococcus, Streptococcus, Streptomyces,* and *Bacillus* (Jacquin et al. 2019). The genus *Bacillus* in particular has potential as a degrader of common plastics, such as PE, PP, PS, and PET (Kumar et al. 2021). As with PET, both PE and PP undergo initial extracellular biotransformation by enzymes secreted by microorganisms, followed by their low-molecular weight products being absorbed into the cell. Intracellular metabolism results in their mineralization (Sivan 2011). *Pseudomonas* sp. E4, for instance, secretes enzymes that breakdown PE (Wilkes and Aristilde 2017), primarily due to its alkane hydroxylase gene (Gravouil et al. 2017). In laboratory tests these bacterial species mineralized up to 28.6% of the PE in 80 days of incubation with the polymer (Yoon et al. 2012).

PE and PP resist biodegradation because of the exceptional stability of their main chain C–C bonds. However, fungi that carry out lignin biodegradation secrete enzymes, such as lignin peroxidases and laccases, capable of breaking the C–C bonds in lignin, and appear to be able to do the same in polyolefins as well. For example, up to 70% mineralization of PE by the common white-rot fungus (*Phanerochaete chrysosporium*) *via* extracellular peroxidases secreted by the fungus, was reported (Mukherjee and Kundu 2014). Laccases capable of relatively fast biodegradation of PE is secreted by several marine species (Santo et al. 2013), including *Actinomycete*s and *Rhodococcus ruber* (Gilan et al. 2004). A strain of the latter species was reported to biodegrade PE aerobically at the rate of 8.0% in four weeks, based on weight loss measurements in the laboratory. Much less is known of hydrocarbon-degrading anaerobic species that may biodegrade polyolefins, even though they are likely present in the bottom sediment (Gittel et al. 2015; Hazen et al. 2016).

Relatively less information is available on the biodegradation of polystyrene [PS]. An extracellular enzyme secreted by the Basidiomycetes fungus, *Lentinus tigrinus,* breaks down PS (Tahir et al. 2013). Several enzymes that can convert styrene intracellularly into phenyl acetate that can participate in the cellular citric acid cycle are known. These include styrene oxide isomerases, styrene mono-oxygenases, and phenylacetyl co-enzyme A ligase (Amobonye et al. 2021).

Table 11.4 provides weight loss data reported in the degradation of common plastics under exposure to seawater or sediment. However, in most cases, the plastic has been pre-oxidized either thermally or photo-oxidatively to some extent, to promote faster biofouling and biodegradation (Sudhakar et al. 2007). Furthermore, the MWDs of the plastic samples used are unspecified in

Table 11.4 Biodegradation of effectively nonbiodegradable common plastics using microbial consortia from natural marine and microcosm environments.

Plastic	Inoculum	Result	Reference
LLDPE films	seawater microcosms, 25 °C, 120 rpm stirring	4.2% weight loss in 6 mo	Syranidou et al. (2017)
LDPE film	Oxic and anoxic sediment slurry, 10 °C for 98 d	No sign of biodegradation	Nauendorf et al. (2016)
PS film	Seawater microcosms 25 °C, 120 rpm stirring	2.3% weight loss in 6 mo	Syranidou et al. (2017b)
LDPE/HDPE/PP	Seawater, shallow sediment ~30 °C	Maximum weight loss of 2.5% for LDPE, 0.8% for HDPE, and 0.5% for PP over 6 mo	Sudhakar et al. (2007)
LDPE	Sediment at 6 m in the Mediterranean Sea up to 33 d	No signs of degradation	Eich et al. (2015)
LDPE	Seawater (1 m depth)	No signs of degradation	Napper and Thompson (2019)
PS	Marine consortia I simulated seawater	4.7% weight loss in 6 mo. Also decrease in Mn (g/mol) by 32%	Syranidou et al. (2017c)

most reports. In any event, different studies, despite their approximate qualitative agreement, are not strictly comparable to each other, not only because of different locations of exposure but also because of potential differences in the fractional crystallinity of samples used. Even with weight loss measurements the true percent biodegradation will be the fraction of the amorphous content (rather than that of the entire sample) that degraded during the exposure. PE and PP do not generally carry high concentrations of additives that may preferentially biodegrade on incubation. However, whether the additives influence the foulant colony composition (for instance because of toxicity) to indirectly affect biodegradation rates, is not clear.

Laboratory studies on the biodegradation of plastics by single organisms are numerous in the literature and typically consist of observations on plastics samples incubated with selected marine microorganisms under controlled incubation conditions. Data from literature was summarized in a recent review (Ali et al. 2021). Gravimetric weight loss of the polymer measured in laboratory exposure studies over extended durations in enriched media, show a few percent decrease in the weight of effectively nonbiodegradable plastics under these enriched biotic conditions. But, the results do not relate to their rates of biodegradation under marine field conditions. This is also true of studies where the micriorganisms were sourced from the marine sediment or sea water. A few recent representative studies on aerobic biodegradation of common plastics in the laboratory are summarized in Table 11.5, illustrating the types of results obtained; the reader is directed to Raddadi and Fava (2019) for a detailed discussion of the topic.

An interesting observation that pertains to microplastics and nanoplastics is the biodegradation of plastic microdebris in the gut of ingesting species. Mechanical stress is a known agent in bringing about fragmentation of ingested plastics (as discussed in Chapter 8) but biotransformation of ingested PE and PS by gut bacteria has also been reported (Yang et al. 2014; Bombelli et al., 2017)). The waxworms, the larvae of *Plodia interpunctella*, ingesting LDPE films were shown to biotransform the polymer with the help of gut bacterial species *Enterobacter asburiae* YT1 and

Table 11.5 Representative weight-loss studies on effectively nonbiodegradable common plastics by selected microorganisms under laboratory conditions.

Plastic	Inoculum	Weight loss	Reference
PP (pre-oxidized)	*Bacillus* sp. strain 27 *Rhodococcus* sp. strain 36 at 29 °C From mangrove sediment	6.4% (*Rhodococcus* sp. and 4% (*Bacillus* sp.) in 40 d	Auta et al. (2018)
LDPE film (with additives)	Marine *Kocuria palustris*, *Bacillus pumilus*, and *Bacillus subtilis* H1584 at 37 °C From pelagic seawater	*Kocuria sp. 1%, B. pumilus* 1.5%, and *B. subtilis* 1.75% in 30 d	Harshvardhan and Jha (2013)
HDPE	*Brevibacillus borstelensis at 37* °C From marine sediment in 30 d	11.4%	Mohanrasu et al. (2018)
LLDPE	*Zalerion maritimum* ATTC 34329 at 25 °C (a marine fungus)	43% in 28 d	Paço et al. (2017)
PS	*Microbulbifer hydrolyticus* IRE-31 Arabian Sea sediment	18% in 30 d and 34% in 60 d.	Kumar et al. (2021)

Bacillus sp. YP1. In 28 days, a weight loss of 10.7% and more significantly, a 13% reduction in the average molecular weight of the polymer, were reported in this study. Also, mealworms, the larvae of *Tenebrio molitor*, were reported to be capable of biotransforming PS (Yang et al. 2015), yielding a 28-day weight loss of 7.4% and a decrease in average molecular weight by 11%.

11.4 Assessing Biodegradation and Mineralization

Respirometry that allows measuring the of rates of mineralization can readily distinguish between the rapidly biodegradable and effecively nonbiodegradable plastics in the laboratory. The chemical equations summarizing biodegradation in general, suggest several basic approaches that might be used to quantify the process for any substrate under controlled incubation. Assuming the plastic to be the sole carbon source in the biotic medium, it will be metabolized by microorganisms either aerobically and anaerobically, converting the polymer carbon into simple compounds or biomass as represented by the simplified equations below. C_{POLYMER} is the carbon content of a hydrocarbon plastic sample at the beginning of the process ($t = 0$), while C_{RESIDUE} is the residual polymer that is yet to be mineralized; at complete carbon conversion, $C_{\text{RESIDUE}} = 0$.

$$C_{\text{POLYMER}} + O_2 \rightarrow CO_2 + H_2O + C_{\text{RESIDUE}} + C_{\text{BIOMASS}} \quad (\text{aerobic})$$

$$C_{\text{POLYMER}} \rightarrow CO_2 + CH_4 + H_2O + C_{\text{RESIDUE}} + C_{\text{BIOMASS}} \quad (\text{anaerobic})$$

The above simplified equations suggest the following four general approaches to assess the progress of biodegradation and mineralization (Andrady 1994):

1) Monitoring the accumulation of biomass
2) Monitoring the depletion of the plastic material
3) Monitoring the evolution of product gases (CO_2 or CH_4) or demand of reactant gas (oxygen)
4) Monitoring any changes in polymer properties.

Of these, monitoring the increase in biomass with the duration of exposure is a qualitative approach that is only indirectly related to mineralization. Older ASTM tests used biomass as an indicator of biodegradation of materials by selected microbial species incubated with the plastic. The second approach of monitoring the depletion of the plastic substrate will yield data on biotransformation, not on mineralization. Weight loss measurements and area loss measurements are based on this approach; however, the results are difficult to interpret because of losses from micro- or nano-fragmentation. It is difficult to measure weight loss in field-exposed samples because of surface fouling; area loss is the better metric especially when using plastic laminates, as biodegradation is primarily a surface phenomenon. As already stated, it is the rate of mineralization that is of particular interest. Therefore, either the biochemical oxygen demand (BOD) associated with the oxidation process, or the CO_2/CH_4 gases evolved during the biodegradation process, needs to be monitored to assess mineralization. Measuring BOD, although straight forward, is not applicable to anaerobic biodegradation. In aerobic biodegradation studies, monitoring CO_2 evolution as a function of time (or respirometry) is the most convenient approach.

11.4.1 Respirometry to Determine Biomineralization

In respirometry, biomineralization of the substrate occurs in a bioreactor or a flask maintained at constant temperature in the laboratory. It typically contains a medium such as soil, sediment, or seawater, carrying a suitable microbial inoculum (Allen et al. 1994). Marine sediment, seawater, sewage sludge, or a tailored consortium of microorganisms, is typically used as the inoculum. Often, the medium is supplemented with N and P minerals to encourage microbial growth and the finely divided plastic sample of known weight is mixed with the medium in the reactor flask, which is continuously aerated and maintained at a constant temperature.

Where continuous air flow is used to monitor the gas, the CO_2 concentrations in the input and exit air streams are monitored and recorded. This is conveniently achieved using a continuous-recording automated infrared detector for the gas (Way et al. 2010). The background respiration rate of the inoculum and medium is determined using a parallel control reactor with no plastic test sample. Subtracting background levels of CO_2 for the control reactor from that of the test reactor, the net evolved CO_2 gas attributed to mineralization of the plastic sample is obtained as a function of the duration of incubation. A plot of the percent carbon conversion of the substrate as a function of time (see Figure 11.4) shows a plateau within a few weeks of incubation, depending on the inherent biodegradability of the polymer. The maximum amount of CO_2 evolved is compared to the theoretical estimate of CO_2 expected for complete mineralization of the sample of known weight (based on the the percent carbon in the plastic determined by elemental analysis). Comparing the maximum CO_2 evolved with the theoretical value, yields a percentage conversion of carbon in polymer or the extent of mineralization achieved.

$$\text{Percent mineralization} = \frac{\text{Observed amount of evolved CO}_2}{\text{Theoretical amount of CO}_2\text{ expected}} \times 100 \qquad (1)$$

Bio-inertness of LDPE is clearly demonstrated in Figure 11.4 that compares data from respirometry of several polyesters in a marine sediment medium. The aliphatic polyesters show maximum extents of aerobic mineralization within about four months of exposure. That no carbon conversion was detectable with LDPE suggests it to be effectively nonbiodegradable under aerobic sediment exposure. It does not, however, preclude biotransformation or very low levels of mineralization below the detection limits of the technique. At such slow rates, biodegradation cannot be considered a significant mechanism for removal of LDPE from the environment.

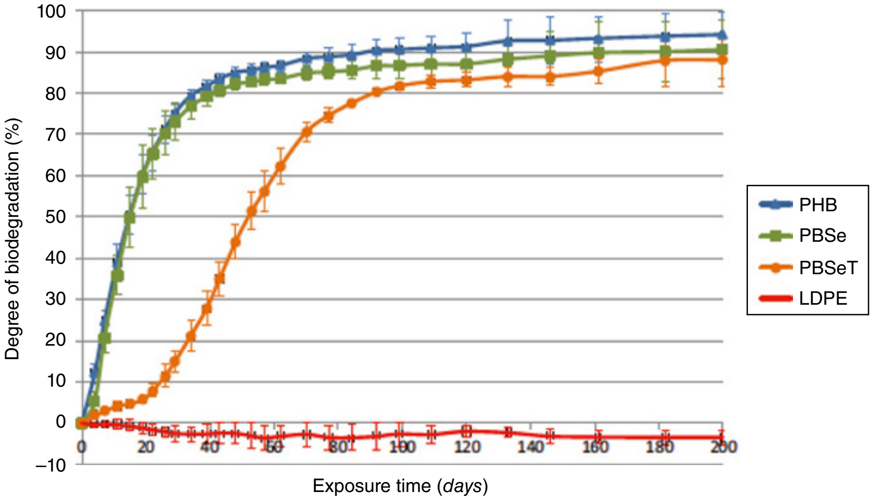


Figure 11.4 Comparison of respirometric data from rapidly biodegrading polyesters versus effectively nonbiodegradable LDPE slowly in seawater mixed with coastal aerobic sediment under aerobic conditions at 25 °C. Film thickness 25–80 μm. *Source:* Courtesy Briassoulis et al. (2020).

Alternatively, a static respirometer technique might be used to generate similar data. In this approach, biodegradation takes place in a sealed biometer flask, again containing the powdered or fragmented plastic sample mixed with the medium carrying the inoculum and incubated at constant temperature. In respirometry, at least three replicates are used for each sample; background, positive and control flasks, each with an adequate air space available in the flask to support the biomass. The respiratory CO_2 produced by microorganisms is absorbed in a quantity dilute alkali placed in a separate compartment within the same flask. The alkali is removed from the flask periodically and titrated against a dilute acid to determine the amount of CO_2 gas absorbed. A design for a simple biometer flask (Andrady 1998) suitable for convenient titration of alkali is shown in Figure 11.5. The upper part of the device that holds the medium, inoculum, and the plastic sample, is fitted on to a flask carrying a quantity of dilute alkali, KOH, through a ground-glass joint. Periodically, the upper compartment carrying the medium is removed and the contents of the flask titrated against a dilute acid using a suitable indicator. The removed upper chamber is immediately fitted on to a fresh flask carrying a fresh aliquot of KOH. Blank flasks, with the same medium, but no plastic substrate, are used as a controls. Also, positive controls consisting of a known readily biodegradable polymer (e.g. cellulose) and a negative control of a recalcitrant material are usually included in the test, and all determinations are made in triplicate. Evolved CO_2 during mineralization of the plastic at different durations of incubation is obtained from the titrimetric results (gas absorbed by the alkali in sample flask, less that in the blank flask).

Mineralization curves as shown in Figure 11.5 can be fitted with a simple first-order function.

$$Y = a\left(1 - \exp\left\{-\left(k - c\right)\cdot t\right\}\right) \qquad \text{for } t > c \tag{2}$$

where Y is the percent mineralization, c is the lag time (where $Y = 0$), and t is the duration of incubation. Maximum mineralization $Y_{\max} = a$ (%) and k (day^{-1}) is a first-order kinetic parameter. Figure 11.5 (right) shows a fit of typical mineralization data to Equation (2) as well as a plot of $Ln\,(1 - y/a)$ versus t (days) as suggested by the equation. Both the initial rate and the maximum extent of mineralization can be obtained from such a plot. A more complicated three-parameter fit has been suggested (Gustafson and Holden 1990), but the simpler two-parameter function is generally adequate.

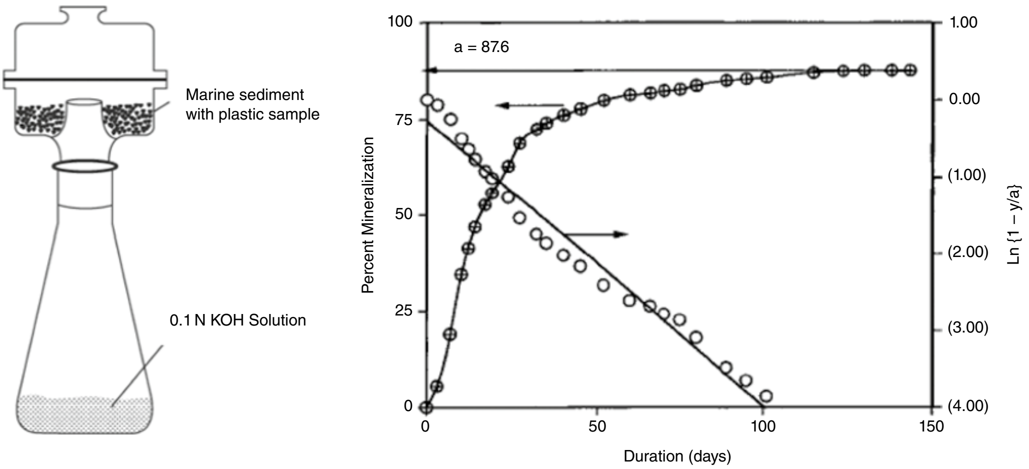


Figure 11.5 Left: Biometer flask with substrate in marine sediment. Right: Filled symbols – percent mineralization of the substrate as a function of the duration of incubation. Open symbols – a plot of the data suggested by Equation (2). *Source:* Courtesy Andrady and Song (1999).

Maximum mineralization obtained will generally be less than 100% because some of the carbon from polymer substrate is sequestered in the yet-to-mineralize biomass. Maximum conversion in the sample can be compared to that obtained with a biomineralizable standard polymer, such as cellulose. Using soil as inoculum, Guo et al. (2012), for instance, compared the aerobic mineralization of rapidly biodegradable esters, expressing the “mineralizability” as the ratio with that obtained for starch in parallel respirometric experiments. No similar data are available for mineralization of plastics under marine conditions.

With anaerobic biodegradation tests, an oxygen-free environment must be maintained in the reactor and CH_4 levels instead of (or in addition to) CO_2 levels) similarly monitored (except that CH_4 cannot be detected titrimetrically). To obtain reproducible data it is important to follow the experimental procedures consistently and closely (Zumstein et al. 2019).

To avoid misinterpreting respirometric data, the following factors need to be taken into account:

1) Mineralization data obtained pertain to the total organic content of the sample that may include additives, oxidation products, sorbed impurities, and residual monomers (Klaeger et al. 2019), in addition to the base polymer (Shiim et al. 2014). Phthalate plasticizers used at high concentrations in PVC, for instance, are readily assimilated by marine organisms (Wright et al. 2020). Photo-oxidation of PE and PP is known to result in numerous water-soluble dicarboxylic acids and carbonyl compounds being released into the biofilm and these may biodegrade preferentially (Romera-Castillo et al. 2018). Even with the base polymer, it will be the low-molecular-weight end of the chain length distribution of the amorphous fraction, that is preferentially mineralized, and initial initially rates cannot therefore be extrapolated reliably to the entire biomineralization process. Unfortunately, neither weight loss data nor mineralization data yields the chain-length fraction being mineralized at a given stage of the process. But this is accessibly *via* analysis of polymer.
2) Some of these non-polymer constituents may leach out of the plastic and either encourage or retard the growth of biomass in the test biometer flasks, causing a priming effect not present in control flasks.

3) The rate of mineralization (but not the maximum extent) depends on the surface area of the sample. Powder samples with a higher specific surface area relative to film samples, for instance, will yield higher biomineralizaton rates. The effect of specific surface area of the sample was demonstrated in the biomineralization of PCL (Funabashi et al. 2007), and poly(ethylene sebacate). The latter is a biodegradable plastic fits a double reciprocal model (or a Lineweaver–Burk plot) with a gradient of 11.56% carbon/day/cm^2 (Chinaglia et al. 2018). The plot of the rate k (per day) versus the area of sample (cm^2) was 11.56 ($r^2 > 0.98$); when the specific surface area was increased (using a finely powdered sample), from 89 to 1650 cm^2, the mineralization rate constant increased from 7.22 to 31.24 mg C/day.
4) With semi-crystalline polymers the respirometric data pertain only to the amorphous fraction while the Th(CO_2) is calculated for the entire sample. This error can be avoided by taking into account the percentage crystallinity of the plastic (determined by DSC.)

When using standardized aerobic respirometry to assess mineralizability, two critical factors need to be considered. First, is the difficulty in controlling or standardizing the inoculum used, as its quality depends on several factors (Baptiste et al. 2019): (i) microbial cell density (Martin et al. 2017), (ii) diversity of the species represented, (iii) ratio of nutrients to biomass in the inoculum (Vazquez-Rodriguez 1999), and (iv) it's exposure history (Kim et al. 2017). Even, merely sampling the seawater or shallow sediment from the natural environment and removing it to the laboratory, affects the microbial consortium (Kowalczyk et al. 2015). Continuously maintaining temperature and aeration can help minimize these effects, but inocula cultured in the laboratory are still likely to be different from natural consortia. Some standardized tests allow the use of synthetic consortia of mixed microorganisms as inocula; these allow a mix of several species of microorganisms selected from a prescribed list and cultured in synthetic seawater to be used as the inoculum. With such an approach, the inter-test variability is likely to be high as the composition of the mix could influence the rate of biodegradation in a polymer-specific manner (Goodhead et al. 2014). The inoculum is quantified in terms of the cell concentration that may not neccessarily be representative of the degrader-cell concentration for a particular substrate. Standardizing microbial cell density in the test environment is a concern that is recognized in the standard test methods, but the methodology provides little guidance on how this might be ensured (Krzan et al. 2006). Where the inoculum is naturally sourced, as with seawater or sediment, the seasonal variations, especially that in temperature, may influence the microbial composition.

The other important consideration is the role of any pre-adapted microorganisms present in the inocula. Some of the biofilm species are believed to evolve or adapt themselves to utilize the polymer substrates they are in contact with (Baptiste et al. 2019; Tribedi et al. 2015) even during the initial settlement stage. If organisms previously exposed to a substrate routinely and already pre-adapted to the plastic are included in the inoculum, the outcome of the test results can be influenced.

11.4.2 Using Radiolabeled Polymers

Though it is convenient to carry out in the laboratory and provides reliable data on mineralization, respirometry uses an atypical biotic environment where the polymer is the sole carbon source. This is in stark contrast to field conditions where other substrates, including readily-biodegradable substances, are also available. This limitation may change the rate or otherwise impact the biodegradation of the plastic material in respirometry. It is a drawback that is avoided when using ^{14}C-labeled polymers as the substrate, that allows metabolic carbon dioxide derived from the polymer to be identified even when other carbon sources (that are not radiolabeled) are present in the medium (Kaplan et al. 1979). Experimentally, it is convenient to use ^{13}C-labeled polymers in biomineralization studies, with the $^{13}CO_2$ from the polymer (identified using isotope-ratio mass spectrometry) easily distinguished from that evolved from other substances in the medium (Wilske et al. 2014). The use of radiolabeled polymers is particularly useful with effectively non-biodegradable plastics such as PE (Albertsson et al. 1993) or cellulose acetate (Komarek et al. 1993).

11.5 Standardized Tests to Assess Biodegradation

Several organizations such as the ASTM or ISO have published standard test methods to establish aerobic biodegradability of plastics in the marine pelagic environment (See Table 11.6). A detailed discussion of different standardized tests is beyond the scope of this chapter. However, an important point to emphasize is that the available tests for marine biodegradation pertain only to aerobic or shallow water environments (Table 11.6). This lack of a suitable anaerobic marine biodegradation test is a very significant drawback in making a balanced assessment of biodegradability of plastics in the ocean, especially because floating plastic debris invariably sink in seawater to reach anoxic deep water regime or the bottom sediment. There are no methods to assess the biodegradation or ecotoxicity associated with plastics littering the bottom sediment environment. It is not reasonable to assume that biodegradation in cold anoxic sediment will neccessarily be extremely slow with all plastics; the biodegradation rates of some plastics obtained in the bottom sediment can be higher (by as much as on order of magnitude) compared to that in seawater (Beltran-Sanahuja 2020).

The many difficulties involved in designing anaerobic test protocols are acknowledged. In-situ weight-loss studies in the sediment do not provide mineralization data, emphasizing the need for a laboratory test. But sampling benthic organisms under native high pressure and maintaining

Table 11.6 A compilation of currently available standardized aerobic biodegradation tests for marine shallow water environments.

	Standard test methods: Pelagic zone (water column scenario)	**Standard test methods: Benthic zone (seafloor scenario)**	**Standard test methods: Eulittoral zone (intertidal beach scenario)**	**Standards specifications**
Laboratory tests	ASTM D6691-17		ASTM D7991-15	ASTM D7081-05: withdrawn 2014
	ASTM D6692-01: withdrawn 2010			ISO 22403:2020
	ISO/FDIS 23977-1	ISO 18830:2016, 2016	ISO22404:2019	
	ISO/FDIS 23977-2	ISO 19679:2016,		
Field tests	ISO 15314:2018. 2018	ISO 22766:2020	(ISO 22766:2020.2020)	
Tank tests		ASTM D7473-12 and WK7193, 2020*		
	ISO/DIS 23832	ISO/DIS 23832*	ISO/DIS 23832*	

Source: Courtesy SAPEA (2020). Reproduced under creative commons license. *-Under development.

them under hyperbaric conditions in the laboratory, are indeed challenging. If the consortia are depressurized in the process, any obligate piezophilic organisms will not survive. Even if these are appropriately sampled and maintained in hyperbaric chambers in the laboratory, sampling the dissolved metabolic gases in the water periodically is also fraught with experimental difficulties. Finally, plastics, especially the glassy polymers such as PET or PS, undergo densification at these high pressures, reducing their fractional free volume. Biodegradation of these, takes place while they are in this densified condition, requiring the plastic samples used in the anaerobic marine biodegradation studies to be preconditioned at high pressure.

An overarching question is the relevance of even the existing laboratory mineralization tests to the biodegradation process that occurs in the marine environment. Biodegradation in laboratory tests where plastic is the sole carbon source contrasts with the field environment where it is a minor, generally unpreferred, carbon source (Ru et al. 2020). How different will the rates of mineralization, and the maximum carbon conversions might be from laboratory respirometry, with competing carbon sources and a wider range of degrading organisms are present, remains unanswered. The question cannot be easily answered even with studies using radiolabeled polymer substrates. This knowledge gap needs to be addressed if the fate of plastics in the marine environment is to be clearly understood.

References

Albertsson, A.-C., Hakkarainen, M., 2017. Designed to degrade. *Science*, 358, 872–873.

Albertsson, A.-C., Karlsson, S.J., 1988. The three stages in degradation of polymers – polyethylene as a model substance. *Journal of Applied Polymer Science*, 35, 1289–1302.

Albertsson, A.C., Barenstedt, C., Karlsson, S., 1993. Increased biodegradation of a low-density polyethylene (LDPE) matrix in starch-filled LDPE materials. *Journal of Environmental Polymer Degradation*, 1, 241–245.

Allen, A.L., Mayer, J., Stote, R., et al., 1994. Simulated marine respirometry of biodegradable polymers. *Journal of Environmental Polymer Degradation*, 2, 237–244. https://doi.org/10.1007/BF02071971

Ali, S.S., Elsamahy, T., Al-Tohamy, R., Zhu, D., Mahmoud, Y.A., G., Koutra, E., Metwally, M.A., Kornaros, M., Sun, J., 2021. Plastic wastes biodegradation: mechanisms, challenges and future prospects. *Science of the Total Environment*, 780, 146590.

Amaral-Zettler, L.A., Zettler, E.R., Mincer, T.J., 2020. Ecology of the Plastisphere. *Nature Reviews Microbiology*, 18, 139–151.

Amaral-Zettler, L.A., Zettler, E.R., Slikas, B., Boyd, G.D., Melvin, D.W., Morrall, C.E., Proskurowski, G., Mincer, T.J., 2015. The bio-geography of the Plastisphere: implications for policy. *Frontiers in Ecology and the Environment*, 13(10), 541–546.

Amobonye, A., Bhagwat, P., Singh, S., Pillai, S., 2021. Plastic biodegradation: frontline microbes and their enzymes. *Science of the Total Environment*, 759, 143536.

Andrady, A., Song, Y., 1999. Aerobic mineralization of paperboard materials used in packaging applications. *Journal of Applied Polymer Science*, 74, 1773–1779.

Andrady, A.L., 1998. Biodegradation of plastics. In: Pritchard, G. (Ed.), *Plastics Additives*, 32–40. London, Chapman Hall.

Andrady, A.L., Song, Y., 1991. Fouling of floating plastic debris under Biscayne Bay exposure conditions. *Marine Pollution Bulletin*, 22(12), 117–122.

Andrady, A.L., 1994. Assessment of environmental biodegradation of synthetic polymers: a review. *Journal of Macromolecular Science, Part C. Polymer Reviews*, 34(1), 25–75.

Auras, R., Harte, B., Selke, S., 2004. An overview of polylactides as packaging materials. *Macromolecular Bioscience*, 4, 835–864.

Auta, H.S., Emenike, C.U., Jayanthi, B., Fauziah, S.H., 2018. Growth kinetics and biodeterioration of polypropylene microplastics by *Bacillus* sp. and *Rhodococcus* sp. isolated from mangrove sediment. *Marine Pollution Bulletin*, 127, 15—21.

Auta, H.S., Emenike, C., Fauziah, S.H., 2017. Screening of *Bacillus* strains isolated from mangrove ecosystems in Peninsular Malaysia for microplastic degradation. *Environmental Pollution*, 231, 1552–1559.

Bagheri, A.R., Laforsch, C., Greiner, A., Agarwal, S., 2017. Fate of so-called biodegradable polymers in seawater and freshwater. *Global Challenges*, 1, 1700048.

Baptiste, A.J., Poursat van Spanning, R.J.M., de Voogt, P., Parsons, J.R., 2019. Implications of microbial adaptation for the assessment of environmental persistence of chemicals. *Critical Reviews in Environmental Science and Technology*, 49(23), 2220–2255.

Barzkar, N., Sohail, M., Tamadoni Jahromi, S., 2021. Marine Bacterial Esterases: Emerging Biocatalysts for Industrial Applications. *Appl Biochem Biotechnol*, 193, 1187–1214.

Beltran-Sanahuja, A., Casado-Coy, N., Simo-Cabrera, L., Sanz-Lazaro, C., 2020. Monitoring polymer degradation under different conditions in the marine environment. *Environmental Pollution*, 259, 113836.

Briand, J.-F., Djeridi, I., Jamet, D., Coupé, S., Bressy, C., Molmeret, M., 2012. Pioneer marine biofilms on artificial surfaces including antifouling coatings immersed in two contrasting French Mediterranean coast sites. *Biofouling*, 28, 453–463.

Briassoulis, D., Pikasi, A., Papardaki, N.G., Mistriotis, A., 2020. Aerobic biodegradation of bio-based plastics in the seawater/sediment interface (sublittoral) marine environment of the coastal zone – test method under controlled laboratory conditions. *Science of the Total Environment*, 722, 137748.

Bryant, J.A., Clemente, T.M., Viviani, D.A., Fong, A.A., Thomas, K.A., Kemp, P., Karl, D.M., White, A.E., Delong, E.F., 2016. Diversity and activity of communities inhabiting plastic debris in the North Pacific Gyre. *MSystems*, 1(3), 1–19.

Cao, S., Wang, J., Chen, H., Chen, D., 2011. Progress of marine biofouling and antifouling technologies. *Chinese Science Bulletin*, 56, 598–612.

Chiellini, E., Corti, A., Swift, G., 2003. Biodegradation of thermally-oxidized, fragmented low-density polyethylenes. *Polymer Degradation and Stability*, 81(2), 341–351.

Chinaglia, S., Tosin, M., Degli-Innocenti, F., 2018. Biodegradation rate of biodegradable plastics at molecular level. *Polymer Degradation and Stability*, 147, 237–244.

Dang, H., Li, T., Chen, M., Huang, G., 2008. Cross-ocean distribution of *Rhodobacterales* bacteria as primary surface colonizers in temperate coastal marine waters. *Applied and Environmental Microbiology*, 74, 52–60.

de Castro, A.M., Carniel, A., Junior, J.N., da Conceição G.A., Valoni, É., 2017. Screening of commercial enzymes for poly (ethylene terephthalate) (PET) hydrolysis and synergy studies on different substrate sources. *Journal of Industrial Microbiology and Biotechnology*, 44, 835–844.

Debroas, D., Mone, A., Ter Halle, A., 2017. Plastics in the North Atlantic garbage patch: a boat-microbe for hitchhikers and plastic degraders. *Science of the Total Environmenr*, 599, 1222–1232.

Decho, A.W., Gutierrez, T., 2017. Microbial extracellular polymeric substances (EPSs) in ocean systems. *Frontiers in Microbiology*, 8, 922.

Denaro, R., Aulenta, F., Crisafi, F., Di Pippo, F., Viggi, C.C., Matturro, B., Tomei, P.F., Smedile, F., Martinelli, A., Di Lisio, V., Venezia, C., Rossetti, S., 2020. Marine hydrocarbon-degrading bacteria breakdown poly(ethylene terephthalate) (PET). *Science of The Total Environment*, 749, 141608.

Deroiné, M., Le Duigou, A., Corre, Y.M., Le Gac, P.-Y., Davies, P., César, P., Bruzaud, S., 2014. Accelerated ageing of polylactide in aqueous environments: comparative study between distilled water and seawater. *Polymer Degradation and Stability*, 108, 319–329.

Devi, R.S., Ramya, R., Kannan, K., Antony, A.R., Kannan, V.R., 2019. Investigation of biodegradation potentials of high density polyethylene degrading marine bacteria isolated from the coastal regions of Tamil Nadu, India. *Marine Pollution Bulletin*, 138, 549–560.

Dey, U., Mondal, N.K., Das, K., Dutta, S., 2012. An approach to polymer degradation through microbes. *Journal of Pharmacy*, 2(3), 385–388.

Didier, D., Anne, M., Alexandra, T.H., 2017. Plastics in the North Atlantic Garbage Patch: a boat-microbe for hitchhikers and plastic degraders. *Science of the Total Environment*, 599–600, 1222–1232.

Dilkes-Hoffman, L.S., Lant, P.A., Laycock, B.., Pratt, S., 2018. The rate of biodegradation of PHA bioplastics in the marine environment: A meta-study, *Marine Pollution Bulletin*, 142, 15–24.

Dussud, C., Hudec, C., George, M., Fabre, P., Higgs, P., Bruzaud, S., et al., 2018. Colonization of non-biodegradable and biodegradable plastics by marine microorganisms. *Frontiers in Microbiology*, 9, 1571.

Dussud, C., Meistertzheim, A.-L., Conan, P., Pujo-Pay, M., George, M., Fabre, P., et al., 2018. Evidence of niche partitioning among bacteria living on plastics, organic particles and surrounding seawaters. *Environmental Pollution*, 236, 807–816.

Dussud, C., Ghiglione, J.-F., 2014. Bacterial degradation of synthetic plastics. In: Briand, F. (Ed.), *Marine Litter in the Mediterranean and Black Seas*. Paris, CIESM Publisher, p. 180.

Eich, A., Mildenberger, T., Laforsch, C., Weber, M., 2015. Biofilm and diatom succession on polyethylene (PE) and biodegradable plastic bags in two marine habitats: early signs of degradation in the pelagic and benthic zone? *PLoS One*, 10, e0137201.

Eyheraguibel, B., Traikia, M., Fontanella, S., Sancelme, M., Bonhomme, S., Fromageot, D., Lemaire, G., Lauranson, J.L., Delort, A.M., 2017. Characterization of oxidized oligomers from polyethylene films by mass spectrometry and NMR spectroscopy before and after biodegradation by a *Rhodococcus rhodochrous* strain. *Chemosphere*, 184, 366–374.

Fazey, F.M.C., Ryan, P.G, 2016. Biofouling on buoyant marine plastics: an experimental study into the effect of size on surface longevity. *Environmental Pollution*, 210, 354–360.

Flemming, H.C., 2016. EPS – then and now. *Microorganisms*, 4, 41.

Funabashi, M., Ninomiya, F., Kunioka, M., 2007. Biodegradation of polycaprolactone powders proposed as reference test materials for international standard of biodegradation evaluation method, *Journal of Polymers and the Environment*, 15, 7–17.

Gallert, C., Winter, J., 2005. *Bacterial Metabolism in Wastewater Treatment Systems*. Wiley-VCH, Weinheim, pp. 1–48.

Gilan, I., Hadar, Y., Sivan, A., 2004. Colonization, biofilm formation and biodegradation of polyethylene by a strain of *Rhodococcus ruber*. *Applied Microbiology and Biotechnology*, 65, 97–104.

Gittel, A., Donhauser, J., Røy, H., Girguis, P.R., Jørgensen, B.B., Kjeldsen, K.U., 2015. Ubiquitous presence and novel diversity of anaerobic alkane degraders in cold marine sediments. *Frontiers in Microbiology*, 6, 1414.

Goodhead, A.K., Head, I.M., Snape, J.R, Davenport, R.J., 2014. Standard inocula preparations reduce the bacterial diversity and reliability of regulatory biodegradation tests. *Environmental Science and Pollution Research*, 21, 9511–9521.

Gravouil, K., Ferru-Clément, R., Colas, S., Helye, R., Kadri, L., Bourdeau, L., Moumen, B., Mercier, A., Ferreira, T., 2017. Transcriptomics and lipidomics of the environmental strain *Rhodococcus ruber* point out consumption pathways and potential metabolic bottlenecks for polyethylene degradation. *Environmental Science & Technology*, 51(9), 5172–5181.

Gu, J.D., 2003. Microbiological deterioration and degradation of synthetic polymeric materials: recent research advances. *International Biodeterioration and Biodegradation*, 52(2), 69–91.

Guo, W., Tao, J., Yang, C., Song, C., Geng, W., Li, Q., 2012. Introduction of environmentally degradable parameters to evaluate the biodegradability of biodegradable polymers. *PLoS ONE*, 7(5), e38341.

Gustafson, D.I., Holden, L.R., 1990. Nonlinear pesticide dissipation in soil: a new model based on spatial variability. *Environmental Science and Technology*, 24, 1032–1038.

Gutierrez-Wing, M.T., Stevens B.E., Theegala, C.S., Negulescu, I.I., Rusch, K.A., 2020. Anaerobic biodegradation of polyhydroxybutyrate in municipal sewage sludge. *Journal of Environmental Engineering*, 136, 709–718.

Hadad, D., Geresh, S., Sivan, A., 2005. Biodegradation of polyethylene by the thermophilic bacterium *Brevibacillus borstelensis*. *Journal of Applied Microbiology*, 98(5), 1093–1100.

Haider, T. P., Voelker, C., Kramm, J., Landfester, K., Wurm, F.R., 2019. Plastics of the future? The impact of biodegradable polymers on the environment and on society. *Angewandte Chemie International Edition*, 58(1), 50—62.

Hakkarainen, M., Albertsson, A.-C., 2004. Environmental degradation of polyethylene. *Advances in Polymer Science*, 169: 177–199.

Hansell, D.A., Carlson, C.A., Repeta, D.J., Schlitzer, R., 2009. Dissolved organic matter in the ocean: a controversy stimulates new insights. *Oceanography*, 22, 202–211.

Harrison, J.P., Schratzberger, M., Sapp, M., Osborn, A.M, 2014. Rapid bacterial colonization of low-density polyethylene microplastics in coastal sediment microcosms. *BMC Microbiology*, 14, 232.

Harshvardhan, K., Jha, B., 2013. Biodegradation of low-density polyethylene by marine bacteria from pelagic waters, Arabian Sea, India. *Marine Pollution Bulletin*, 77(1-2), 100–106.

Harrison, J.P., Boardman, C., O'Callaghan, K., Delort, A.M., Song, J., 2018. Biodegradability standards for carrier bags and plastic films in aquatic environments: a critical review. *Royal Society Open Science*, 5, 171792.

Hazen, T.C., Prince, R.C., Mahmoudi, N., 2016. Marine oil biodegradation. *Environmental Science & Technology*, 50, 2121–2129.

Ishigaki, T., Sugano, W., Nakanishi, A., Tateda, M., Ike, M., Fujita, M. (2004). The degradability of biodegradable plastics in aerobic and anaerobic waste landfill model reactors. *Chemosphere*, 54, 225–233.

Itrich, N.R., McDonough, K.M., van Ginkel, C.G., Bisinger, E.C., LePage, J.N., Schaefer, E.C., Menzies, J.Z., Casteel, K.D., Federle, T.W., 2015. Widespread microbial adaptation to L-glutamate-N,N-diacetate (L-GLDA) following its market introduction in a consumer cleaning product. *Environmental Science & Technology*, 49(22), 13314–13321.

Jacquin, J., Cheng, J., Odobel, C., Pandin, C., Conan, P., Pujo-Pay, M., Barbe, V., Meistertzheim, A.L. Ghiglione, J.-F., 2019. Microbial ecotoxicology of marine plastic debris: a review on colonization and biodegradation by the "Plastisphere". *Frontiers in Microbiology*, 10, 865.

Jambeck, J.R., Andrady, A., Geyer, R., Narayan, R., Perryman, M., Siegler, T., Wilcox, C., Lavender Law, K., 2015. Plastic waste inputs from land into the ocean. *Science*, 347, 768–771.

Joo, S., Cho, I.J., Seo, H., Son, H.F., Sagong, H.-Y., Shin, T.J., Chi, S.Y., Lee, S.Y., Kim, K., 2018. Structural insight into molecular mechanism of poly (ethylene terephthalate) degradation. *Nature Communications*, 9, 382.

Kaplan, D.L., Hartenstein, R., Sutter, J., 1979. Biodegradation of polystyrene, poly(methyl methacrylate), and phenol formaldehyde. *Applied and Environmental Microbiology*, 38(3), 551—553.

Kasuya, K., Takagi, K., Ishiwatari, S., Yoshida, Y., Doi, Y., 1998. Biodegradabilities of various aliphatic polyesters in natural waters. *Polym Degrad Stab*, 59(1–3), 327–332.

Khandare, S.D., Chaudhary, D., Jha, B., 2021. Marine bacterial biodegradation of low-density polyethylene (LDPE) plastic. *Biodegradation*, 32, 127–143.

Kim, S., Rossmassler, K., Broeckling, C.D., Galloway, S., Prenni, J., De Long, S.K., 2017. Impact of inoculum sources on biotransformation of pharmaceuticals and personal care products. *Water Research*, 125, 227–236.

Klaeger, F., Tagg, A.S., Otto, S., 2019. Residual monomer content affects the interpretation of plastic degradation. *Scientific Reports*, 9, 2120.

Kolvenbach, B.A., Helbling, D.E., Kohler, H.-P.E., Corvini, P.F.-X., 2014. Emerging chemicals and the evolution of biodegradation capacities and pathways in bacteria. *Current Opinion in Biotechnology*, 27, 8–14.

Komarek, R.J., Gardner, R.M., Buchanan, C.M., Gedon, S., 1993. Biodegradation of radiolabeled cellulose acetate. *Journal of Applied Polymer Science*, 50, 1739.

Kowalczyk, A., Martin, T.J., Price, O.R., Snape, J.R., van Egmond, R.A., Finnegan, C.J., Schäfer, H., Davenport, R.J., Bending, G.D., 2015. Refinement of biodegradation tests methodologies and the proposed utility of new microbial ecology techniques. *Ecotoxicology and Environmental Safety*, 111, 9–22.

Kristensen, E., Ahmed, S., Devol, A.H., 1995. Aerobic and anaerobic decomposition of organic matter in marine sediment: which is fastest? *Limnology and Oceanography*, 40(8), 1430–1437.

Kuwae, T., Hosokawa, Y., 1999. Determination of abundance and biovolume of bacteria in sediments by dual staining with 4′,6-diamidino-2-phenylindole and acridine orange: relationship to dispersion treatment and sediment characteristics. *Applied and Environmental Microbiology*, 65, 3407–3412.

Kumar, A.A., Karthick, K., Arumugam, K.P., 2011. Biodegradable polymers and its applications. *International Journal of Bioscience, Biochemistry and Bioinformatics*, 1(3), 173–176.

Kumar, G., Hinduja, M., Sujitha, K., Rajan, N.N., Dharani, G., 2021. Biodegradation of polystyrene by deep-sea *Bacillus paralicheniformis* G1 and genome analysis. *Science of the Total Environment*, 774, 145002.

Lambert, S., Wagner, M., 2017. Environmental performance of bio-based and biodegradable plastics: the road ahead. *Chemical Society Reviews*, 46, 6855–6871.

Lee, J.W., Nam, J.H., Kim, Y.H., Lee, K., Lee D., 2008. Bacterial communities in the initial stage of marine biofilm formation on artificial surfaces. *Journal of Microbiology*, 46, 174–182.

Leja, K., Lewandowicz, G., 2010. Polymer biodegradation and biodegradable polymers—a review. *Polish Journal of Environmental Studies*, 19(2), 255–266.

Ioakeimidis, C., Fotopoulou, K., Karapanagioti, H., Gerage, M., 2016. The degradation potential of PET bottles in the marine environment: an ATR-FTIR based approach. *Scientific Reports*, 6, 23501.

Lobelle, D., Cunliffe, M., 2011. Early microbial biofilm formation on marine plastic debris. *Marine Pollution Bulletin*, 62(1), 197–200.

Lu, B., Wang, G., Huang, D., Ren, Z., Wang, X., Wang, P., Zhen, Z., Zhang, W., Ji, J., 2018. Comparison of PCL degradation in different aquatic environments: effects of bacteria and inorganic salts. *Polymer Degradation and Stability*, 150, 133–139.

Matjašič, T., Simčič, T., Medvešček, N., Bajt, O., Dreo, T., Mori, N., 2021. Critical evaluation of biodegradation studies on synthetic plastics through a systematic literature review. *Science of the Total Environment*, 752, 141959.

Martin, T.J., Snape, J.R., Bartram, A., Robson, A., Acharya, K., Davenport, R.J., 2017. Environmentally relevant inoculum concentrations improve the reliability of persistent assessments in biodegradation screening tests. *Environmental Science & Technology*, 51(5), 3065–3073.

Michels, J., Stippkugel, A., Lenz, M., Wirtz, K., Engel, A., 2018. Rapid aggregation of biofilm-covered microplastics with marine biogenic particles. *Proceedings of the Royal Society B: Biological Sciences*, 285, 20181203.

Mohee, R., Unmar, G.D., Mudhoo, A., Khadoo, P., 2008. Biodegradability of biodegradable/degradable plastic materials under aerobic and anaerobic conditions. *Waste Management*, 28, 1624–1629.

Mohanrasu, K., Premnath, N., Siva, Prakash, G., Sudhakar, M., Boobalan, T., Arun, A., 2018. Exploring multi potential uses of marine bacteria; an integrated approach for PHB production, PAHs and polyethylene biodegradation. *Journal of Photochemistry and Photobiology B*, 185, 55–65.

Mukherjee, S., Kundu, P.P., 2014. Alkaline fungal degradation of oxidized polyethylene in black liquor: studies on the effect of lignin peroxidases and manganese peroxidases. *Journal of Applied Polymer Science*, 131, 40738.

Müller, R.-J., Kleeberg, I., Deckwer, W.D., 2001. Biodegradation of polyesters containing aromatic constituents. *Journal of Biotechnology*, 6, 87–95.

Muthukrishnan, T., Khaburi, M., Abed, R.M.M., 2019. Fouling microbial communities on plastics compared with wood and steel: are they substrate- or location-specific? *Microbial Ecology*, 78, 361.

Nakayama, A., Yamano, N., Kawasaki, N., 2019. Biodegradation in seawater of aliphatic polyesters. *Polymer Degradation and Stability*, 166, 290.

Napper, I.E., Thompson, R.C., 2019. Environmental deterioration of biodegradable, oxo-biodegradable, compostable, and conventional plastic carrier bags in the sea, soil, and open-air over a 3-year period. *Environmental Science & Technology*, 53, 4775–4783.

Nauendorf, A., Krause, S., Bigalke, N.K., Gorb, E.V., Gorb, S.N., Haeckel, M., Wahl, M., Treude, T., 2016. Microbial colonization and degradation of polyethylene and biodegradable plastic bags in temperate fine-grained organic-rich marine sediments. *Marine Pollution Bulletin*, 103, 168–178.

Oberbeckmann, S., Loeder, M.G.J., Labrenz, M., 2015. Marine microplastic-associated biofilms – a review. *Environmental Chemistry*, 12, 551–562.

Oberbeckmann, S., Loeder, M.G.J., Gerdts, G., Osborn, A.M., 2014. Spatial and seasonal variation in diversity and structure of microbial biofilms on marine plastics in Northern European waters. *FEMS Microbiology Ecology*, 49, 478–492.

Oberbeckmann, S., Osborn, A.M., Duhaime, M.B., 2016. Microbes on a bottle: substrate, season and geography influence community composition of microbes colonizing marine plastic debris. *PLoS One*, 11(8), e0159289.

Ogonowski, M., Motiei, A., Ininbergs, K., Hell, E., Gerdes, Z., Udekwu, K.I., Bacsik, Z., Gorokhova, E., 2018. Evidence for selective bacterial community structuring on microplastics. *Environmental Microbiology*, 20(8), 2796–2808.

Ohkita, Y., Lee, S.H., 2006. Thermal degradation and biodegradability of poly (lactic acid)/corn starch biocomposites. *Journal of Applied Polymer Science*, 100, 3009–3017.

Paço, A., Duarte, K., da Costa, J.P., Santos, P.S., Pereira, R., Pereira, M.E., Freitas, A.C., Duarte, A.C., Rocha-Santos, T.A., 2017. Biodegradation of polyethylene microplastics by the marine fungus *Zalerion maritimum*. *Science of the Total Environment*, 586, 10–15.

Pantani, R., Sorrentino, A., 2013. Influence of crystallinity on the biodegradation rate of injection-molded poly(lactic acid) samples in controlled composting conditions, *Polymer Degradation and Stability*, 98(5), 1089–1096.

Pinto, M., Langer, T.M., Hüffer, T., Hofmann, T., Herndl, G.J., 2019. The composition of bacterial communities associated with plastic biofilms differs between different polymers and stages of biofilm succession. *PLoS One*, 14, e0217165.

Porter, A.B., Lyons, P., Galloway, T., S., Lewis, T., 2018. Role of marine snows in microplastic fate and bioavailability. *Environmental Science & Technology*, 52, 7111–7119.

Premraj, R., Doble, M., 2005. Biodegradation of polymer. *Indian Journal of Biotechnology*, 4, 186–193.

Raddadi, N., Fava, E., 2019. Biodegradation of oil-based plastics in the environment: existing knowledge and needs of research and innovation. *Science of the Total Environment*, 679, 148–158.

Rongrong, G., Chaomin S., 2021. A marine bacterial community that degrades poly(ethylene terephthalate) and polyethylene, Rongrong Gao. *Journal of Hazardous Materials*, 416, 125928.

Reischwitz, A., Stoppok, E., Buchholz, K., 1997. Anaerobic degradation of poly-3-hydroxybutyrate and poly-3-hydroxybutyrate-co-3-hydroxyvalerate. *Biodegradation*, 8, 313–319

Roager, L., Sonnenschein, E.C., 2019. Bacterial candidates for colonization and degradation of marine plastic debris. *Environmental Science & Technology*, 53(20), 11636–11643.

Romera-Castillo, C., Pinto, M., Langer, T.M., Álvarez-Salgado, X.A., Herndl, G.J., 2018. Dissolved organic carbon leaching from plastics stimulates microbial activity in the ocean. *Nature Communications*, 9, 1–7.

Ru, J., Huo, Y., Yang, Y., 2020. Microbial degradation and valorization of plastic wastes. *Frontiers in Microbiology*, 11, 442.

Rummel, C.D., Jahnke, A., Gorokhova, E.K ühnel, D., Schmitt-Jansen, M., 2017. Impacts of biofilm formation on the fate and potential effects of microplastic in the aquatic environment. *Environmental Science & Technology Letters*, 4(17), 258–267.

Saez, J.M., Aparicio, J.D., Amoroso, M.J., Benimeli, C.S., 2015. Effect of the acclimation of a *Streptomyces* consortium on lindane biodegradation by free and immobilized cells. *Process Biochemistry*, 50(11), 1923–1933.

Santo, M., Weitsman, R., Sivan, A., 2013. The role of the copper-binding enzyme – laccase – in the biodegradation of polyethylene by the actinomycete *Rhodococcus ruber*. *International Biodeterioration & Biodegradation*, 84, 204–210.

SAPEA (Science Advice for Policy by European Academies). 2020. *Biodegradability of Plastics in the Open Environment*. SAPEA, Berlin. doi:10.26356/biodegradabilityplastics

Sekiguchi, T., Saika, A., Nomura, K., Watanabe, T., Fujimoto, Y., Enoki, M., Sato, T., Kato, C., Kanehiro, H., 2011. Biodegradation of aliphatic polyesters soaked in deep seawaters and isolation of poly (ε-caprolactone)-degrading bacteria. *Polymer Degradation and Stability*, 96(7), 1397–1403.

Shah, A.A., Hasan, F., Hameed, A., Ahmed, S., 2008. Biological degradation of plastics: a comprehensive review. *Biotechnology Advances*, 26(3), 246–265.

Lee, H., Shim, W.J., Kwon, J.-H., 2014. Sorption capacity of plastic debris for hydrophobic organic chemicals. *Science of the Total Environment*, 470-471, 1545–1552.

Shimao, M., 2001. Biodegradation of plastics. *Current Opinion in Biotechnology*, 12(3), 242–247.

Singh, B., Sharma, N., 2008. Mechanistic implications of plastic degradation. *Polymer Degradation and Stability*, 93, 561–584.

Simoes, M., Simões, L.C., Vieira, M.J., 2010. A review of current and emergent biofilm control strategies. *LWT – Food Science and Technology*, 43(4), 573–583.

Sivan, A., 2011. New perspectives in plastic biodegradation. *Current Opinion in Biotechnology*, 22, 422–42.

Son, H.F., Cho, I.J., Joo, S., Seo, H., Sagong, H.Y., Choi, S.Y., Lee, S.Y., Kim, K.J., 2019. Rational protein engineering of thermo-stable PETase from *Ideonella sakaiensis* for highly efficient PET degradation. *ACS Catalysis*, 9, 3519–3526.

Steinberg, N., Kolodkin-Gal, I., 2015. The matrix reloaded: how sensing the extracellular matrix synchronizes bacterial communities. *Journal of Bacteriology*, 197, 2092–2103.

Sudhakar, M., Doble, M., Murthy, P.S., Venkatesan, R., 2008. Marine microbe-mediated biodegradation of low- and high-density polyethylenes. *International Biodeterioration and Biodegradation*, 61, 203–213.

Sudhakar, M., Trishul, A., Doble, M., Kumar, K.S., Jahan, S.S., Inbakandan, D., Viduthalai, R.R., Umadevi, V.R., Murthi, P.S., Venkatesan, R., 2007. Biofouling and biodegradation of polyolefins in ocean waters. *Polymer Degradation and Stability*, 92, 1743–1752.

Syranidou, E., Karkanorachaki, K., Amorotti, F., Franchini, M., Repouskou, E., Kaliva, M., Vamvakaki, M., Kolvenbach, B., Fava, F., Corvini, P.F.X., Kalogerakis, N., 2017. Biodegradation of weathered polystyrene films in seawater microcosms. *Scientific Reports*, 7, 17991.

Syranidou, E., Karkanorachaki, F., Amorotti, M., Franchini, E., Repouskou, E., Kaliva, M., Vamvakaki, M., Kolvenbach, B., Fava, F., Corvini, P.F., Kalogerakis, N., 2017b. Biodegradation of weathered polystyrene films in seawater microcosms. *Science Reports*, 7, 17991.

Tahir, L., Ali, M.I., Zia, M., Atiq, N., Hasan, F., Ahmed, S., 2013. Production and characterization of esterase in *Lantinus tigrinus* for degradation of polystyrene. *Polish Journal of Microbiology*, 62(2013), 101–108.

Taniguchi, I., Yoshida, S., Hiraga, K., Miyamoto, K., Kimura, Y., Oda, K., 2019. Biodegradation of PET: current status and application aspects. *ACS Catalysis*, 9, 4089–4105.

Tokiwa, Y., Calabia, B.P., Ugwu, C.U., Aiba, S., 2009. Biodegradability of plastics. *International Journal of Molecular Science*, 10, 3722–3742.

Tribedi, P., Gupta, A.D., Sil, A.K., 2015. Adaptation of *Pseudomonas* sp. AKS2 in biofilm on low-density polyethylene surface: an effective strategy for efficient survival and polymer degradation. *Bioresources and Bioprocessing*, 2(14), 1–10.

Upreti, M. C., Srivastava, R. B., 2003. A potential *Aspergillus* species for biodegradation of polymeric materials. *Current Science*, 84(11), 1399–1402.

Urbanek, A.K., Rymowicz, W., Mirończuk, A.M., 2018. Degradation of plastics and plastic-degrading bacteria in cold marine habitats. *Applied Microbiology and Biotechnology*, 102(18), 7669–7678.

van der Meer, J. R., 2006. Environmental pollution promotes selection of microbial degradation pathways. *Frontiers in Ecology and the Environment*, 4(1), 35–42.

Vazquez-Rodriguez, G., Palluy, F., Goma, G., Rols, J.L., 1999. Procedures in ready biodegradability testing: effects of the inoculation and the monitored parameter. *Environmental Technology*, 20(3), 301–308.

Wang, G.-X., Huang, D., Ji, J.-H., Völker, C., Wurm, F.R., 2021. Seawater-degradable polymers—fighting the marine plastic pollution. *Advanced Science*, 8, 2001121.

Wei, R., Zimmermann, W., 2017. Biocatalysis as a green route for recycling the recalcitrant plastic polyethylene terephthalate. *Microbial Biotechnology*, 10, 1302–1307.

Wei, R., Breite, D., Song, C., Gräsing, D., Ploss, T., Hille, P., Schwerdtfeger, R., Matysik, J., Schulze, A., Zimmermann, W., 2019. Biocatalytic degradation efficiency of postconsumer polyethylene terephthalate packaging determined by their polymer microstructures. *Advanced Science*, 6, 1900491.

Wilkes, R.A., Aristilde, L., 2017. Degradation and metabolism of synthetic plastics and associated products by *Pseudomonas* sp. capabilities and challenges. *Journal of Applied Microbiology*, 123, 582–593.

Wilske, B., Bai, M., Lindenstruth, B., Bach, M., Rezaie, Z., Frede, H.-G., Breuer, L., 2014. Biodegradability of a polyacrylate superabsorbent in agricultural soil. *Environmental Science and Pollution Research*, 21(16), 9453—9460.

Wright, R.J., Bosch, R., Gibson, M.I., Christie-Oleza, J.A., 2020. Plasticizer degradation by marine bacterial isolates: a proteogenomic and metabolomic characterization. *Environmental Science & Technology*, 54(4), 2244–2256.

Wright, R., 2019. Food or just a free ride? Exploring marine microbial community dynamics on natural and synthetic polymers. PhD thesis, University of Warwick.

Yagi, H., Ninomiya, F., Funabashi, M., Kunioka, M., 2009. Anaerobic biodegradation tests of poly(lactic acid) and polycaprolactone using new evaluation system for methane fermentation in anaerobic sludge. *Polymer Degradation and Stability*, 94, 1397–1404.

Yang, Y., Yang, J., Jiang, L., 2016. A bacterium that degrades and assimilates poly(ethylene terephthalate). *Science*, 353, 759.

Yang, J., Yang, Y., Wu, W.M., Zhao, J., Jiang, L., 2014. Evidence of polyethylene biodegradation by bacterial strains from the guts of plastic-eating waxworms *Environmental Science & Technology*, 48, 13776–13784.

Yang, J., Yang, Y., Wu, W.M., Zhao, J., Song, Y., Gao, L.L., Yang, R., Jiang, 2015. Biodegradation and mineralization of polystyrene by plastic-eating mealworms: Part 2. Role of gut microorganisms. *Environmental Science & Technology*, 49, 12087–12093.

Yang, H-S., Yoon, J-S., Kim, M-N., 2005. Dependence of biodegradability of plastics in compost on the shape of specimens. *Polymer Degradation and Stability*, 87, 131–135.

Yoon M.G., Jeon J.H., Kim M.N., 2012. Biodegradation of polyethylene by a soil bacterium and AlkB cloned recombinant cell. *J. Bioremed. Biodegrad*., 3:145.

Yoshida, S., Takehana, T., Kazumi, H., Taniguchi, I., 2016. A bacterium that degrades and assimilates poly(ethylene terephthalate). *Science*, 351, 1196–1199.

Zambrano, M.C., Pawlak, J.J., Daystar, J., Ankeny, M., Goller, C.C., Venditti, R.A., 2020. Aerobic biodegradation in freshwater and marine environments of textile microfibers generated in clothes laundering: effects of cellulose and polyester-based microfibers on the microbiome. *Marine Pollution Bulletin*, 151, 110826.

Zhu, L., Zhao, S., Bittar, T. B., Stubbins, A., D. Li., 2020. Photochemical dissolution of buoyant microplastics to dissolved organic carbon: rates and microbial impacts, *J. Hazard. Mater.,* 383, 121065.

Zettler, E.R., Mincer, T.J., Amaral-Zettler, L.A., 2013. Life in the “Plastisphere”: microbial communities on plastic marine debris. *Environmental Science & Technology*, 47, 7137–7146.

Zumstein, M., Narayan, R., Kohler, H.E., McNeill, K., Sander, M., 2019. Dos & Do Nots when assessing the biodegradation of plastics. *Environmental Science & Technology.*, 53(17), 9967–9969.

12

Ingestion of Microplastics by Marine Animals

Winnie Courtene-Jones, Nathaniel J. Clark, Astrid C. Fischer, Natalie S. Smith, and Richard C. Thompson

International Marine Litter Research Unit, School of Biological and Marine Sciences, University of Plymouth, Drake Circus, Plymouth, Devon, United Kingdom

12.1 Introduction

Over recent years, awareness of the ecological consequences of marine plastic debris has increased considerably. Vast quantities of plastic waste emanating from land-based sources (Borrelle et al. 2020; Geyer et al. 2017) have entered and accumulated in the marine environment, where they can fragment to form smaller micro- and potentially nano-sized fragments. Due to their small size, which for many marine creatures can be similar to that of their prey, microplastics have considerable potential to be ingested. Further, the prevalence of microplastics throughout the global ocean, from tropical to Polar regions (Bergmann et al. 2019; Kanhai et al. 2020) and from sea surface to the deepest parts of our ocean (Peng et al. 2017; Thompson et al. 2004; Courtene-Jones et al. 2020), indicates the widescale potential for biota to encounter microplastics in their ambient environment.

The presence of small plastic pieces in the environment was first documented in the early 1970s (Buchanan 1971; Carpenter et al. 1972; Carpenter and Smith 1972), but it was not until the late 1980s that interest into the biological impacts of this pollutant began to be investigated more extensively (Laist 1987). Early work was primarily concerned with the effects of macroplastics such as fishing and maritime debris on marine megafauna, for example seals, seabirds, and turtles (Bjorndal et al. 1994). The stomach contents of beached seabirds were examined, evidencing their consumption of plastics (Franeker 1985; Fry et al. 1987; Furness 1985). The first assessment of the number of marine species impacted by plastics in terms of both ingestion and entanglement totaled 267 species, and almost exclusively focused on large vertebrates, with the exception of a small number of fish ($n = 34$) and crustaceans ($n = 8$) (Laist 1997).

As knowledge regarding the presence of microplastics in the environment has increased (Thompson et al. 2004) so too has the concern for their ecological impacts, and research efforts have been focused to address such questions. Indeed, using the search terms “(microplastic OR microplastics) AND (ingestion OR uptake)” in Web of Science indicated a substantial growth in research activity over the past decade (Figure 12.1). A notable shift in investigation has also occurred with research moving away from simply considering the presence of internalized microplastics (Cadée 2002) to wider examination of the multitude of ways microplastics may cause

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

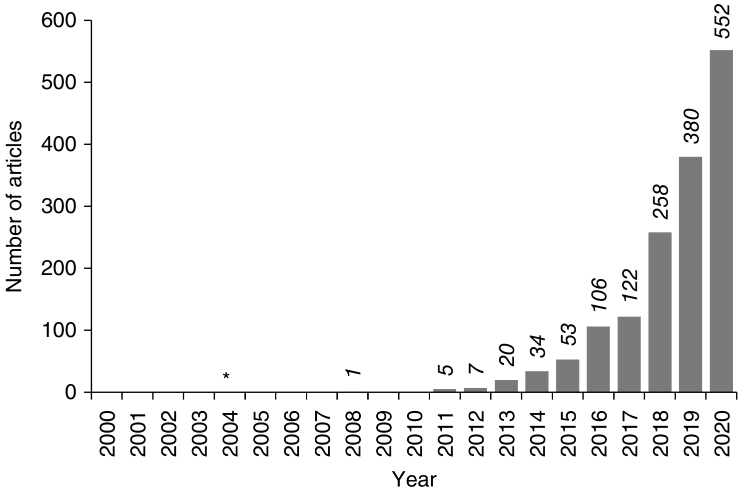


Figure 12.1 The number of articles published (stated above the bars) over the past two decades using the terms *microplastic* and *ingestion/uptake*. Results obtained from Web of Science on 18 December 2020. The star indicates the first use of the term "microplastic" (Thompson et al. 2004), which was used in the body of the text rather than the title and so it was not detected in this search.

biological harm (see Section 12.5), including the availability and toxicity of co-contaminants (Fred-Ahmadu et al. 2020) and the possibility of trophic transfer (Walkinshaw et al. 2020).

12.1.1 Defining Harm

There are many ways in which harm can be defined. A report by Werner et al. (2016) investigated the numerous ways in which litter and its degradation products can have impacts on organisms and the economy. As an example, a discarded plastic bag can cause entanglement to marine birds and mammals. Plastic bags can smother habitats, altering species assemblages and biogeochemical processes that may detrimentally impact the ecosystem as a whole (Green et al. 2015). They can also reduce the aesthetics of the beach and consequently have an impact on human well-being (Wyles et al. 2016). The same bag can degrade over time and produce microparticles and nanoparticles, which, in turn, can be consumed by marine life. The ingestion of plastics can cause toxicological effects (see Section 12.3) and microplastics can pass up through the food chain, potentially causing harm at different trophic levels (Carbery et al. 2018; Welden et al. 2018). The accumulation of litter can also impact the economy through reduced tourism and the financial burden of costs associated with clean-ups (Werner et al. 2016). This chapter focuses on the ingestion of plastics; therefore, harm is defined here within the ecotoxicological context of impacts on organisms and ecosystems.

12.2 Ingestion of Microplastics by Marine Organisms

Owing to the small size of microplastics and their near ubiquitous presence throughout the marine environment, concern for marine life arises from their ingestion. The bioavailability of microplastics to a specific organism is determined by the size, density, abundance, and color of microplastic (Wright et al. 2013), as well as biological factors such as biofilm and aggregation with organic material (Figure 12.2). The size fraction ingested will depend on the size of the mouth/buccal

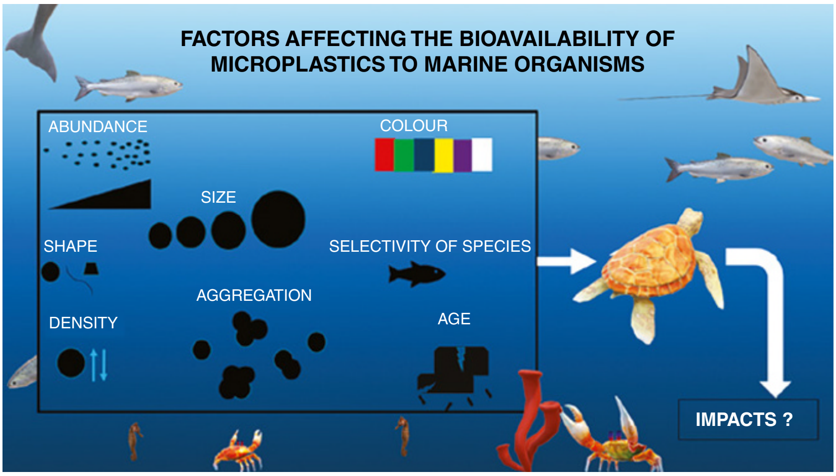


Figure 12.2 Factors influencing the bioavailability of microplastics to marine organism.

cavity of the animal (Jâms et al. 2020). Due to their small size (<5 mm in diameter), microplastics are available via ingestion to a wide range of organisms as they overlap with the size range of their prey (Galloway et al. 2017) and can be readily ingested along with prey items (e.g. Goncalves et al. 2019; Hall et al. 2015; Lee et al. 2013). The specific density of the polymer will affect its position within the water column and thus the potential that a species will interact with the plastic. As such, the types of plastics ingested may vary between organisms. Those inhabiting the upper water column will likely encounter low-density, buoyant polymers such as polystyrene (PS) and polyethylene (PE) on the sea surface, while benthic species may have a greater likelihood of ingesting high-density negatively buoyant polymers, such as polyester. This is an over-simplification, as biofilms can rapidly form on the surface of plastics (Lobelle and Cunliffe 2011) and cycles of fouling and de-fouling can occur (Kooi et al. 2017), altering their buoyancy and position in the water column. The abundance of microplastics in the marine environment will also affect its bioavailability, i.e. where microplastic abundances are greater, there is a higher chance that an organism will encounter a particle and thus a greater likelihood of ingestion. For example, rotifers exposed to 1.0 and 10.0 mg/L microplastics showed ingestion in all individuals; however, at 0.1 mg/L, the incidence of ingestion was less than 30% (Beiras et al. 2018). It is hypothesized that benthic detritivores and deposit feeders may be more susceptible to plastic ingestion due to the high quantities of microplastics found in sediments (Bour et al. 2018; Browne et al. 2010). Finally, color may influence the likelihood of ingestion due to prey item resemblance: for example some species of fish that prey upon zooplankton may ingest white, tan, or yellow microplastics that most resemble their prey (Ory et al. 2018; Shaw and Day 1994). Microplastics can also be ingested through consumption of contaminated prey items (e.g. da Costa Araújo et al. 2020), i.e. trophic transfer, which is discussed further in Section 12.3.3.

Microplastic bioavailability can be influenced by biological factors: for example the growth of biofilms on the surface of plastics may enhance their likelihood of being consumed (Hodgson et al. 2018) through the secretion of exopolymeric substances and aggregation with organic matter. Vroom et al. (2017) demonstrated that aging in seawater may make PS beads more likely to be ingested by marine zooplankton, as many of the species ingested aged PS in preference to pristine PS beads. In addition, phytoplankton colonizing the surface of plastics can produce infochemicals such as dimethyl sulfide (DMS) that are chemical cues. Empirical studies found that microplastics can acquire DMS signatures, which can subsequently enhance their ingestion by seabirds (Savoca et al. 2019) and zooplankton (Botterell et al. 2020; Procter et al. 2019).

Field and laboratory studies have demonstrated the wide and increasing range of organisms spanning numerous habitats and taxonomic levels that ingest microplastics, including fish (Lusher et al. 2013), seabirds (Puskic et al. 2020), zooplankton (Cole et al. 2015), corals (Hall et al. 2015), molluscs (Al-Sid-Cheikh et al. 2018; Green et al. 2017), and crustaceans (Watts et al. 2014; Welden and Cowie 2016). The first comprehensive review indicated that 177 species had ingested plastics (Laist 1997), which increased to 208 species (Gall and Thompson 2015), then 331 species (Kühn et al. 2015), and more recently 701 species were reported (Kühn and van Franeker 2020), illustrating the development in our understanding of species affected by plastic ingestion (Table 12.1). Many of the species were listed as near threatened, vulnerable, endangered, or critically endangered on the International Union for Conservation of Nature (IUCN) RedList (Gall and

Table 12.1 Summary of the number of species within each taxa documented to have ingested plastics, as reviewed by Laist (1997), Kühn et al. (2015), and Kühn and van Franeker (2020).

	Laist (1997)	Kühn et al. (2015)	Kühn and van Franeker (2020)
Seabirds			
Anseriformes (marine ducks)		1	2
Podicipediformes (grebes)	0	0	0
Phaethontiformes (tropicbirds)		2	2
Gaviiformes (loons)		3	4
Sphenisciformes (penguins)	1	5	5
Procellariiformes (tubenoses)	62	84	91
Pelecaniformes (pelicans)	8	2	3
Suliformes (gannets, cormorants)		12	15
Charadriiformes (gulls, terns, skuas, auks)	40	55	58
Total seabirds	**111**	**164**	**180**
Marine mammals			
Ursidae (polar bears)		0	0
Mustelidae (marine otters)	0	0	0
Pinnipedia (all seals)	2	12	15
Mysticeti (baleen whales)	2	7	8
Odontoceti (toothed whales)	21	40	44
Sirenia (manatees, dugongs)	1	3	2
Total marine mammals	**26**	**62**	**69**
Other taxa			
All turtles	6	7	7
All sea snakes	—	0	0
All fish	33	92	363
All invertebrates	1	6	82
Grand total	**177**	**331**	**701**

Thompson 2015), indicating additional anthropogenic stressors on already vulnerable species. Few taxa have been routinely monitored to investigate temporal trends in plastic ingestion; however, data from seabirds and turtles reveal that their ingestion frequency has increased over the past few decades (Senko et al. 2020). Large-scale monitoring of northern fulmars (*Fulmarus glacialis*) has indicated that between 1969 and 2010, both the incidence of ingestion and the mass of plastics ingested have increased (Avery-Gomm et al. 2012). Although these studies are valuable in assessing the temporal trends in the quantities of plastics ingested, understanding the impacts remains more challenging (discussed in Section 12.3).

12.3 The Impacts of Microplastic Ingestion on Marine Organisms

With a growing geographical database of wild collected biota that had ingested microplastics (e.g. fish; Wang et al. 2020), there is increasing focus to determine whether the presence of these materials is hazardous to organisms. Studies have reported detrimental impacts caused by microplastic ingestion across different levels of biological organization (Rochman et al. 2016), from those at the individual-level (including subcellular, cellular, and organ-specific effects) to ecosystem-level effects (Sections 12.3.1–12.3.3). Reporting the presence of microplastics in an organism does not indicate harmful consequences. As with all xenobiotic compounds (i.e. chemical substances found within an organism that are not naturally produced by that organism; or otherwise), there will be a concentration or dose at which negative effects (i.e. toxicological) will begin to be observed, indicating a decline in health. The exposure concentrations where toxicological effects begin to be observed are likely to change depending on the physicochemical properties of the plastic (e.g. size, shape, polymer, and associated chemicals), the organism and its life history.

12.3.1 Individual-Level Impacts

The result of the microplastic exposure can lead to effects at different levels of biological functioning, including those on the individual, at site-specific target organs, on certain cell types, and even subcellular effects. Once ingested, microplastics can either remain in the gut, or if the particles are smaller than that of the cells lining the gut lumen (which will vary between organisms), they may be absorbed across the gut tissue and into the animal. In both of these scenarios, microplastics may be egested by the organism with no detrimental effects (Jovanović et al. 2018), or direct toxicity due to the physical impacts of plastic ingestion, or indirect toxicity related to the release of chemicals from the plastic may occur (see Section 12.4).

Direct physical impacts may occur whereby microplastics block the gastrointestinal tract or microplastics may interact with and irritate the cells lining the gut tissue, which may cause the mucous present to slough away (Williams et al. 2015). This sloughing effect is finite, and if exhausted will reveal the underlying tissue, causing further damage to the underlying musculature.

When trying to understand the effects of ingestion, fish have widely been studied through the incorporation of microplastics to a diet that can be fed to fish at a fixed dose for a period of time. The effect of microplastics on fish following ingestion varies widely between observed and no-observed effects. *Medaka* displayed altered gene expression, following a two-month dietary exposure to virgin PE and to PE that had previously been weathered in the environment for three months (Rochman et al. 2014). Downregulation of choriogenin (Chg H) occurred in males, and downregulation of vitellogenin, Chg H, and the estrogen receptor (ERα) was documented in females, indicating plastic exposure can cause an endocrine-disrupting effect (Rochman et al. 2014). Another study which fed *Medaka* diets containing 0.01, 0.1, or 1.0% of microplastics isolated from environmental samples caused death, decreased head-to-body ratios, and alterations to swimming behavior in larvae, in a dose-dependent manner (Pannetier et al. 2020). Following 60–90 days exposure to 0.1% polyvinyl chloride (PVC) microplastics, there is some evidence of intestinal upset, with the presence of edema of the tissue layers making up the gut in seabass (Pedà et al. 2016). However, fish fed a diet containing 0.01% microplastics showed no effect on growth rate, pathology in the intestine or liver to gilthead bream (Jovanović et al. 2018). This may represent a concentration-dependent effect in the exposures of the two studies.

Prolonged exposure to plastics or other xenobiotics can upset normal functioning of oxidative pathways, causing build-ups of potentially toxic by-products (e.g. superoxide) known as oxidative stress. These molecules are often highly charged, with the ability to damage subcellular components such as proteins and DNA. In laboratory studies, they can be measured either directly (e.g. reactive oxygen species) or indirectly through associated detoxification enzyme concentrations (e.g. catalase [CAT]) or damaged products (e.g. thiobarbituric acid reactive substances [TBARS]). These end points have been common among microplastic exposures; however, there is no clear consensus on these systems. For example, fish fed a diet containing 33.3 mg/kg microplastics for five days showed significant elevation in CAT, glutathione-*S*-transferase (GST), and superoxide dismutase activity and TBARS concentrations compared to control fish where no microplastics were present (Zitouni et al. 2020). However, fish fed PS microplastics for 28 days showed no effects on hepatic CAT or GST activity (Ašmonaite et al. 2018). To unravel the effect of particle size and polymer, a systematic approach needs adopting.

12.3.2 Population-Level Impacts

As summarized in the previous section, a number of detrimental impacts can occur to an organism as a result of ingesting microplastics. Whether or not risk is posed to a population as a whole depends on a number of factors including the life history of a species (e.g. rate of reproduction), foraging strategy, species range, and the population size. Individual-level effects, such as reduced feeding ability (Bergami et al. 2016; Yin et al. 2018) or altered reproduction (Sussarellu et al. 2016), may affect an entire population by causing an overall population decline or can cause successive generations to become less evolutionarily fit. For example, copepods, which had been exposed continuously to microplastics over two generations, showed increased mortality rates across life stages and a higher proportion of the female egg sacs failed to develop (Lee et al. 2013). The study indicates that there could be detrimental impacts to recruitment on successive generations, ultimately causing a reduction in the population size and in turn reducing food availability for higher trophic levels. Sussarellu et al. (2016) reported that oysters exposed to micro-PS particles produced 38% fewer oocytes and sperm velocity was reduced by 23%; also, there were marked carryover effects with significant impacts on progeny, potentially reducing evolutionary fitness. Observation of polychlorinated biphenyls (PCBs) in the soft tissues of the lugworm *Arenicola marina* following ingestion of PS microplastics with surface-sorbed PCBs (Besseling et al. 2013) showed these could reduce overall fitness.

Filter-feeding megafauna (i.e. mobulid rays, filter-feeding sharks, and baleen whales) may be susceptible to high levels of microplastic pollution and exposure to any associated contaminants due to their feeding strategy, life history, and habitat overlap with dense aggregations of plastics located in the gyres (Eriksen et al. 2013; Law et al. 2010), as well as in other regions such as the Coral Triangle (Germanov et al. 2018; Worm et al. 2017). Within manta ray feeding areas in the Coral Triangle, it was found that between 4.4 and 62.7 pieces of microplastics could be ingested per hour, depending on the season (dry/wet) (Germanov et al. 2019). While the extent of the impact of microplastic ingestion by filter-feeding megafauna is not fully understood, populations are already threatened with other anthropogenic pressures such as poaching, by-catch from fisheries, habitat destruction, and boat strikes. Nearly half of mobulid rays, two-thirds of filter-feeding sharks, and over a quarter of baleen whale species are listed by the IUCN as globally threatened (IUCN RedList) and are prioritized for conservation. Megafauna exhibit k-selective life history strategies, which are characterized by slow reproductive rates, late sexual maturity, and low offspring numbers, meaning populations can be slow to recover after decline. Marine megafauna are charismatic species, with the potential to act as flagship species for marine conservation (Bowen-Jones and Entwistle 2002). The use of iconic megafauna as flagship species can bring awareness to the impacts of microplastics to marine life, enhancing communication and public engagement, and stimulating community action (Pahl et al. 2017).

As mass production of plastics only commenced within the past 70 years, plastics in the marine environment present a relatively novel substrate for the colonization and dispersal of species. Bacteria that colonize plastics were shown to differ from the surrounding water (Zettler et al. 2013), sediment (Harrison et al. 2014), and colonizing nonplastic/natural debris (Ogonowski et al. 2018). As such, plastics provide a different ecological niche to natural debris, supporting different populations and communities of bacteria. Furthermore, plastics offer a vector for long-range dispersal of organisms. While natural materials, such as wood and seaweeds, tend to degrade and sink within months, plastics persist over much longer time scales (decades or longer) and so offer a mechanism for species to be transported over much greater distances (Barnes et al. 2009; Barnes and Milner 2004) and time scales. With the quantities of plastics in the marine environment increasing over the past seven decades (Borrelle et al. 2020), the potential for plastic-associated dispersal presents a viable opportunity for the movement of species. Indeed, some 270 species have been identified to disperse via plastic debris, including some invasive species (Secretariat of the Convention on Biological Diversity and the Scientific and Technical Advisory Panel—GEF, 2012). This list was expanded a few years later to include a further 25 taxa, including bryozoans, molluscs, crustaceans, and polychaetes, that had not been previously reported in rafting assemblages (Goldstein et al. 2014). Plastic debris stranded in northern Spain was found to contain three different invasive species (Miralles et al. 2018). If an invasive species is able to establish and proliferate outside its native distribution, this may threaten native species due to increased resource competition. Such effects could cascade through the ecosystem and the Convention on Biological Diversity indicates that this is both a biological and economic challenge (Secretariat of the Convention on Biological Diversity, 2016).

12.3.3 Ecosystem-Level Impacts

To date, few studies have quantified the effects of microplastic pollution on ecosystem functioning. In part, this is due to the profound challenges in linking suborganism-level effects to the ecosystem level. Yet, it is the ecosystem-wide consequences of a pollutant that bring the greatest concern. Ecosystem-wide effects could result where sublethal effects on a particular species or population prevent them from performing certain functions on which other parts of the ecosystems rely, for example bioturbation of sediments, or carbon and nutrient export.

Bioturbation of sediments by plants and animals is a fundamental process redistributing nutrients and oxygen across the benthic boundary layer and altering the habitat structure for other benthic organisms (Meadows et al. 2012). After a two-month exposure to PVC-containing sediment, the lugworm *A. marina* showed a significant reduction in feeding activity and the passage of this material through the gut was 1.5 times slower (Wright et al. 2013). Extrapolating this to the Wadden Sea, the authors report that this could mean that 130 m^3 less sediment is reworked annually. Another study exposing *A. marina* to PE, PVC, and the biodegradable polymer polylactic acid-containing sediments also reports reduced feeding and burrowing activity, causing a 10–16% reduction in burrow surface area and hence less water and nutrient exchange (Green et al. 2016). The behavior and action of bioturbators could alter the distribution of microplastics within the sediment itself, enhancing mixing of microplastics into deeper sediments (Nakki et al. 2017) and interaction with infauna.

Mussels and clams are considered “ecosystem engineers” due to the fundamental role they play in creating biogenic reefs, which act as refugia and nursery grounds for diverse communities including commercially important seafood species. The reefs also play an important function in increasing turbulent mixing and particle resuspension, which provides food for filter feeders (Drost 2013). Green (2016) demonstrated that mussels that ingested microplastics had 50% less byssal attachment strength, potentially causing mortality through dislodgement by wave action and compromising their ability to form or maintain reef structures, which could have ramifications on the ecosystem as a whole.

Within the global ocean, the vertical flux of organic material, such as detritus and fecal pellets, is fundamental to the “biological pump” (Turner 2015), the mechanism by which carbon-containing compounds are exported to the deep ocean. Many species of zooplankton and mesopelagic fish undertake vertical migrations, travelling long distances from the epipelagic zone where they feed to the deeper ocean where they deposit fecal material. This provides carbon and nutrients to the ocean interior and the benthos and also promotes oceanic storage of atmospheric carbon (e.g. Buesseler 2012; Giering et al. 2014). Following the ingestion of microplastics, zooplankton species can expel them with other organic material. Laboratory studies utilizing some of the most commonly manufactured polymers, which were fed to zooplankton, showed that the subsequent microplastic containing fecal pellets had modified buoyancies compared to controls (Cole et al. 2016; Coppock et al. 2019). Those containing low-density polymers (PS, low-density PE) had reduced settling velocities, while those with high-density polymers (polyethylene terephthalate, polyamide) sunk at either the same or an increased rate to controls (Cole et al. 2016; Coppock et al. 2019). Extrapolating these results to the average depth of the ocean would hypothetically result in fecal pellets taking between 10 days less and 53 days longer to sink to the benthos respectively. While modifications to fecal pellet sinking rates have only been studied in copepods (Cole et al. 2016; Coppock et al. 2019) and Antarctic krill (Bergami et al. 2020), a considerable diversity of organisms are reported to ingest and subsequently expel microplastics (Nelms et al. 2018). If similar results are found across species and taxonomic assemblages, there could be profound ramifications to pelagic and benthic ecosystems on a global scale.

Increasing numbers of studies have shown that many lower trophic-level organisms are able to ingest microplastics. Microplastics may, therefore, be indirectly assimilated as a result of trophic transfer, whereby predators consume contaminated prey items and as such microplastics can spread through the food chain. Laboratory studies have shown that microplastics can be transferred indirectly between trophic levels, i.e. from prey to predator. The trophic transfer of microplastics has been recorded from mussels to crabs (Farrell and Nelson 2013; Watts et al. 2014), between planktonic trophic levels (Setälä et al. 2014) and between herring and captive seals (Nelms et al. 2018). Trophic transfer relies upon microplastics being retained in the body of an organism long enough for it to be predated upon, thereby passing on the plastics. The duration that microplastics remain within an organism following consumption are not well known and results differ considerably between species. Mussels can rapidly (within 24 hours) expel the majority of ingested microplastics in their pseudofeces (Goncalves et al. 2019; Woods et al. 2018); however, this rate may slow when food is abundant (Chae and An 2020). Copepods display microplastic retention rates comparable to natural food items (Vroom et al. 2017), while egestion of microplastics by the planktivorous fish *Seriolella violacea* took on average 7 days (longer than food items) and 49 days at most (Ory et al. 2018). Small microplastic particles also have the ability to translocate once ingested (Al-Sid-Cheikh et al. 2018; Browne et al. 2008; von Moos et al. 2012), increasing the potential for them to be retained in an organism's body and be passed to higher trophic predators.

12.4 Impacts of Plastic-Associated Chemicals on Organisms

During production, chemicals are added to plastics to alter or improve their desired properties, such as plasticizers, flame-retardants, antimicrobial agents, or UV inhibitors. Many of these additive chemicals, such as bisphenol A, polybrominated diphenyl ethers (PBDE), and phthalates, are also known to be endocrine-disrupting compounds, owing to their ability to modulate the endocrine system. These additive chemicals can subsequently leach from the plastic into the environment (Markic et al. 2019; Turner 2018) or, if ingested, into organisms (Bakir et al. 2014; Coffin et al. 2019; Hermabessiere et al. 2017). Studies have indicated that plastic additives can cause toxicological impacts, such as mortality; however, attributing impacts to specific chemical compounds remains challenging (Bejgarn et al. 2015; Gandara et al. 2016).

In addition to the chemicals intentionally added into plastics, other compounds present in the environment due to agricultural and industrial processes may become adsorbed onto microplastics. Toxic hydrophobic organic compounds, often termed "persistent organic pollutants" (POPs) due to their slow degradation rates, have been identified in plastics collected from the environment (Mato et al. 2001; Rios et al. 2007; Teuten et al. 2009). Samples of plastics pellets collected globally were found to have adsorbed PCBs, hexachlorocyclohexane (HCH) pesticides and dichlorodiphenyltrichloroethane (DDT), and its breakdown products dichlorodiphenyldichloroethane and dichlorodiphenyldichloroethylene (Ogata et al. 2009). Indeed, plastics have been shown to readily adsorb hydrophobic organic chemicals, such as polycyclic aromatic hydrocarbons (PAHs) and HCHs (Lee et al. 2014). Microplastics in the presence of up to 25 ng/g of different PCB congeners can bind up to 65% present in solution (Llorca et al. 2020). Due to their large surface area-to-volume ratio, microplastics can acquire a considerable loading of chemicals, up to six orders of magnitude greater than in the surrounding seawater (Hirai et al. 2011; Mato et al. 2001). These chemicals can remain attached to the surface of the microplastic and can dissociate once ingested (Teuten et al. 2009), where they can potentially become bioavailable for uptake across the gut. A recent study indicated that although bioavailable to copepods, microplastic-sorbed PAHs did not cause significant toxicity (Sørensen et al. 2020), while other studies have shown altered gene expression following exposure to microplastic sorbed with contaminants (PCBs, brominated flame retardants, perfluorinated chemicals, PAHs, PCBs, PBDEs) (Rainieri et al. 2018; Rochman et al. 2013).

Although studies indicate that microplastic-associated POPs can be transferred once the microplastics are ingested (Athey et al. 2020), it is not clear what role microplastics play, compared to other sources of exposure, i.e. uptake through food. Modeling studies suggest that the amount of hydrophobic organic contaminants sorbed onto plastic is expected to be negligible (<0.001%; Koelmans et al. 2016). Even under modeled gut conditions, the co-exposure of ingested microplastics with DDT, phenanthrene, and bis-2-ethylhexyl phthalate is minimum compared to other routes (water or diet alone rather than microplastic; Bakir et al. 2016).

12.4.1 Laboratory Studies: Limitations and Discrepancies Between Laboratory and Field Observations

Despite growing knowledge of the ubiquitous presence of microplastics in the environment, assessing the risks they pose to marine life is challenging and, in part, is hampered by the variability in laboratory protocols and types of microplastic particle used (de Ruijter et al. 2020; Hermsen et al. 2018).

There are many technical challenges to performing robust laboratory exposures that are environmentally representative. Some of these challenges surround the exposure conditions; for instance, exposing animals to microplastics via the ambient water can lead to incidental ingestion, making it difficult to extrapolate whether any observed effects are from exposure via the gill or gut, or both. Another challenge that has been commonly identified in the literature is the concentration of microplastics used in laboratory experiments, which often exceeds those detected in the environment (Burns and Boxall 2018; Lenz et al. 2016). However, selecting appropriate microplastic concentrations are, for laboratory studies, confounded by the high variability of microplastics reported between different environmental studies, localities, and sampling methods (Barrows et al. 2017; Kanhai et al. 2017; Rist et al. 2020), making it difficult to suggest a single environmentally realistic concentration. Further, the abundance of small microplastics in the natural environment is very likely to a have been underestimated due to methodological constrains. For example, surface water samples are typically collected with a 333-μm aperture net, resulting in the absence of data for smaller microplastic sizes (GESAMP 2016). This is an area of particular concern as smaller microplastic particles are bioavailable to a wider range of organisms such as zooplankton (Botterell et al. 2019; Vroom et al. 2017). Under sampling of smaller microplastics in the environment means that there are few estimates that can contribute toward making laboratory methodologies more relevant to environmental conditions, and very few that can simulate environmental concentrations of nanoplastic particles in a laboratory setting (Al-Sid-Cheikh et al. 2018).

Within the environment, thermoplastics such as PE, polypropylene, PS, and polyethylene terephthalate occur most frequently (SAPEA 2019) and are thus likely to be ingested. Field studies often report the occurrence of polyester, polyamide, and acrylic fibers, which can contribute to >90% of the total microplastics ingested for certain species (Beer et al. 2018; Courtene-Jones et al. 2017). The majority of laboratory studies have, however, used spherical PS microplastics to examine impacts; while beads are ingested by wild populations, fibers and fragments are more typically identified (Burns and Boxall 2018). One reason why PS spheres are so widely used is their commercial availability in reproducible form, whereas microfibers would have to be extracted from larger materials before use. Microplastics, which were previously underrepresented in laboratory studies, in terms of polymers, morphologies, and sizes, are increasingly receiving research focus (Al-Sid-Cheikh et al. 2018; Bucci et al. 2020; Cole et al. 2020), which will advance understanding of the impacts posed by these different particles.

12.5 Conclusion

Over the past 40 years, an increasing number of organisms spanning different habitats, taxonomic groups, and feeding guilds have been reported to ingest microplastics. By comparison, the ecotoxicological impacts of ingesting microplastics and the mechanisms by which these are caused are still poorly understood. Challenges in addressing the impacts of microplastics are, in part, presented by the (i) diversity and complexity of physicochemical properties of “microplastics,” (ii) variability and environmental relevancy of laboratory protocols, and (iii) physiology and life history of the study species. Evidence shows that microplastics and their associated co-contaminants can cause detrimental impacts to organisms across all levels of biological organization, from subcellular to ecosystem-wide effects (Section 12.4). Exposure to microplastics can trigger inflammatory responses, oxidative stress, and suppressed feeding and reproduction, which over successive generations may reduce evolutionary fitness. Increasing numbers of studies have shown that many lower trophic-level organisms are able to ingest microplastics and may suffer detrimental impacts.

What this effect, at the base of the food chain, may have for long-term productivity and resilience of the ecosystem is unknown, especially when considering cumulative impacts with other anthropogenic pollutants in a warming climate (Horton and Barnes 2020; Lamb et al. 2018; Welden and Lusher 2017). There is broad consensus between the public, policy makers, and industry that the current levels of plastic pollution in the environment are unacceptable. Continued efforts are, therefore, required to reduce plastic inputs and to focus research to address key knowledge gaps regarding the impacts of microplastics and their associated chemicals on marine life and the environment as a whole, which can help to inform and prioritize solutions.

References

Al-Sid-Cheikh, M., Rowland, S. J., Stevenson, K., et al. (2018). Uptake, whole-body distribution, and depuration of nanoplastics by the scallop *Pecten maximus* at environmentally realistic concentrations. *Environmental Science & Technology*, 52: 14480–14486. doi:10.1021/acs.est.8b05266

Ašmonaite, G., Larsson, K., Undeland, I., et al. (2018). Size matters: ingestion of relatively large microplastics contaminated with environmental pollutants posed little risk for fish health and fillet quality. *Environmental Science & Technology*, 52: 14381–14391. doi:10.1021/acs.est.8b04849

Athey, S. N., Albotra, S. D., Gordon, C. A., et al. (2020). Trophic transfer of microplastics in an estuarine food chain and the effects of a sorbed legacy pollutant. *Limnology and Oceanography Letters*, 5: 154–162. doi:10.1002/lol2.10130

Avery-Gomm, S., O'Hara, P. D., Kleine, L., et al. (2012). Northern fulmars as biological monitors of trends of plastic pollution in the eastern North Pacific. *Marine Pollution Bulletin*, 64: 1776–1781. doi:10.1016/j.marpolbul.2012.04.017

Bakir, A., O'Connor, I. A., Rowland, S. J., et al. (2016). Relative importance of microplastics as a pathway for the transfer of hydrophobic organic chemicals to marine life. *Environmental Pollution*, 219: 56–65. doi:10.1016/j.envpol.2016.09.046

Bakir, A., Rowland, S. J., Thompson, R. C. (2014). Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions. *Environmental Pollution*, 185: 16–23. doi:10.1016/j.envpol.2013.10.007

Barnes, D. K., Galgani, F., Thompson, R. C., et al. (2009). Accumulation and fragmentation of plastic debris in global environments. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364: 1985–1998. doi:10.1098/rstb.2008.0205

Barnes, D. K. A., Milner, P. (2004). Drifting plastic and its consequences for sessile organism dispersal in the Atlantic Ocean. *Marine Biology*, 146: 815–825. doi:10.1007/s00227-004-1474–1478.

Barrows, A. P. W., Neumann, C. A., Berger, M. L., et al. (2017). Grab vs. neuston tow net: a microplastic sampling performance comparison and possible advances in the field. *Analytical Methods*, 9: 1446–1453. doi:10.1039/c6ay02387h

Beer, S., Garm, A., Huwer, B., et al. (2018). No increase in marine microplastic concentration over the last three decades – a case study from the Baltic Sea. *Science of the Total Environment*, 621: 1272–1279. doi:10.1016/j.scitotenv.2017.10.101

Beiras, R., Bellas, J., Cachot, J., et al. (2018). Ingestion and contact with polyethylene microplastics does not cause acute toxicity on marine zooplankton. *Journal of Hazardous Materials*, 360: 452–460. doi:10.1016/j.jhazmat.2018.07.101

Bejgarn, S., Macleod, M., Bogdal, C., et al. (2015). Toxicity of leachate from weathering plastics: an exploratory screening study with *Nitocra spinipes*. *Chemosphere*, 132: 114–119. doi:10.1016/j.chemosphere.2015.03.010

Bergami, E., Bocci, E., Vannuccini, M. L., et al. (2016). Nano-sized polystyrene affects feeding, behavior and physiology of brine shrimp *Artemia franciscana* larvae. *Ecotoxicology and Environmental Safety*, 123: 18–25. doi:10.1016/j.ecoenv.2015.09.021

Bergami, E., Manno, C., Cappello, S., et al. (2020). Nanoplastics affect moulting and faecal pellet sinking in Antarctic krill (*Euphausia superba*) juveniles. *Environment International*, 143. doi:10.1016/j.envint.2020.105999

Bergmann, M., Mützel, S., Primpke, S., et al. (2019). White and wonderful? Microplastics prevail in snow from the Alps to the Arctic. *Science Advances*, 5: eaax1157.

Besseling, E., Wegner, A., Foekema, E. M., et al. (2013). Effects of microplastic on fitness and PCB bioaccumulation by the lugworm *Arenicola marina* (L.). *Environmental Science & Technology*, 47: 593–600. doi:10.1021/es302763x

Bjorndal, K. A., Bolten, A. B., Lagueux, C. J. (1994). Ingestion of marine debris by juvenile sea turtles in coastal Florida habitats. *Marine Pollution Bulletin*, 28: 154–158. https://doi.org/10.1016/0025-326X(94)90391-3

Borrelle, S. B., Ringma, J., Law, K. L., et al. (2020). Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. *Science*, 369: 1515–1518. doi:10.1126/science.aba3656

Botterell, Z. L. R., Beaumont, N., Cole, M., et al. (2020). Bioavailability of microplastics to marine zooplankton: effect of shape and infochemicals. *Environmental Science & Technology*, 54: 12024–12033. doi:10.1021/acs.est.0c02715

Botterell, Z. L. R., Beaumont, N., Dorrington, T., et al. (2019). Bioavailability and effects of microplastics on marine zooplankton: a review. *Environmental Pollution*, 245: 98–110.

Bour, A., Haarr, A., Keiter, S., et al. (2018). Environmentally relevant microplastic exposure affects sediment-dwelling bivalves. *Environmental Pollution*, 236: 652–660. doi:10.1016/j.envpol.2018.02.006

Bowen-Jones, E., Entwistle, A. (2002). Identifying appropriate flagship species: the importance of culture and local contexts. *Oryx*, 36: 189–195. doi:10.1017/s0030605302000261

Browne, M. A., Dissanayake, A., Galloway, T. S., et al. (2008). Ingested microscopic plastic translocates to the circulatory system of the mussel, *Mytilus edulis* (L.). *Environmental Science & Technology*, 42: 5026–5031.

Browne, M. A., Galloway, T. S., Thompson, R. C. (2010). Spatial patterns of plastic debris along estuarine shorelines. *Environmental Science & Technology*, 44: 3404–3409. doi:10.1021/es903784e

Bucci, K., Tulio, M., Rochman, C. M. (2020). What is known and unknown about the effects of plastic pollution: a meta-analysis and systematic review. *Ecological Applications*, e02044.

Buchanan, J. B. (1971). Pollution by synthetic fibres. *Marine Pollution Bulletin*, 2: 23. https://doi.org/10.1016/0025-326X(71)90136-6

Buesseler, K. O. (2012). The great iron dump. *Nature*, 487: 305–306.

Burns, E. E., Boxall, A. B. A. (2018). Microplastics in the aquatic environment: evidence for or against adverse impacts and major knowledge gaps. *Environmental Toxicology and Chemistry*, 37: 2776–2796. doi:10.1002/etc.4268

Cadée, G. C. (2002). Seabirds and floating plastic debris. *Marine Pollution Bulletin*, 44: 1294–1295.

Carbery, M., O'Connor, W., Palanisami, T. (2018). Trophic transfer of microplastics and mixed contaminants in the marine food web and implications for human health. *Environment International*, 115: 400–409. doi:10.1016/j.envint.2018.03.007

Carpenter, E. J., Anderson, S. J., Harvey, G. R., et al. (1972). Polystyrene spherules in coastal waters. *Science*, 178: 749–750. doi:10.1126/science.178.4062.749

Carpenter, E. J., Smith, K. L. (1972). Plastics on the sargasso sea surface. *Science*, 175: 1240–1241. doi:10.1126/science.175.4027.1240

Chae, Y., An, Y.-J. (2020). Effects of food presence on microplastic ingestion and egestion in *Mytilus galloprovincialis*. *Chemosphere*, 240: 124855 (6 pages). doi:10.1016/j.chemosphere.2019.124855

Coffin, S., Huang, G. Y., Lee, I., et al. (2019). Fish and seabird gut conditions enhance desorption of estrogenic chemicals from commonly-ingested plastic items. *Environmental Science & Technology*, 53: 4588–4599. doi:10.1021/acs.est.8b07140

Cole, M., Liddle, C., Consolandi, G., et al. (2020). Microplastics, microfibres and nanoplastics cause variable sub-lethal responses in mussels (*Mytilus* spp.). *Marine Pollution Bulletin*, 160: 111552. doi:10.1016/j.marpolbul.2020.111552

Cole, M., Lindeque, P., Fileman, E., et al. (2015). The impact of polystyrene microplastics on feeding, function and fecundity in the marine copepod *Calanus helgolandicus*. *Environmental Science & Technology*, 49: 1130–1137. doi:10.1021/es504525u

Cole, M., Lindeque, P. K., Fileman, E., et al. (2016). Microplastics alter the properties and sinking rates of zooplankton faecal pellets. *Environmental Science & Technology*, 50: 3239–3246. doi:10.1021/acs.est.5b05905

Coppock, R. L., Galloway, T. S., Cole, M., et al. (2019). Microplastics alter feeding selectivity and faecal density in the copepod, *Calanus helgolandicus*. *Science of the Total Environment*, 687: 780–789. doi:10.1016/j.scitotenv.2019.06.009

Courtene-Jones, W., Quinn, B., Ewins, C., et al. (2020). Microplastic accumulation in deep-sea sediments from the Rockall Trough. *Marine Pollution Bulletin*, 154: 111092. doi:10.1016/j.marpolbul.2020.111092

Courtene-Jones, W., Quinn, B., Gary, S. F., et al. (2017). Microplastic pollution identified in deep-sea water and ingested by benthic invertebrates in the Rockall Trough, North Atlantic Ocean. *Environmental Pollution*, 231: 271–280. doi:10.1016/j.envpol.2017.08.026

Da Costa Araújo, A. P., DE Andrade Vieira, J. E., Malafaia, G. (2020). Toxicity and trophic transfer of polyethylene microplastics from *Poecilia reticulata* to *Danio rerio*. *Science of the Total Environment*, 742: 140217. doi:10.1016/j.scitotenv.2020.140217

De Ruijter, V. N., Redondo-Hasselerharm, P. E., Gouin, T., et al. (2020). Quality criteria for microplastic effect studies in the context of risk assessment: a critical review. *Environmental Science & Technology*, 54: 11692–11705. doi:10.1021/acs.est.0c03057

Drost, E. (2013). *Hydrodynamics over a patch structure on an intertidal mussel bed*. MSc, Universiteit Utrecht. p. 64.

Eriksen, M., Maximenko, N., Thiel, M., et al. (2013). Plastic pollution in the South Pacific subtropical gyre. *Marine Pollution Bulletin*, 68: 71–76. doi:10.1016/j.marpolbul.2012.12.021

Farrell, P., Nelson, K. (2013). Trophic level transfer of microplastic: *Mytilus edulis* (L.) to *Carcinus maenas* (L.). *Environmental Pollution*, 177: 1–3. doi:10.1016/j.envpol.2013.01.046

Franeker, J. A. V. (1985). Plastic Ingestion in the North Atlantic Fulmar. *Marine Pollution Bulletin*, 16: 367–369.

Fred-Ahmadu, O. H., Bhagwat, G., Oluyoye, I., et al. (2020). Interaction of chemical contaminants with microplastics: principles and perspectives. *Science of the Total Environment*, 706: 135978. doi:10.1016/j.scitotenv.2019.135978

Fry, D. M., Fefer, S. I., Sileo, L. (1987). Ingestion of plastic debris by Laysan Albatrosses and wedge-tailed shearwaters in the Hawaiian Islands. *Marine Pollution Bulletin*, 18: 339–343.

Furness, R. W. (1985). Ingestion of plastic particles by seabirds at Gough Island, South Atlantic Ocean. *Environmental Pollution (Series A)*, 38: 261–272.

Gall, S. C., Thompson, R. C. (2015). The impact of debris on marine life. *Marine Pollution Bulletin*, 92: 170–179. doi:10.1016/j.marpolbul.2014.12.041

Galloway, T. S., Cole, M., Lewis, C. (2017). Interactions of microplastic debris throughout the marine ecosystem. *Nature Ecology & Evolution*, 1: 116. doi:10.1038/s41559-017-0116

Gandara, E. S. P. P., Nobre, C. R., Resaffe, P., et al. (2016). Leachate from microplastics impairs larval development in brown mussels. *Water Research*, 106: 364–370. doi:10.1016/j.watres.2016.10.016

Germanov, E. S., Marshall, A. D., Bejder, L., et al. (2018). Microplastics: no small problem for filter-feeding megafauna. *Trends in Ecology & Evolution*, 33: 227–232. doi:10.1016/j.tree.2018.01.005

Germanov, E. S., Marshall, A. D., Hendrawan, I. G., et al. (2019). Microplastics on the menu: plastics pollute Indonesian Manta Ray and whale shark feeding grounds. *Frontiers in Marine Science*, 6: 1–21. doi:10.3389/fmars.2019.00679

GESAMP (2016). *Sources, Fate and Effects of Microplastics in the Marine Environment: Part Two of a Global Assessment*. IMO/FAO/UNESCO-IOC/ÚNIDO/WMO/IAEA/UN/UNEP/UNDP, 220.

Geyer, R., Jambeck, J. R., Law, K. L. (2017). Production, use, and fate of all plastics ever made. *Science Advances*, 3: e1700782. doi:10.1126/sciadv.1700782

Giering, S. L., Sanders, R., Lampitt, R. S., et al. (2014). Reconciliation of the carbon budget in the ocean's twilight zone. *Nature*, 507: 480–483. doi:10.1038/nature13123

Goldstein, M. C., Carson, H. S., Eriksen, M. (2014). Relationship of diversity and habitat area in North Pacific plastic-associated rafting communities. *Marine Biology*, 161: 1441–1453. doi:10.1007/s00227-014-2432-8

Goncalves, C., Martins, M., Sobral, P., et al. (2019). An assessment of the ability to ingest and excrete microplastics by filter-feeders: a case study with the Mediterranean mussel. *Environmental Pollution*, 245: 600–606. doi:10.1016/j.envpol.2018.11.038

Green, D. S. (2016). Effects of microplastics on European flat oysters, *Ostrea edulis* and their associated benthic communities. *Environmental Pollution*, 216: 95–103. doi:10.1016/j.envpol.2016.05.043

Green, D. S., Boots, B., Blockley, D. J., et al. (2015). Impacts of discarded plastic bags on marine assemblages and ecosystem functioning. *Environmental Science & Technology*, 49: 5380–5389. doi:10.1021/acs.est.5b00277

Green, D. S., Boots, B., O'Connor, N. E., et al. (2017). Microplastics affect the ecological functioning of an important biogenic habitat. *Environmental Science & Technology*, 51: 68–77. doi:10.1021/acs.est.6b04496

Green, D. S., Boots, B., Sigwart, J., et al. (2016). Effects of conventional and biodegradable microplastics on a marine ecosystem engineer (*Arenicola marina*) and sediment nutrient cycling. *Environmental Pollution*, 208: 426–434. doi:10.1016/j.envpol.2015.10.010

Hall, N. M., Berry, K. L. E., Rintoul, L., et al. (2015). Microplastic ingestion by Scleractinian corals. *Marine Biology*, 162: 725–732. doi:10.1007/s00227-015-2619-7

Harrison, J. P., Schratzberger, M., Sapp, M., et al. (2014). Rapid bacterial colonization of low-density polyethylene microplastics in coastal sediment microcosms. *BMC Microbiology*, 14: 1–15.

Hermabessiere, L., Dehaut, A., Paul-Pont, I., et al. (2017). Occurrence and effects of plastic additives on marine environments and organisms: a review. *Chemosphere*, 182: 781–793. doi:10.1016/j.chemosphere.2017.05.096

Hermsen, E., Mintenig, S. M., Besseling, E., et al. (2018). Quality criteria for the analysis of microplastic in biota samples: a critical review. *Environmental Science & Technology*, 52: 10230–10240. doi:10.1021/acs.est.8b01611

Hirai, H., Takada, H., Ogata, Y., et al. (2011). Organic micropollutants in marine plastics debris from the open ocean and remote and urban beaches. *Marine Pollution Bulletin*, 62: 1683–1692. doi:10.1016/j.marpolbul.2011.06.004

Hodgson, D. J., Brechon, A. L., Thompson, R. C. (2018). Ingestion and fragmentation of plastic carrier bags by the amphipod *Orchestia gammarellus*: effects of plastic type and fouling load. *Marine Pollution Bulletin*, 127: 154–159. doi:10.1016/j.marpolbul.2017.11.057

Horton, A. A., Barnes, D. K. A. (2020). Microplastic pollution in a rapidly changing world: implications for remote and vulnerable marine ecosystems. *Science of the Total Environment.* doi:10.1016/j.scitotenv.2020.140349

Jâms, I. B., Windsor, F. M., Poudevigne-Durance, T., et al. (2020). Estimating the size distribution of plastics ingested by animals. *Nature Communications*, 11. doi:10.1038/s41467-020-15406-6

Jovanović, B., Gokdag, K., Guven, O., et al. (2018). Virgin microplastics are not causing imminent harm to fish after dietary exposure. *Marine Pollution Bulletin*, 130: 123–131. doi:10.1016/j.marpolbul.2018.03.016

Kanhai, D. K., Gardfeldt, K., Krumpen, T., et al. (2020). Microplastics in sea ice and seawater beneath ice floes from the Arctic Ocean. *Scientific Reports*, 10: 5004. doi:10.1038/s41598-020-61948-6

Kanhai, D. K., Officer, R., Lyashevska, O., et al. (2017). Microplastic abundance, distribution and composition along a latitudinal gradient in the Atlantic Ocean. *Marine Pollution Bulletin*, 115: 307–314. doi:10.1016/j.marpolbul.2016.12.025

Koelmans, A. A., Bakir, A., Burton, G. A., et al. (2016). Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies. *Environmental Science & Technology*, 50: 3315–3326. doi:10.1021/acs.est.5b06069

Kooi, M., Nes, E. H. V., Scheffer, M., et al. (2017). Ups and downs in the ocean: effects of biofouling on vertical transport of microplastics. *Environmental Science & Technology*, 51: 7963–7971. doi:10.1021/acs.est.6b04702

Kühn, S., Bravo Rebolledo, E. L., Van Franeker, J. A. (2015). Deleterious effects of litter on marine life. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), *Marine Anthropogenic Litter*. Springer Open, Cham; New York. 75–116.

Kühn, S., Van Franeker, J. A. (2020). Quantitative overview of marine debris ingested by marine megafauna. *Marine Pollution Bulletin*, 151: 110858. doi:10.1016/j.marpolbul.2019.110858

Laist, D. W. (1987). Overview of the biological effects of lost and discarded plastic debris in the marine environment. *Marine Pollution Bulletin*, 18: 319–326. https://doi.org/10.1016/S0025-326X(87)80019-X

Laist, D. W. (1997). Impacts of marine debris: entanglement of marine life in marine debris including a comprehensive list of species with entanglement and ingestion records. *In:* Coe, J. M., Rogers, D. B. (eds.) *Marine Debris*. Springer. 319–326.

Lamb, J. B., Willis, B. L., Fiorenza, E. A., et al. (2018). Plastic waste associated with disease on coral reefs. *Science*, 359: 460–462.

Law, K. L., Moret-Ferguson, S., Maximenko, N. A., et al. (2010). Plastic accumulation in the North Atlantic subtropical gyre. *Science*, 329: 1185–1188. doi:10.1126/science.1192321

Lee, H., SHIM, W. J., Kwon, J. H. (2014). Sorption capacity of plastic debris for hydrophobic organic chemicals. *Science of the Total Environment*, 470–471: 1545–1552. doi:10.1016/j.scitotenv.2013.08.023

Lee, K. W., Shim, W. J., Kwon, O. Y., et al. (2013). Size-dependent effects of micro polystyrene particles in the marine copepod *Tigriopus japonicus*. *Environmental Science & Technology*, 47: 11278–11283. doi:10.1021/es401932b

Lenz, R., Enders, K., Nielsen, T. G. (2016). Microplastic exposure studies should be environmentally realistic. *Proceedings of the National Academy of Sciences of the United States of America*, 113: E4121–E4122. doi:10.1073/pnas.1606615113

Llorca, M., Abalos, M., Vega-Herrera, A., et al. (2020). Adsorption and desorption behaviour of polychlorinated biphenyls onto microplastics' surfaces in water/sediment systems. *Toxics*, 8(3): 59. doi:10.3390/toxics8030059

Lobelle, D., Cunliffe, M. (2011). Early microbial biofilm formation on marine plastic debris. *Marine Pollution Bulletin*, 62: 197–200. doi:10.1016/j.marpolbul.2010.10.013

Lusher, A. L., Mchugh, M., Thompson, R. C. (2013). Occurrence of microplastics in the gastrointestinal tract of pelagic and demersal fish from the English Channel. *Marine Pollution Bulletin*, 67: 94–99. doi:10.1016/j.marpolbul.2012.11.028

Markic, A., Gaertner, J.-C., Gaertner-Mazouni, N., et al. (2019). Plastic ingestion by marine fish in the wild. *Critical Reviews in Environmental Science and Technology*: 1–41. doi:10.1080/10643389.2019.1631990

Mato, Y., Isobe, T., Takada, H., et al. (2001). Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environmental Science & Technology*, 35: 318–324. doi:10.1021/es0010498

Meadows, P. S., Meadows, A., Murray, J. M. H. (2012). Biological modifiers of marine benthic seascapes: their role as ecosystem engineers. *Geomorphology*, 157–158: 31–48. doi:10.1016/j.geomorph.2011.07.007

Miralles, L., Gomez-Agenjo, M., Rayon-Viña, F., et al. (2018). Alert calling in port areas: marine litter as possible secondary dispersal vector for hitchhiking invasive species. *Journal for Nature Conservation*, 42: 12–18. doi:10.1016/j.jnc.2018.01.005

Nakki, P., Setala, O., Lehtiniemi, M. (2017). Bioturbation transports secondary microplastics to deeper layers in soft marine sediments of the northern Baltic Sea. *Marine Pollution Bulletin*, 119: 255–261. doi:10.1016/j.marpolbul.2017.03.065

Nelms, S. E., Galloway, T. S., Godley, B. J., et al. (2018). Investigating microplastic trophic transfer in marine top predators. *Environmental Pollution*, 238: 999–1007. doi:10.1016/j.envpol.2018.02.016

Ogata, Y., Takada, H., Mizukawa, K., et al. (2009). International Pellet Watch: global monitoring of persistent organic pollutants (POPs) in coastal waters. 1. Initial phase data on PCBs, DDTs, and HCHs. *Marine Pollution Bulletin*, 58: 1437–1446. doi:10.1016/j.marpolbul.2009.06.014

Ogonowski, M., Motiei, A., Ininbergs, K., et al. (2018). Evidence for selective bacterial community structuring on microplastics. *Environmental Microbiology*, 20: 2796–2808. doi:10.1111/1462-2920.14120

Ory, N. C., Gallardo, C., Lenz, M., et al. (2018). Capture, swallowing, and egestion of microplastics by a planktivorous juvenile fish. *Environmental Pollution*, 240: 566–573. doi:10.1016/j.envpol.2018.04.093

Pahl, S., Wyles, K. J., Thompson, R. C. (2017). Channelling passion for the ocean towards plastic pollution. *Nature Human Behaviour*, 1: 697–699. doi:10.1038/s41562-017-0204-4

Pannetier, P., Morin, B., Le Bihanic, F., et al. (2020). Environmental samples of microplastics induce significant toxic effects in fish larvae. *Environment International*, 134: 105047. doi:10.1016/j.envint.2019.105047

Pedà, C., Caccamo, L., Fossi, M. C., et al. (2016). Intestinal alterations in European sea bass *Dicentrarchus labrax* (Linnaeus, 1758) exposed to microplastics: preliminary results. *Environmental Pollution*, 212: 251–256. doi:10.1016/j.envpol.2016.01.083

Peng, J., Wang, J., Cai, L. (2017). Current understanding of microplastics in the environment: occurrence, fate, risks, and what we should do. *Integrated Environmental Assessment and Management*, 13: 476–482. doi:10.1002/ieam.1912

Procter, J., Hopkins, F. E., Fileman, E. S., et al. (2019). Smells good enough to eat: dimethyl sulfide (DMS) enhances copepod ingestion of microplastics. *Marine Pollution Bulletin*, 138: 1–6. doi:10.1016/j.marpolbul.2018.11.014

Puskic, P. S., Lavers, J. L., Bond, A. L. (2020). A critical review of harm associated with plastic ingestion on vertebrates. *Science of the Total Environment*, 743: 140666. doi:10.1016/j.scitotenv.2020.140666

Rainieri, S., Conlledo, N., Larsen, B. K., et al. (2018). Combined effects of microplastics and chemical contaminants on the organ toxicity of zebrafish (*Danio rerio*). *Environmental Research*, 162: 135–143. doi:10.1016/j.envres.2017.12.019

Rios, L. M., Moore, C., Jones, P. R. (2007). Persistent organic pollutants carried by synthetic polymers in the ocean environment. *Marine Pollution Bulletin*, 54: 1230–1237. https://doi.org/10.1016/j.marpolbul.2007.03.022

Rist, S., Vianello, A., Winding, M. H. S., et al. (2020). Quantification of plankton-sized microplastics in a productive coastal Arctic marine ecosystem. *Environmental Pollution*, 266: 115248. doi:10.1016/j.envpol.2020.115248

Rochman, C. M., Browne, M. A., Underwood, A. J., et al. (2016). The ecological impacts of marine debris: unraveling the demonstrated evidence from what is perceived. *Ecology*, 97: 302–312.

Rochman, C. M., Hoh, E., Kurobe, T., et al. (2013). Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress. *Scientific Reports*, 3: 3263. doi:10.1038/srep03263

Rochman, C. M., Kurobe, T., Flores, I., et al. (2014). Early warning signs of endocrine disruption in adult fish from the ingestion of polyethylene with and without sorbed chemical pollutants from the marine environment. *Science of the Total Environment*, 493: 656–661. doi:10.1016/j.scitotenv.2014.06.051

SAPEA (2019). *A Scientific Perspective on Microplastics in Nature and Society*. In: *Evidence Review Report No. 4*. Science Advice for Policy by European Academies. 176.

Savoca, S., Capillo, G., Mancuso, M., et al. (2019). Microplastics occurrence in the Tyrrhenian waters and in the gastrointestinal tract of two congener species of seabreams. *Environmental Toxicology and Pharmacology*, 67: 35–41. doi:10.1016/j.etap.2019.01.011

Secretariat of the Convention on Biological Diversity (2016). Marine Debris: Understanding, Preventing and Mitigating the Significant Adverse Impacts on Marine and Coastal Biodiversity. *Technical Series No.*83: 78.

Secretariat of the Convention on Biological Diversity and the Scientific and Technical Advisory Panel—GEF (2012). *Impacts of Marine Debris on Biodiversity: Current Status and Potential Solutions*. Technical Series Report Number 67. Secretariat of the Convention on Biological Diversity and the Scientific and Technical Advisory Panel—GEF, Montreal. ISBN 92-9225-444-8.

Senko, J. F., Nelms, S. E., Reavis, J. L., et al. (2020). Understanding individual and population-level effects of plastic pollution on marine megafauna. *Endangered Species Research*, 43: 234–252. doi:10.3354/esr01064

Setälä, O., Fleming-Lehtinen, V., Lehtiniemi, M. (2014). Ingestion and transfer of microplastics in the planktonic food web. *Environmental Pollution*, 185: 77–83. doi:10.1016/j.envpol.2013.10.013

Shaw, D. G., Day, R. H. (1994). Colour- and form-dependent loss of plastic micro-debris from the North Pacific Ocean. *Marine Pollution Bulletin*, 28: 39–43. https://doi.org/10.1016/0025-326X(94)90184-8

Sørensen, L., Rogers, E., Altin, D., et al. (2020). Sorption of PAHs to microplastic and their bioavailability and toxicity to marine copepods under co-exposure conditions. *Environmental Pollution*, 258: 113844. doi:10.1016/j.envpol.2019.113844

Sussarellu, R., Suquet, M., Thomas, Y., et al. (2016). Oyster reproduction is affected by exposure to polystyrene microplastics. *Proceedings of the National Academy of Sciences of the United States of America*, 113: 2430–2435. doi:10.1073/pnas.1519019113

Teuten, E. L., Saquing, J. M., Knappe, D. R., et al. (2009). Transport and release of chemicals from plastics to the environment and to wildlife. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364: 2027–2045. doi:10.1098/rstb.2008.0284

Thompson, R. C., Olsen, Y., Mitchell, R. P., et al. (2004). Lost at sea: where is all the plastic. *Science*, 304: 838.

Turner, A. (2018). Mobilisation kinetics of hazardous elements in marine plastics subject to an avian physiologically-based extraction test. *Environmental Pollution*, 236: 1020–1026. doi:10.1016/j.envpol.2018.01.023

Turner, J. T. (2015). Zooplankton fecal pellets, marine snow, phytodetritus and the ocean's biological pump. *Progress in Oceanography*, 130: 205–248. doi:10.1016/j.pocean.2014.08.005

Von Moos, N., Burkhardt-Holm, P., Kohler, A. (2012). Uptake and effects of microplastics on cells and tissue of the blue mussel *Mytilus edulis* L. after an experimental exposure. *Environmental Science & Technology*, 46: 11327–11335. doi:10.1021/es302332w

Vroom, R. J. E., Koelmans, A. A., Besseling, E., et al. (2017). Aging of microplastics promotes their ingestion by marine zooplankton. *Environmental Pollution*, 231: 987–996. doi:10.1016/j.envpol.2017.08.088

Walkinshaw, C., Lindeque, P. K., Thompson, R., et al. (2020). Microplastics and seafood: lower trophic organisms at highest risk of contamination. *Ecotoxicology and Environmental Safety*, 190: 110066. doi:10.1016/j.ecoenv.2019.110066

Wang, W., Ge, J., Yu, X. (2020). Bioavailability and toxicity of microplastics to fish species: a review. *Ecotoxicology and Environmental Safety*, 189: 109913. doi:10.1016/j.ecoenv.2019.109913

Watts, A. J., Lewis, C., Goodhead, R. M., et al. (2014). Uptake and retention of microplastics by the shore crab *Carcinus maenas*. *Environmental Science & Technology*, 48: 8823–8830. doi:10.1021/es501090e

Welden, N. A., Abylkhani, B., Howarth, L. M. (2018). The effects of trophic transfer and environmental factors on microplastic uptake by plaice, *Pleuronectes plastessa*, and spider crab, *Maja squinado*. *Environmental Pollution*, 239: 351–358. doi:10.1016/j.envpol.2018.03.110

Welden, N. A., Lusher, A. L. (2017). Impacts of changing ocean circulation on the distribution of marine microplastic litter. *Integrated Environmental Assessment and Management*, 13: 483–487. doi:10.1002/ieam.1911

Welden, N. A. C., Cowie, P. R. (2016). Long-term microplastic retention causes reduced body condition in the langoustine, *Nephrops norvegicus*. *Environmental Pollution*, 218: 895–900. doi:10.1016/j.envpol.2016.08.020

Werner, S., Budziak, A., van Franeker, J., et al. (2016). *Harm caused by Marine Litter* MSFD GES TG Marine Litter – Thematic Report; JRC Technical report. doi:10.2788/690366.

Williams, J. M., Duckworth, C. A., Burkitt, M. D., et al. (2015). Epithelial cell shedding and barrier function: a matter of life and death at the small intestinal villus tip. *Veterinary Pathology*, 52: 445–455. doi:10.1177/0300985814559404

Woods, M. N., Stack, M. E., Fields, D. M., et al. (2018). Microplastic fiber uptake, ingestion, and egestion rates in the blue mussel (*Mytilus edulis*). *Marine Pollution Bulletin*, 137: 638–645. doi:10.1016/j.marpolbul.2018.10.061

Worm, B., Lotze, H. K., Jubinville, I., et al. (2017). Plastic as a persistent marine pollutant. *Annual Review of Environment and Resources*, 42: 1–26. doi:10.1146/annurev-environ-102016-060700

Wright, S. L., Thompson, R. C., Galloway, T. S. (2013). The physical impacts of microplastics on marine organisms: a review. *Environmental Pollution*, 178: 483–492. doi:10.1016/j.envpol.2013.02.031

Wyles, K. J., Pahl, S., Thomas, K., et al. (2016). Factors that can undermine the psychological benefits of coastal environments: exploring the effect of tidal state, presence, and type of litter. *Environment and Behavior*, 48: 1095–1126. doi:10.1177/0013916515592177

Yin, L., Chen, B., Xia, B., et al. (2018). Polystyrene microplastics alter the behavior, energy reserve and nutritional composition of marine jacopever (*Sebastes schlegelii*). *Journal of Hazardous Materials*, 360: 97–105. doi:10.1016/j.jhazmat.2018.07.110

Zettler, E. R., Mincer, T. J., Amaral-Zettler, L. A. (2013). Life in the "plastisphere": microbial communities on plastic marine debris. *Environmental Science & Technology*, 47: 7137–7146. doi:10.1021/es401288x

Zitouni, N., Bousserrhine, N., Missawi, O., et al. (2020). Uptake, tissue distribution and toxicological effects of environmental microplastics in early juvenile fish *Dicentrachus labrax*. *Journal of Hazardous Materials*. doi:10.1016/j.jhazmat.2020.124055

13

Microplastics in Fish and Seafood Species

Amy L. Lusher[1,2] *and Garth A. Covernton*[3]

[1] *Norwegian Institute for Water Research (NIVA), Oslo, Norway*
[2] *Department of Biological Science, University of Bergen, Bergen, Norway*
[3] *Department of Ecology and Evolutionary Biology, University of Toronto, Toronto, Ontario, Canada*

13.1 Introduction

Microplastics and other small anthropogenic items are now regularly identified in the global environment, and the interactions between animals and this heterogeneous contaminant have not gone unnoticed. Researchers have focused on the ingestion of these particles by different species from small planktonic organisms to large invertebrates, fish, birds, and mammals. The widespread nature of microplastics means that they can be ingested by a variety of animals, including species of commercial interest like fish and shellfish. Research has begun to be directed toward the consequences that microplastics can have on seafood species, not only to the individual organisms themselves but also to the production of sustainable fish and seafood value chains; an important topic within the United Nations Sustainable Development Goals.

Researchers have been investigating the consequences of interactions between seafood species and microplastics since the 1970s, with the number of studies released each year now growing exponentially. Despite some initial struggle with methodologies in the early years of publishing on microplastics, studies currently tend to have a much stronger focus on optimizing methods, rigorously testing approaches, and harmonizing methods and results where possible (Brander et al. 2020; Cowger et al. 2020; Dehault et al. 2019), although more work in this area needs to be done. As of 2020, 60% of the most farmed aquaculture species and 80% of the most caught fish have been investigated for the presence of microplastics (Walkinshaw et al. 2020), although the lack of harmonized approaches often makes it difficult to compare studies. There is, however, some potential for probabilistic methods to harmonize data by accounting for missing data, such as smaller size categories in certain studies (Koelmans et al. 2020; Kooi and Koelmans 2019).

For many seafood species, other than bivalves, the digestive tract is commonly removed prior to consumption, while microplastics investigations have focused on the digestive tracts of animals – stomachs and intestines. Researchers have only recently begun to utilize methods allowing the observation of microplastics as well as nanoplastics in the edible tissues of fish and other seafood species, beginning in 2018 (Abbasi et al. 2018; Akhbarizadeh et al. 2018). In this way, our best estimates of human exposure to microplastics via seafood come primarily from the consumption of bivalve species, for which whole-body studies have been conducted since the early days of

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

microplastics research (Van Cauwenberghe and Janssen 2014; Walkinshaw et al. 2020). Additional complexities arise when considering smaller microplastics and nanoplastics (<100 μm) which are currently very difficult to identify, and attempts to quantify them are highly prone to contamination. New technologies are beginning to address these issues, but it is still early days in the study of these smaller particles.

Recent literature on microplastics in the human diet, including seafood (Cox et al. 2019) has led to a great deal of public concern relating to the consumption of microplastics. While recent findings of high numbers of microplastics released from teabags and baby bottles (Hernandez et al. 2019; Li et al. 2020) may have begun to shift public attention away from seafood, much of the early media coverage on microplastics was related to seafood, especially fish and shellfish. This may have led to concerned consumers reducing their seafood consumption. While research has not yet provided a complete picture of the degree to which various seafood items are contaminated with microplastics, our knowledge of the contamination of other food items is limited to a much greater extent (Cox et al. 2019). In order to characterize any health risks arising for humans due to exposure to microplastic *via* seafood, consumption will need to be considered in the context of global and regional intake and in proportion to other food items and their degree of contamination.

If we want to understand the risk to humans, we need to use comparable, validated, and harmonized (and where possible – standardized) approaches, an aspect of microplastic research that has been identified to compromise risk assessments for both the environment and human health (VKM 2019). The FAO conducted a thorough review of this situation in 2016 (Lusher et al. 2017) which was followed by a barrage of publications investigating uptake and implications to individual species. Since 2016, at least 353 studies on fish, 187 on bivalves, 1 on cephalopods, and 27 on seafood arthropod species have been published. The high variety of commercially important seafood species reported to contain microplastics includes many of the most caught (tonnage) wild and aquaculture species (Lusher and Welden 2020). The goal of this chapter is not to repeat the assessment conducted in 2016 (Lusher et al. 2017) or subsequent detailed reviews on seafood uptake (Walkinshaw et al. 2020), but rather to present an update on the status of knowledge surrounding microplastics in fish and seafood species and the consequences to the seafood supply chain.

13.2 How Microplastics Can Enter Seafood and Transfer to Humans

Seafood species can uptake microplastics through a variety of pathways, such as in a wild or aquaculture setting. The most studied routes are via ingestion, either directly from the environment or indirectly via trophic transfer from prey (detailed in Walkinshaw et al. 2020). The extent to which either of these pathways occurs may depend on the feeding and/or dietary strategy of individual species. Microplastics can also end up in the gills and digestive tracts of animals due to the unintentional intake of microplastics in seawater during respiration. Ingested and inhaled microplastics will mostly be egested by the animal, although there is some potential for translocation and accumulation to occur in tissues beyond the digestive tract, which could lead to human consumption.

13.2.1 Seaweed and Aquatic Plants

Seaweeds are important ingredients in many kinds of seafood, especially in Asian and Polynesian cuisine (Mouritsen et al. 2018). Compared to other groups of organisms, macroalgae and macrophytes, including seaweeds and seagrasses, are far less studied, with few investigations into either the external presence of microplastics or the impacts of microplastics on their growth and developments (Gao et al. 2021). Consequently, only limited research has been carried out on the quantities of microplastics present in seaweeds consumed as seafood.

Gao et al. (2020) demonstrated that seaweed can concentrate microplastics from seawater, with *Ulva prolifera* collected from beaches in Qingdao, China containing an average abundance of 4603.3 particles/kg dry weight, and Feng et al. (2020a) further showed that drifting *U. prolifera* concentrated microplastics (830.0 particles/g wet weight) at levels higher than attached seaweed (490.0 particles/g wet weight). Feng et al. (2020b) found mean concentrations of 0.06–0.19 particles/g wet weight trapped by six species of cultured macroalgae in China. It appears that the microplastics adhere to thali on seaweed surfaces and become trapped. The presence of microplastics associated with seaweeds has been raised as a possible route of entry for microplastics into food supply chains as seaweeds are used in animal feed and food products for humans. Given that seaweeds are often described as a superfood and there is increasing cultivation as an aquaculture product (Sundbæk et al. 2018), it is necessary to conduct further investigations into the concentration of microplastics and potential transfer to consumers. There is already some evidence showing that seaweed can represent a pathway for microplastic uptake by herbivorous gastropods and fish (Goss et al. 2018; Gutow et al. 2016).

In the first study to look at direct human exposure to microplastics through the consumption of processed seaweed, between 0.9 and 3.0 particles/g microplastics were identified in 24 brands of commercially packaged nori *Pyropia* spp. (Li et al. 2020). It is possible that the preparation processes contributed to the number of microplastics identified. Washing was seen to remove 94.5% of trapped particles from *Fucus* sp. (Sundbæk et al. 2018), but this was not the case for washing *Pyropia* sp. (Li et al. 2020). The former was a laboratory method whereas the latter was conducted in commercial processing facilities. In addition, the packaging process may also contribute to microplastics identified in commercial products. Future research should investigate the introduction of microplastics throughout the processing chain of seaweed products.

There is also potential for smaller microplastics and nanoplastics, which are mostly missed by current quantification methodologies, to transfer to humans, either attached to the surface or internalized into the cells of seaweed, but little to no research has been done in this area. For instance, Y. Chen et al. (2020) reported that microalgae could internalize 2-μm or smaller-sized polystyrene microbeads within their cells, although it is not clear whether their methods were stringent enough to measure only the particles and not any leached fluorescent dye (Schür et al. 2019). Further work is needed to determine whether these findings apply to macroalgae and whether other polymer types and particle shapes can be internalized and transferred by seaweeds.

13.2.2 Bivalves

Bivalve mollusks that are commonly consumed as seafood include clams, oysters, mussels, and scallops. Most of the bivalves are filter-feeders and can efficiently capture particles in the size range of 5–300 μm, with some, less-efficient capture occurring for smaller particles, dependent on species (Ward et al. 2019a). During human consumption, the entire soft body of bivalves is usually eaten, which is part of the reason they have received so much attention as a transfer risk for humans. While many publications have stated that bivalves are non-selective filter feeders, they perform particle selection on their gills – also with labial palps for some species – and reject many particles prior to ingestion *via* accumulation and removal as pseudofeces. In general, spheres approaching 1 mm will be rejected nearly 100% of the time, with decreasing rejection rates down to around 20–30% for particles below 100 μm, while fibers are consistently rejected, across size ranges, about 20%–80% of the time (Ward et al. 2019b). Once ingested, the majority of microplastics are egested following a period of between nine hours and five days, with smaller particles the slowest to be passed and potentially able to remain in tissues for longer periods (Fernández and Albentosa 2019; Graham et al. 2019; Van Cauwenberghe and Janssen 2014; Woods et al. 2018).

Studies over large spatial scales have reported mixed results in terms of patterns in bivalve microplastic concentrations, with several studies finding associations between bivalve concentrations and sources of pollution (Bråte et al. 2018, Klasios et al. 2021), and others not (Cho et al. 2021; Li et al. 2018). Where associations exist, they are primarily for highly contaminated areas, suggesting that accumulation potential is low, and thus minimal transfer risk to humans when environmental contamination is not high. Given the above evidence, it is likely that human exposure to microplastics - as a result of bivalves directly ingesting the particles - will primarily relate to the degree of microplastic contamination in the time just preceding harvest in the area where the animals were grown if no depuration is performed (Section 13.3.2).

13.2.3 Crustaceans

Crustaceans consumed as seafood are primarily within the order Decapoda, including crabs, lobsters, crayfish, and shrimp. Krill may also be consumed, although most often it is the extracted oils that are consumed as supplements. This route has yet to be investigated, but the oils are highly processed so contamination would likely occur during the refinement and packaging of the oils. Crabs, lobsters, and crayfish are primarily generalist scavengers and predators, and consume a wide range of food items. However, there are some decapods that use suspension feeding, capturing particles from the water column. For example, the Norway lobster (*Nephrops norvegicus*), an important commercial fishery species in Europe, has been demonstrated to feed on particulate organic material for nearly half of its diet (Santana et al. 2020). *N. norvegicus* has also been demonstrated to show a high frequency of microplastic ingestion (67%–98% of individuals), and it is possible that its scavenging feeding strategy, combined with particulate filtering from the water column, would make it more susceptible to ingesting microplastics (Cau et al. 2019; Hara et al. 2020; Murray and Cowie 2011; Welden and Cowie 2016). Decapod stomachs contain a chitinous foregut, known as the gastric mill, which may slow the passing of fibrous microplastics, especially fiber bundles, through their digestive tracts leading to accumulation (McGoran et al. 2020; Murray and Cowie 2011; Torn 2020). The animals might then later be able to shed these accumulated particles in their stomach lining during moulting (Welden and Cowie 2016).

The digestive tracts of larger decapod crustaceans, such as crabs, lobsters, and crayfish, which are expected to accumulate the most microplastics, are generally not consumed as seafood, and usually, muscles are eaten. However, microplastics have been detected in the edible portion of some crustaceans, including in abdominal muscles of the commercial shrimp species *Pleoticus muelleri*, the exoskeleton, muscle, and gills of the tiger prawn *Panaeus semisulcatus*, and the soft tissues of the crab *Portunus pelagicus*, suggesting that microplastics can be transferred to humans *via* consumption of other parts of decapod crustaceans (Abbasi et al. 2018; Akhbarizadeh et al. 2019; Daniel et al. 2021; Fernández Severini et al. 2020). In contrast, the edible tissues of the shrimp *Metapenaeus dobsoni* and *Fenneropenaeus indicus* were not found to contain microplastics (Daniel et al. 2021). In a laboratory study, >20 μm microplastic particles could not translocate into the tissue of the brown shrimp *Crangon crangon*, following ingestion, suggesting that it is the smaller, understudied fraction of microplastics that is most likely to transfer from crustaceans to humans (Devriese et al. 2015).

13.2.4 Other Invertebrate Species

Other animals that are eaten as seafood worldwide include cephalopods (squid and octopuses), gastropod mollusks (marine and freshwater snails), holothurians (sea cucumbers), and echinoids (sea urchins). The body parts commonly consumed as seafood are the mantle for squid, tentacles for octopuses, whole body for gastropods, muscle or whole body for sea cucumbers, and gonads for sea urchins. Overall, limited research has been conducted on species from these taxa. A single study found that the edible portions of the squid *Uroteuthis duvaucelii*, contained an average of 7.7 particles/kg (Daniel et al. 2020). Few to no studies have looked at a microplastic concentration in seafood gastropod species, although laboratory studies have shown that gastropod pedal mucus can retain suspected microplastic particles (Gutow et al. 2019). Mohsen et al. (2019) found 0–30 particles and 0–19 particles/individual in the intestines and coelomic fluid, respectively of farmed sea cucumbers *Apostichopus japonicus* in China. Murano et al. (2020) found that 10- and 45-μm polystyrene spheres could translocate into the gonads of the sea urchin *Paracentrotus lividus*. Interestingly, only 1% of 10-μm particles reached the gonads in contrast with 12% of 45-μm particles.

13.2.5 Fish

Fish species that are consumed as seafood come from a wide range of habitats, with a variety of feeding strategies, body sizes, and trophic positions. Variations in microplastics uptake by fish species are generally attributed to feeding strategy, gastrointestinal structure, and background contamination in a habitat (Walkinshaw et al. 2020). For example, planktivorous, filter-feeding species, such as many Engraulids and Clupeids (including anchovies and herring) may be more likely to consume microplastics from their environment. When nutrient-rich particle concentrations are high, these fish swim with their mouth open and filter particles from the water column using their gill rakers, generally only selecting by particle size, which might predispose them to ingest floating/suspended microplastics (Drenner et al. 1986; Heidman et al. 2012). Filter-feeding fish will also selectively particle feed under certain conditions (James and Findlay 1989), but might then selectively ingest microplastics due to the resemblance in size, shape, and/or color to prey (Ory et al. 2017, 2018). These factors might explain why filter-feeding, planktivorous species have been found to contain higher concentrations of microplastics in their viscera and gills in comparison with other seafood species (Daniel et al. 2020). On the other hand, piscivores would be expected to uptake microplastics either through trophic transfer via prey, or feedstock, or accidental ingestion when feeding.

Trophic transfer is the way in which microplastics can move from lower species to predatory species when microplastics have been internalized by the prey species (Miller et al. 2020; Walkinshaw et al. 2020). It can also refer to the transfer of microplastics from contaminated feedstock in aquaculture to the cultured species. Trophic transfer has been demonstrated to occur in fish and other organisms (Nelms et al. 2018; Welden et al. 2018). If particles are transferred and accumulated past a certain threshold, magnification would occur with increasing trophic position. If trophic biomagnification of microplastics is occurring, it would be expected that fish such as tuna and sharks, which feed at the top of marine food webs, would be exposed to the highest concentrations of microplastics and thus present the greatest risk to humans when eaten as seafood. However, current evidence suggests that larger microplastics (generally >100 μm) are not biomagnifying in the digestive tract of fishes, or seafood species in general (Covernton et al. 2021; Gouin 2020; Miller et al. 2020; Walkinshaw et al. 2020). Still, smaller microplastics might be able to translocate into certain tissues and organs, where they may accumulate and magnify (Collard et al. 2017).

Many commercial fish species have been investigated for the presence of microplastics (Danopoulos et al. 2020; Lusher and Welden 2020). When consumed, it is most often the body muscle of fish that is eaten, like a fillet, although smaller fish may also be eaten whole. The presence of microplastics in the digestive tracts of commercial species does not necessarily provide direct evidence for human exposure as these organs are not always consumed. However, non-edible tissues of fish are often used for other purposes, such as a fish meal for farmed animals (fish and poultry), which may further represent a route of entry into human food chains (Karbalaei et al. 2020). Current methodological limitations make it difficult to study the presence of smaller microplastics in fish fillets, although several results have emerged. Ribeiro et al. (2020) used pyrolysis to detect mass concentrations of plastics in the edible portions of various seafood and found that sardines contained more than 6× as much plastic as crabs, and crabs more than 3× as much as oysters, with squids and prawns containing the lowest concentrations. Daniel et al. (2020) examined the difference in presence of microplastics between edible (muscle and skin) and inedible (gill and viscera) portions of nine commercially important pelagic fish from Kerala, India. The authors found that 41.1% of the inedible tissues contained microplastics compared with 7% of edible tissues. In contrast, Akoueson et al. (2020) found evidence of microplastics present in the gills and digestive tracts of several seafood fish species, but not in the edible flesh. Zeytin et al. (2020) experimentally incorporated 1–5 μm fluorescently-labeled microspheres into feed for European sea bass *Dicentrachus labrax* and found that one particle reached the fish fillet for every 1.8×10^7 ingested microplastics particles, which is equivalent to 0.00005% of particles. This suggests that translocation of ingested microplastics will be minimal in fish, although further work is needed.

13.2.6 Other Marine Vertebrates (Mammals and Sea Turtles)

Even though mammals and reptiles are consumed as seafood in some places around the world, there have been limited investigations into microplastic presence in these species (Duncan et al. 2019; Zantis et al. 2021). Of the studies that do exist most focus on digestive tracts, which are not consumed by humans. Some studies have looked into the guts of hunted whales and seals (including commercial and community hunts), these studies have shown limited microplastics quantities, and are yet to investigate edible tissues. For example, Beluga whale species, *Delphinapterus leucas* hunted in the Northwest Territories, Canada were found to have between 18 and 147 microplastics in their digestive tracts (Moore et al. 2020) whereas no microplastics were identified in any of the 142 seals harvested from communities around Nunavut, Canada (Bourdages et al. 2020). Some investigations on the blubber of live individuals suggest that chemicals associated with plastics can be identified (Panti et al. 2019), although concentrations could be associated with transfer from larger plastic or already contaminated prey species.

13.3 Microplastics in the Seafood Supply Chain

As shown above, microplastics that are internalized by, or in terms of seaweeds – adhered to, species targeted as seafood could represent one way in which microplastics enter the seafood supply chain. Microplastics may further be introduced along the seafood supply chain up from culture and capture to the preparation of meals by vendors or during preparation by the consumer (Figure 13.1).

13.3.1 Culture and Harvesting Conditions

Animals harvested from the wild or culture facilities can ingest microplastics from the capture environment as well as during the collection process. In some studies, microplastics matching the fishing equipment have been identified in the digestive tract of fish (Lusher et al. 2013; Neto et al. 2020; Possatto et al. 2011). It has been suggested that species grown or reared in mariculture and aquaculture facilities might be exposed more to microplastics due to the use of ropes, nets, cages, fences, and feeding tubes (Gomiero et al. 2020; Jang et al. 2020; Kazmiruk et al. 2018; Lv et al. 2020). Where aquaculture intensity is high and seawater turnover is low, the use of plastic equipment might contribute to the ingestion of microplastic by the cultured animals (Chen et al. 2018, B. Chen et al. 2020). However, where aquaculture activity is diffuse and seawater turnover high, the ingestion of microplastics by cultured animals will primarily be determined by other inputs (Covernton et al. 2019; Li et al. 2016; Schoof and DeNike 2017). Individuals may be exposed to microplastics through their feed as well. Several previous studies have shown that fish feed contains microplastics (Castelvetro et al. 2020; Gündoğdu et al. 2021; Hanachi et al. 2019; Lv et al. 2020). Furthermore, fish meals produced from fish waste pose an additional risk. As they are made from fish waste including digestive tracts and other inedible tissues, microplastic exposure could be at a higher level for cultured species (Daniel et al. 2020; Gomiero et al. 2020; Hantoro et al. 2019).

13.3.2 Processing

Microplastics could also be introduced into seafood products during processing. For example, Li et al. (2020) found that the intermediate processing stages during the commercial production of nori had increased numbers of larger microplastic particles (1–5 mm) compared with the preprocessed samples. Fish and seafood are processed in many different ways, including cleaning, depuration, deshelling, sold alive, cooked, filtered, dried, frozen, and canned.

During ***Depuration*** contaminant levels in bivalve shellfish are reduced by placing them in clean seawater in facilities where filtration rates are maximized, promoting the removal of harmful substances from the bivalves via the natural passing of waste (Lee et al. 2008). The shellfish aquaculture industry commonly uses this practice to remove contaminants such as fecal bacteria from individuals that growers have cultivated in areas where these microbes might occur in harmful amounts. This

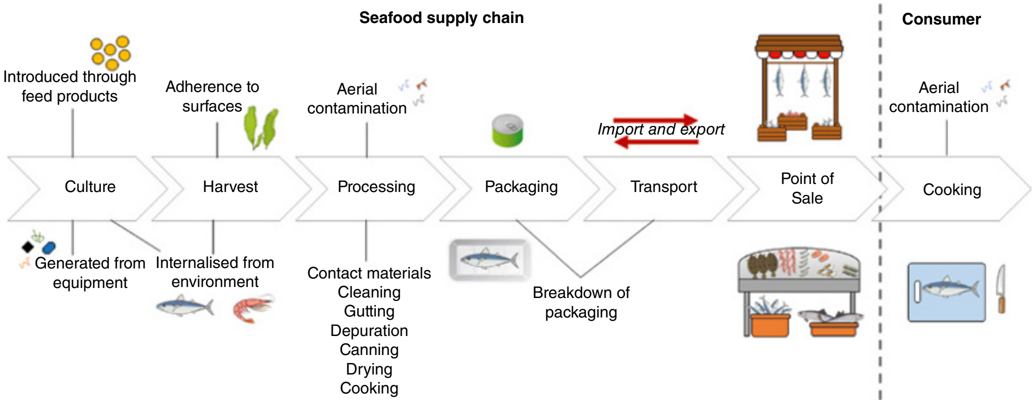


Figure 13.1 Potential routes for microplastics to enter seafood throughout the supply chain.

technique has also been used by microplastics researchers to clear microplastics from the digestive tracts of bivalves before analysis (Van Cauwenberghe and Janssen 2014). The feasibility and efficacy of depuration for eliminating microplastics from bivalves or other seafood, before human consumption has not yet been investigated from an industry perspective. Laboratory studies have shown that depurating bivalves for several days in clean seawater can lower the concentrations of microplastics present in their tissues (Van Cauwenberge and Janssen 2014, Saputri et al. 2020). It is possible that depurating shellfish could reduce the degree of microplastic contamination in shellfish harvested from highly contaminated areas; however, these studies were not carried out under large-scale depuration facility conditions. It is highly possible that background contamination from the depuration facility might be a potentially insurmountable issue, and the depuration tanks might become more concentrated in microplastics, due to settling and contamination from equipment, than the seawater from which the shellfish were harvested.

Canning is a widely used method for fish and shellfish preservation. Approximately 11% of the global consumption of fisheries products (17 million tonnes) of prepared and preserved fish, including canning (FAO 2020). Canning includes multiple steps which vary with the species used. Fish may be washed and dressed, soaked, have viscera removed, be precooked and steamed (Featherstone 2016). All of these steps could involve the introduction of airborne particles. Furthermore, additives such as salt may be included, which themselves may contain microplastics. Interestingly, a significant correlation was observed between the salt contents of canned fish and microplastics (Akhbarizadeh et al. 2020). The most important fish species which are canned are tuna, anchovies, bonito, sardines, and mackerels (ElShehawy and Farag 2019). During investigations of canned tuna and mackerel, Akhbarizadeh et al. (2020) found that 80% of samples had at least one particle. In contrast, Karami et al. (2018) reported that only 20% of 20 different brands of canned sardines and sprats displayed microplastics >149 μm. The source of the microplastics was unclear and was predicted to be from the fish themselves, food additives, as well as any contact materials during the cleaning and canning process. The presence of microplastics (as well as metals and other contaminants) has raised concerns for the hygiene and safety of canned seafood. Furthermore, sometimes high temperatures are used for sterilization and steaming. Microplastics have been shown to be affected by high temperatures which raise concern surrounding the release of any additive chemicals associated with these particles.

Gutting and filleting of fish may reduce the number of microplastics destined for dinner tables. The removal of viscera, gills, and digestive tracts will remove any internalized materials but not any micro- or nanoplastics that have translocated into the edible tissues of the fish. However, the processing phase itself may introduce microplastics to the surface of filets if there are microplastics on the work surfaces or settling from the factory air. The introduction of microplastics during this processing step should be further investigated as it is relevant not only in commercial settings but also in the home of the consumer preparing their meals.

Dried fish and shellfish are regular food commodities in Asia. In most instances, species are dried whole, including the viscera and gills. Karami et al. (2017) investigated samples of commonly consumed dried fish from local markets in Malaysia and found that the viscera and gills of these species contained fewer numbers of microplastics than the remaining flesh.

13.3.3 Packaging

Packaging could further introduce microplastics to the surface of food products. Two studies have thus far investigated microplastics generated from plastic food containers with size between 3 and 38 mg (Fadare et al. 2020) and 3 to 29 items per package (Du et al. 2020). Furthermore, packing materials could transfer the particles to the product, as has been shown for meat products (Kedzierski et al. 2020). No parallel studies are available for the packaging of seafood products.

13.3.4 Transport

Seafood products are often packaged in plastics before transport. The transport itself will probably not introduce microplastics to seafood products that are processed and packaged, although depending on how the products are handled, jostling, compressing, or exposure to sunlight might increase degradation of the packaging. The export and import of products such as frozen squid (Daniel et al. 2021) highlight that contaminated seafood products are not contained in one country. The exchange of goods within and between countries will influence how a risk assessment can be performed (Hantoro et al. 2019). There are currently no studies investigating how trade could be affected related to the growing evidence of microplastic contamination of products.

13.3.5 Cooking and Food Preparation

Recent work has demonstrated that microplastics are generated during the opening of plastic packaging, with generated numbers dependent on the type of plastic (thickness, density, stiffness) (Sobhani et al. 2020). As mentioned above, the packing materials may transfer microplastics to a food product. Whether these microplastics transfer to the consumer depends on the food preparation method. Kedzierski et al. (2020) found that microplastics were hard to remove from meat products by rinsing alone and that they could be cooked along with food. In contrast, cooking seafood in water might cause transfer into the cooking water and reduce the microplastics content in the food (Renzi et al. 2018). Heating seafood in plastic containers or using plastic cooking utensils might further contaminate the food with microplastics, especially of smaller fragments, as has been demonstrated to occur in large numbers when heating plastic baby bottles and tea bags (Hernandez et al. 2019; Li et al. 2020).

Microplastics may be introduced to seafood products by preparations before and at the point of sale the point of sale. An assessment of 41 different vendors of traditionally stuffed mussels at Turkish markets revealed that microplastic concentrations varied between vendors. The highest average concentrations were identified in Istanbul (0.9 particles/mussel, while the lowest number was found in Bodrum with 0.3 particles/mussel (Gündoğdu et al. 2020). Similarly, microplastics were identified in delicatessen products (fish, mussels, and tofu) from vendors at local markets in Thailand (40.6% of products, Tokhun and Somparn 2020). Supermarkets may also contribute to different levels of microplastics. Supermarket-bought seafood showed significantly different microplastics concentrations with pre-cooked mussels (1.4 per g) contaminated with more microplastics than live mussels (0.9 per g) (Li et al. 2018).

Further contamination can occur during both food preparation *via* fallout from indoor air. Catarino et al. (2018) estimated a fallout rate of 1 fiber per 4.32 cm^2 for mealtimes and 5 fibers per 4.32 cm^2 for cooking time during 20 minutes and calculated that a 12.5 cm dinner plate would receive 114 particles during a 20-minute mealtime. Assuming 33% microplastics, they estimated human ingestion of settled microplastics during evening meals as 13 731–68 415 particles/year.

13.4 Consequences of Microplastics in Seafood

Microplastics are a complex contaminant, with toxicity dependent on the size, shape, polymeric composition, environmentally adsorbed chemicals, and chemicals added during plastics production (Rochman et al. 2019). The consequences to specific species and the seafood supply chain will therefore be dependent on the type of microplastic contamination present in the environment of the harvested species, the processing area, and where preparation and consumption of the ultimate food product occurs. Furthermore, the transfer and toxicity of any adsorbed chemicals will depend on a variety of factors, including the plastic polymer type, its crystallinity, particle size, age, and degree of weathering, as well as environmental pH, salinity, and ionic strength, and the chemical properties of the contaminant (Fred-Ahmadu et al. 2020). As previously discussed, the lack of harmonization among methodologies used by microplastics researchers makes it even more difficult to perform risk assessments. As a result, there is currently limited data surrounding the complete potential for microplastics to adversely affect human and environmental health in the long term, which makes it difficult to inform management action and consumer advice or infer risk to seafood supply chains (Faraday 2019).

13.4.1 Producers and Consumers

Current evidence cannot determine whether there have been significant consequences for seafood producers related to the direct effects of contamination concerns surrounding microplastics. On the other hand, there is evidence that the industry may be adversely impacted, to some extent, by public perception of microplastics in seafood. As Deng et al. (2020) found in a survey of 437 Shanghai residents, 72.3% of respondents believed that microplastics entered human bodies via seafood, while 62.9% believed they entered via water and 49.4% via breathing air. When asked what actions they would take if they discovered that seafood contained microplastics, only 9.0% of respondents said that they would continue consumption as usual, compared with 16.6% who would consider using toothpaste as usual after discovering it contained microplastics. In 2019, Völker et al. reported that studies on microplastics in seafood were more likely to be covered by media articles communicating a higher level of concern in relation to studies demonstrating global abundance or effects on marine organisms. Reduced seafood consumption caused by concerns about microplastic would be in opposition to the advice from nutritional authorities recommending an increase in the consumption of seafood (Smith et al. 2018).

The high intake of seafood (fish and shellfish) in few countries has been raised as a concern for the potential implications on consumers and human health (Barboza et al. 2018). Studies from around the world have reported varying estimates of human consumption of microplastics from different seafood products (Table 13.1). A recent review and meta-analysis by Danopoulos et al. (2020) using reported seafood microplastics concentrations and FAO consumption data estimated global microplastics consumption at 0–27 825 particles/person/year for mollusks, 206–17 716 particles/person/year for crustaceans, and 31–8 323 particles/person/year for fish. They projected that the total maximum per person yearly uptake from all seafood could be as high as 53 864 particles based on average global seafood consumption, but could range up to 298 535 particles for Hong Kong, where per capita seafood consumption rates are high, especially of bivalve mollusks. This is within the same order of magnitude of yearly consumption for combined sources that have been reported by other studies (Cox et al. 2019). However, limited knowledge of microplastics contamination of other food groups or dose-dependent hazards to human health makes it currently impossible to conclude whether this level of exposure is detrimental to human health, either in the short or long term.

Seafood consumption is one of the pathways for human exposure to microplastics, but it might not be the biggest when compared to other routes of exposure. There are still several gaps existing in our understanding of human exposure pathways, especially red meat and poultry, dairy, vegetables, grains, and rice which occupy a large proportion of humans' diets. Considering that humans are exposed to microplastics in air, drinking water, and more commonly consumed foods, the relative dietary exposure from seafood consumption is likely to be low, and maybe overestimated (Barboza et al. 2018; Lusher et al. 2017). Many studies on microplastics in seafood report low concentrations. Possibly the best example of differing microplastic exposure concentrations for different exposure sources reported within a single study was demonstrated by Catarino et al. (2018) who showed that

Table 13.1 Estimated seafood dietary intake of microplastics by humans (could be horizontal).

Product type	Location	Seafood consumption (data source)	Plastic consumption rate	Reference
Molluscs	Global	2.5 kg/capita/year (FAO)	500–32 750 items/capita/year	Hantoro et al. (2019)
Molluscs	Europe	11.8–72.1 g/capita/day (EFSA)	1800–11 000 items/capita/year	Van Cauwenberghe and Janssen (2014)
Molluscs (*Mytilus* sp. and *Modiolus modiolus*)	Europe (Spain, France, Belgium)	3.08 kg/capita/year (SEAFISH)	4620 items/capita/year	Catarino et al. (2018)
Molluscs (*Mytilus sp. and Modiolus modiolus*)	UK	82 g (SEAFISH)	123 items/capita/year	Catarino et al. (2018)
Molluscs (5× species)	Iran	2.4 kg/capita/year (FAO)	4800 items/capita/year	Naji et al. (2018)
Mytilus edulis	Korea	0.67 g/capita/day (KNHANES)	29 items/capita/year	Cho et al. (2019)
Mytilus edulis	UK	100 g live mussels/portion 100 g frozen, chilled, or processed mussels/portion	100/100g portion 140/100g portion	Li et al. (2019)
Mytilus galloprovincialis	Tunisia	31.2 g/capita/year (consumer) 3510 g/capita/year (fisherman)	25 items/capita/year (consumer) 2757 items/capita/year (fisherman)	Abidli et al. (2019)
Mytilus sp. (stuffed – sold by street vendors)	Turkey		0–11 000 items/capita/year based on different portion sizes	Gündoğdu et al. (2020)
Crassostrea gigas	Korea	0.84 g/capita/day (KNHANES)	21 items/capita/year	Cho et al. (2019)
Crassostrea gigas	Tunisia	27.2 g/capita/year (consumer) 3060 g/capita/year (fisherman)	40 items/capita/year (consumer) 4437 items/capita/year (fisherman)	Abidli et al. (2019)
Carpet shell *Ruditapes decussatus*	Tunisia	30.4 g/capita/year (consumer) 3420 g/capita/year (fisherman)	44 items/capita/year (consumer) 4920 items/capita/year (fisherman)	Abidli et al. (2019)
Tapes philippinarum	Korea	1.25 g/capita/day (KNHANES)	155 items/capita/year	Cho et al. (2019)
Perna viridis, Meretrix meretrix	India	121 g per portion	3918 items/capita/year	Dowarah et al. (2020)
Patinopecten yessoensio	Korea	0.25 g/capita/day(KNHANES)	7 items/capita/year	Cho et al. (2019)
Scallop *Pectin maximus*	UK	7.5 kg/capita/year (DEFRA) 20.8 kg/capita/year (FAO)	1267 ± 679 items/capita/year 3494 ± 1872 items/capita/year	Akoueson et al. (2020)

(*Continued*)

Table 13.1 (Continued)

Product type	Location	Seafood consumption (data source)	Plastic consumption rate	Reference
Patagonian scallops *Zygochlamys patagonica*	UK	7.5 kg/capita/year (DEFRA) 20.8 kg/capita/year (FAO)	2449 ± 808 items/capita/year 6756 ± 2230 items/capita/year	Akoueson et al. (2020)
Hexaplex trunculus	Tunisia	39.2 g/capita/year (consumer) 4410 g/capita/year (fisherman)	28 items/capita/year (consumer) 3104 items/capita/year (fisherman)	Abidli et al. (2019)
Bolinus brandaris	Tunisia	21.6 g/capita/year (consumer) 2430 g/capita/year (fisherman)	23 items/capita/year (consumer) 2558 items/capita/year (fisherman)	Abidli et al. (2019)
Uroteuthis (Photololigo) duvaucelii	India	4.9 kg/capita/year (2016)	13 items/capita/year	Daniel et al. (2021)
Crustaceans	Global	1.79 kg/capita/year (FAO)	322–1951 items/capita/year	Hantoro et al. (2019)
Langoustine *Nephrops norvegicus*	Ireland	7 g/day (2014)	15–4471 items/capita/year	Hara et al. (2020)
Prawn *Penaeus semisulcatus*	Iran	100 g (USEPA) per meal adults 50 g (USEPA) per meal children	36 per meal 19 per meal	Akhabarizadeh et al. (2019)
Portunus armatus	Iran	100 g (USEPA) per meal adults 50 g (USEPA) per meal children	26 per meal 13 per meal	Akhabarizadeh et al. (2019)
Marine fish	Global	1.25 kg/capita/year (FAO)	25–32 375 items/capita/year	Hantoro et al. (2019)
Marine fish	Europe	15.6 kg/capita/year (EFSA)	842 items/capita/year	Barboza et al. (2020)
Marine fish	Portugal	57.0 kg/capita/year (EUMOFA)	3078 items/capita/year	Barboza et al. (2020)
Marine fish	Spain	47.7 kg/capita/year (EUMOFA)	2576 items/capita/year	Barboza et al. (2020)
Marine fish	Italy	31.1 kg/capita/year (EUMOFA)	1679 items/capita/year	Barboza et al. (2020)
Marine fish	USA	21.4 kg/capita/year (NOAA)	1156 items/capita/year	Barboza et al. (2020)
Marine fish	Brazil	9.6 kg/year/capita (NOAA)	518 items/capita/year	Barboza et al. (2020)
Marine fish (9 pelagic species)	India	8–9 kg kg/year/capita	40–45 items/capita/year	Daniel et al. (2020)
Bartail flathead *Platycephalus indicus*	Iran	300 g per week (adults) 50 g per week (children)	555 items/week (adults) 92 items /week (children)	Akhabarizadeh et al. (2018)

Bartail flathead *Platycephalus indicus*	Iran	227 g (USEPA) per meal (adults) 116 g (USEPA) per meal (children)	41 items/meal (adults) 20 items/meal (children)	Akhabarizadeh et al. (2019)
Grouper *Epinephelus coioides*	Iran	300 g per week (adults) 50 g per week (children)	240 items/week (adults) 40 items/week (children)	Akhabarizadeh et al. (2018)
Grouper *Epinephelus coioides*	Iran	227 g (USEPA) per meal (adults) 116 g (USEPA) per meal (children)	36 items/meal (adults) 18 items/meal (children)	Akhabarizadeh et al. (2019)
Scad *Alepes djedaba*	Iran	300 g per week (adults) 50 g per week (children)	233 items/week (adults) 39 items/week (children)	Akhabarizadeh et al. (2018)
Liza klunzingeri	Iran	227 g (USEPA) per meal (adults) 116 g (USEPA) per meal (children)	61 items/meal (adults) 30 items/meal (children)	Akhabarizadeh et al. (2019)
Pickhandle baracuda *Sphyraena jello*	Iran	300 g per week (adults) 50 g per week (children)	169 items/week (adults) 28 items/week (children)	Akhabarizadeh et al. (2018)
Haddock *Melanogrammus aeglefinus*	UK	7.5 kg/capita/year (DEFRA) 20.8 kg/capita/year (FAO)	1614 items/gram/year 4451 items/gram/year	Akoueson et al. (2020)
Seabass *Dicentrarchus labrax*	UK	7.5 kg/capita/year (DEFRA) 20.8 kg/capita/year (FAO)	1333 items/gram/year 3677 items/gram/year	Akoueson et al. (2020)
Mackerel *Scomber scombrus*	UK	7.5 kg/capita/year (DEFRA) 20.8 kg/capita/year (FAO)	2187 items/gram/year 6032 items/gram/year	Akoueson et al. (2020)
Plaice *Pleuronectes platessa*	UK	7.5 kg/capita/year (DEFRA) 20.8 kg/capita/year (FAO)	5828 items/gram/year 16076 items/gram/year	Akoueson et al. (2020)
Canned tuna and mackerel (50 samples, 7 brands)	Iran	Adult: 4.94 g/person/day Children: 1.53 g/person/day	234 items/gram/year 72 items/gram/year	Akhbarizadeh et al. (2020)
Canned Sardine and sprat (20 brands)	US	90 g/capita/year	1–5 items/capita/year	Karami et al. (2018)

Data sources reported by cited publications: FAO (Food and Agriculture Organisation of the United Nations), KNHANES (Korea Center for Disease Control and Prevention), DEFRA (Department for Environment, Food and Rural Affairs – UK), USEPA (the United States Environmental Protection Agency), NOAA (National Oceanographic and Atmospheric Administration – USA), EUMOFA (European Market Observatory for Fisheries and Aquaculture Products), EFSA (European Food Safety Authority), SEAFISH-UK (The Sea Fish Industry Authority).

domestic dust contamination during a meal (13 731–68 415 particles/person/year) may be higher than the fiber intake through consumption of mussels (123–4620 particles/person/year).

It is the responsibility of producers to ensure that their products are safe for consumption. As with other environmental contaminants, producers can take measures such as routine monitoring to determine that levels of microplastics in their products are within safe values. Such "safe values" are yet to be determined and there are currently no standards or management actions in place for monitoring seafood for microplastics. This has also been linked to the limited understanding of the consequences of microplastics at environmental levels. In general, standards need to be introduced for monitoring microplastics in seafood, including methods that focus on smaller particles and nanoplastics, which may be present in the edible tissue. Producers may be able to take preventive steps to reduce microplastic contamination of their products, such as eliminating microplastics from aquaculture fish meals.

13.4.2 Seafood Security

Fisheries and aquaculture provide a large proportion of the world's food supply, with an estimated per capita consumption of 20.5 kg in 2018, providing 17% of animal protein consumption, or 7% of all protein in 2017 (FAO 2020). For around 3.3 billion people, fish makes up almost 20% of average per capita animal protein intake, and in a few developing countries, fish contributes 50% or more of animal protein intake. Food security is defined by the FAO as a situation that exists "when all people, at all times, have physical, social and economic access to sufficient, safe and nutritious food that meets their dietary needs and food preferences for an active and healthy life" (FAO 1996). There are many risks to food security, for example, climate change, eutrophication, and overexploitation of fisheries stocks. It is currently unclear whether microplastics pose a risk to global food security.

Preliminary risk assessments have concluded that microplastics do not currently pose a substantial risk to marine and freshwater biological communities, which would suggest no current food security threat (Everaert et al. 2020; Garrido Gamarro et al. 2020; Koelmans et al. 2020). However, these risk assessments are based on traditional toxicology testing, which occurs at the individual level and does not consider chronic exposure effects or indirect effects to ecological communities (such as modifications to species interactions). They are also unable to take into consideration the complex toxicology of microplastics, as different polymers, shapes, sizes, and chemical mixtures have different interactions with different species. Even under these current assessments, most researchers concede that some parts of the global ocean and freshwater bodies will be under significant threat from microplastics pollution by the end of the century if emissions continue to rise as currently projected.

Thus, while microplastics may or may not represent a current threat to global food security, proactive measures to reduce emissions may be necessary to prevent future threats. Management schemes should be developed to test the safety and quality of end products. Having action levels will ensure that food safety management regularly checks the presence of microplastics and will give clear signals to consumers and stakeholders that the threat to seafood is being adequately addressed (Faraday 2019). As the field develops and data and models more thoroughly cover the breadth of microplastics types and mixtures, future risk assessments will ideally allow for the creation of standards for limiting food security threats due to microplastics exposure.

13.5 Conclusion

The information regarding microplastics in seafood items is globally patchy, with the most data existing for bivalve shellfish and the digestive tracts of fish, and missing data for some species and regions. Exposure and risks will be associated with regional diets, as well as the levels of microplastics contamination in the capture environment, and processing, packaging, and food preparation methods. More in-depth local and global monitoring of the degree on microplastic contamination of the edible tissues of seafood species throughout the supply chain will be necessary to inform risk assessments and strategies for mitigating harm to the public. However, these steps will be of limited use until comprehensive data and understanding of the human and environmental health effects of microplastics and their associated chemicals are present. There is currently enough knowledge available to confirm that microplastics are being transferred to humans *via* seafood, but other routes of transfer may be more relevant for overall chronic exposure. More complete knowledge of the overall contamination of various food products is needed before the relative contribution of seafood can be understood. Acting to regulate seafood projects based on the current best available science runs the risk of being counterproductive given the known health benefits of consuming seafood. Considering the ubiquitous nature of microplastics, special consideration should be given to understanding the chronic effects of human exposure to ensure that seafood or other food products are not negatively impacting the health and wellbeing of any human populations, especially those, often already impoverished or underrepresented populations, that relies so heavily on the consumption of seafood to meet their dietary needs.

References

Abbasi, S., Soltani, N., Keshavarzi, B., et al. 2018. Microplastics in different tissues of fish and prawn from the Musa Estuary, Persian Gulf. *Chemosphere*, 205: 80–87. https://doi.org/10.1016/j.chemosphere.2018.04.076

Abidli, S., Lahbib, Y., Trigui El Menif, N. 2019. Microplastics in commercial molluscs from the lagoon of Bizerte (Northern Tunisia). *Marine Pollution Bulletin*, 142: 243–252. https://doi.org/10.1016/j.marpolbul.2019.03.048

Akhbarizadeh, R., Moore, F., Keshavarzi, B. 2018. Investigating a probable relationship between microplastics and potentially toxic elements in fish muscles from northeast of Persian Gulf. *Environmental Pollution*, 232: 154–163. https://doi.org/10.1016/j.envpol.2017.09.028

Akhbarizadeh, R., Moore, F., Keshavarzi, B. 2019. Investigating microplastics bioaccumulation and biomagnification in seafood from the Persian Gulf: a threat to human health? *Food Additives & Contaminants: Part A*, 36: 1696–1708. https://doi.org/10.1080/19440049.2019.1649473

Akhbarizadeh, R., Dobaradaran, S., Nabipour, I., et al. 2020. Abundance, composition, and potential intake of microplastics in canned fish. *Marine Pollution Bulletin*, 160: 111633. https://doi.org/10.1016/j.marpolbul.2020.111633

Akoueson, F., Sheldon, L. M., Danopoulos, E., et al. 2020. A preliminary analysis of microplastics in edible versus non-edible tissues from seafood samples. *Environmental Pollution*, 262: 114452. https://doi.org/10.1016/.envpol.2020.114452

Barboza, L. G. A., Vethaak, A. D., Lavorante, B. R. B. O., et al. 2018. Marine microplastic debris: an emerging issue for food security, food safety and human health. *Marine Pollution Bulletin*, 133: 336–348. https://doi.org/10.1016/j.marpolbul.2018.05.047

Barboza, L. G. A., Lopes, C., Oliveira, P., et al. 2020. Microplastic in wild fish from North East Atlantic Ocean and its potential for causing neurotoxic effects, lipid oxidative damage, and human health risks associated with ingestion exposure. *Science of the Total Environment*, 717: 134625. https://doi.org/10.1016/j.scitotenv.2019.134625

Bourdages, M. P. T., Provencher, J. F., Sudlovenick, E., et al. 2020. No plastics detected in seal (*Phocidae*) stomachs harvested in the eastern Canadian Arctic. *Marine Pollution Bulletin*, 150: 110772. https://doi.org/10.1016/j.marpolbul.2019.110772

Brander, S. M., Renick, V. C., Foley, et al. 2020. Sampling and QA/QC: a guide for scientists investigating the occurrence of microplastics across matrices. *Applied Spectroscopy*, 74: 1099–1125. https://doi.org/10.1177/0003702820945713

Bråte, I. L. N., Hurley, R., Iversen, K., et al. 2018. *Mytilus* spp. as sentinels for monitoring microplastic pollution in Norwegian coastal waters: a qualitative and quantitative study. *Environmental Pollution*, 242: 383–393. https://doi.org/10.1016/j.envpol.2018.08.077

Castelvetro, V., Corti, A., Bianchi, S., et al. 2020. Microplastics in fish meal: contamination level analyzed by polymer type, including polyester (PET), polyolefins, and polystyrene. *Environmental Pollution*, 115792. https://doi.org/10.1016/j.envpol.2020.115792

Catarino, A. I., Macchia, V., Sanderson, W. G., et al. 2018. Low levels of microplastics (MP) in wild mussels indicate that MP ingestion by humans is minimal compared to exposure via household fibres fallout during a meal. *Environmental Pollution*, 237: 675–684. https://doi.org/10.1016/j.envpol.2018.02.069

Cau, A., Avio, C. G., Dessì, C., Follesa, M. C., Moccia, D., Regoli, F., Pusceddu, A., 2019. Microplastics in the crustaceans *Nephrops norvegicus* and *Aristeus antennatus*: flagship species for deep-sea environments? *Environmental Pollution*, 255: 113107. https://doi.org/10.1016/j.envpol.2019.113107

Chen, B., Fan, Y., Huang, W., et al. 2020. Observation of microplastics in mariculture water of Longjiao Bay, southeast China: influence by human activities. *Marine Pollution Bulletin*, 160, 111655. https://doi.org/10.1016/j.marpolbul.2020.111655

Chen, M., Jin, M., Tao, P., et al. 2018. Assessment of microplastics derived from mariculture in Xiangshan Bay, China. *Environmental Pollution*, 242: 1146–1156. https://doi.org/10.1016/j.envpol.2018.07.133

Chen, Y., Ling, Y., Li, X., et al. 2020. Size-dependent cellular internalization and effects of polystyrene microplastics in microalgae *P. helgolandica* var. *tsingtaoensis* and *S. quadricauda*. *Journal of Hazardous Materials*, 399: 123092. https://doi.org/10.1016/j.jhazmat.2020.123092

Cho, Y., Shim, W. J., Jang, M., et al. 2019. Abundance and characteristics of microplastics in market bivalves from South Korea. *Environmental Pollution*, 245: 1107–1116. https://doi.org/10.1016/j.envpol.2018.11.091

Cho, Y., Shim, W.J., Jang, M., et al. 2021. Nationwide monitoring of microplastics in bivalves from the coastal environment of Korea. *Environmental Pollution*, 270: 116175. https://doi.org/10.1016/j.envpol.2020.116175

Collard, F., Gilbert, B., Compère, P., et al. 2017. Microplastics in livers of European anchovies (*Engraulis encrasicolus*, L.). *Environmental Pollution*, 229: 1000–1005. https://doi.org/10.1016/j.envpol.2017.07.089

Covernton, G., Collicutt, B., Gurney-Smith, H., et al. 2019. Microplastics in bivalves and their habitat in relation to shellfish aquaculture proximity in coastal British Columbia, Canada. *Aquaculture Environment Interactions*, 11: 357–374. https://doi.org/10.3354/aei00316

Covernton, G. A., Davies, H. L., Cox, K. D., et al. 2021. A Bayesian analysis of the factors determining microplastics ingestion in fish. *Journal of Hazardous Materials*, 413: 125405. https://doi.org/10.1016/j.jhazmat.2021.125405

Cowger, W., Booth, A., Hamilton, B., et al. 2020. Reporting guidelines to increase the reproducibility and comparability of research on microplastics. *Applied Spectroscopy*, 74: 1066–1077. https://doi.org/10.1177/0003702820930292

Cox, K. D., Covernton, G. A., Davies, H. L. 2019. Human consumption of microplastics. *Environmental Science and Technology*, 53: 7068–7074. https://doi.org/10.1021/acs.est.9b01517

Daniel, D. B., Ashraf, P. M., Thomas, S. N. 2020. Microplastics in the edible and inedible tissues of pelagic fishes sold for human consumption in Kerala, *India. Environmental Pollution*, 266: 115365. https://doi.org/10.1016/j.envpol.2020.115365

Daniel, D. B., Ashraf, P. M., Thomas, S.N., et al. 2021. Microplastics in the edible tissues of shellfishes sold for human consumption. *Chemosphere*, 264: 128554. https://doi.org/10.1016/j.chemosphere.2020.128554

Danopoulos, E., Jenner, L. C., Twiddy, M., et al. 2020. Microplastic contamination of seafood intended for human consumption: a systematic review and meta-analysis. *Environmental Health Perspectives*, 128, 126002. https://doi.org/10.1289/EHP7171

Dehaut, A., Hermabessiere, L., Duflos, G. 2019. Current frontiers and recommendations for the study of microplastics in seafood. *Trends in Analytical Chemistry*, 116: 346–359. https://doi.org/10.1016/j.trac.2018.11.011

Deng, L., Cai, L., Sun, F., et al. 2020. Public attitudes towards microplastics: perceptions, behaviors and policy implications. *Resources, Conservation and Recycling*, 163: 105096. https://doi.org/10.1016/j.resconrec.2020.105096

Devriese, L. I., van der Meulen, M. D., Maes, T., et al. 2015. Microplastic contamination in brown shrimp (*Crangon crangon*, Linnaeus 1758) from coastal waters of the Southern North Sea and Channel area. *Marine Pollution Bulletin*, 98: 179–187. https://doi.org/10.1016/j.marpolbul.2015.06.051

Dowarah, K., Patchaiyappan, A., Thirunavukkarasu, C., et al. 2020. Quantification of microplastics using Nile Red in two bivalve species *Perna viridis* and *Meretrix meretrix* from three estuaries in Pondicherry, India and microplastic uptake by local communities through bivalve diet. *Marine Pollution Bulletin*, 153: 110982. https://doi.org/10.1016/j.marpolbul.2020.110982

Drenner, R. W., Threlkeld, S. T., McCracken, M. D. 1986. Experimental analysis of the direct and indirect effects of an omnivorous filter-feeding Clupeid on plankton community structure. *Canadian Journal of Fisheries and Aquatic Sciences*, 43: 1935–1945.

Du, F., Cai, H., Zhang, Q., et al. 2020. Microplastics in take-out food containers. *Journal of Hazardous Materials*, 399: 122969. https://doi.org/10.1016/j.jhazmat.2020.122969

Duncan, E. M., Broderick, A. C., Fuller, W. J., et al. 2019. Microplastic ingestion ubiquitous in marine turtles. *Global Change Biology*, 25: 744–752. https://doi.org/10.1111/gcb.14519

ElShehawy, S. M., Farag, Z. S. 2019. Safety assessment of some imported canned fish using chemical, microbiological and sensory methods. *The Egyptian Journal of Aquatic Research*, 45: 389–394. https://doi.org/10.1016/j.ejar.2019.08.005

Everaert, G., De Rijcke, M., Lonneville, B., et al. 2020. Risks of floating microplastic in the global ocean. *Environmental Pollution*, 267: 115499. https://doi.org/10.1016/j.envpol.2020.115499

FAO. 1996. *Rome Declaration on World Food Security*. Food and Agriculture Organization of the United Nations, Rome, Italy (13 November 1996). Available from: <http://www.fao.org/fileadmin/templates/faoitaly/documents/pdf/pdf_Food_Security_Cocept_Note.pdf> ().

FAO. 2020. *The State of World Fisheries and Aquaculture 2020. Sustainability in action*. Food and Agriculture Organization of the United Nations, Rome, Italy. https://doi.org/10.4060/ca9229en

Fadare, O. O., Wan, B., Guo, L.-H., et al. 2020. Microplastics from consumer plastic food containers: are we consuming it? *Chemosphere*, 253: 126787. https://doi.org/10.1016/j.chemosphere.2020.126787

Faraday, S. E. 2019. Microplastics as a new, ubiquitous pollutant: strategies to anticipate management and advise seafood consumers. *Marine Policy*, 104: 103–107. https://doi.org/10.1016/j.marpol.2019.02.020

Featherstone, S. 2016. Canning of fish and seafood. In: Fetherstone, S. (ed.), *A Complete Course in Canning and Related Processes: Volume 3 Processing Procedures for Canned Food Products*, 231–265. Woodhead Publishing. https://doi.org/10.1016/C2013-0-16340-4

Feng, Z., Zhang, T., Shi, H., et al. 2020a. Microplastics in bloom-forming macroalgae: distribution, characteristics and impacts. *Journal of Hazardous Materials*, 397: 122752. https://doi.org/10.1016/j.jhazmat.2020.122752

Feng, Z., Zhang, T., Wang, J., et al. 2020b. Spatio-temporal features of microplastics pollution in macroalgae growing in an important mariculture area, *China. Science of the Total Environment*, 719: 137490. https://doi.org/10.1016/j.scitotenv.2020.137490

Fernández, B., Albentosa, M. 2019. Insights into the uptake, elimination and accumulation of microplastics in mussel. *Environmental Pollution*, 249: 321–329. https://doi.org/10.1016/j.envpol.2019.03.037

Fernández Severini, M. D., Buzzi, N. S., Forero López, A. D., et al. 2020. Chemical composition and abundance of microplastics in the muscle of commercial shrimp *Pleoticus muelleri* at an impacted coastal environment (Southwestern Atlantic). *Marine Pollution Bulletin*, 161: 111700. https://doi.org/10.1016/j.marpolbul.2020.111700

Fred-Ahmadu, O. H., Bhagwat, G., Oluyoye, I., et al. 2020. Interaction of chemical contaminants with microplastics: principles and perspectives. *Science of the Total Environment*, 706: 135978. https://doi.org/10.1016/j.scitotenv.2019.135978

Garrido Gamarro, E., Ryder, J., Elvevoll, E. O., et al. 2020. Microplastics in fish and shellfish–a threat to seafood safety? *Journal of Aquatic Food Product Technology*, 29(4): 417–425. https://doi.org/10.1080/10498850.2020.1739793

Gao, F., Li, J., Hu, J., et al. 2020. Occurrence of microplastics carried on *Ulva prolifera* from the Yellow Sea, China. *Case Studies in Chemical and Environmental Engineering.* 2: 100054. https://doi.org/10.1016/j.cscee.2020.100054

Gao, G., Zhao, X., Jin, P., et al. 2021. Current understanding and challenges for aquatic primary producers in a world with rising micro- and nano-plastic levels. *Journal of Hazardous Materials* 406: 124685. https://doi.org/10.1016/j.jhazmat.2020.124685

Gomiero, A., Haave, M., Bjorøy, Ø., et al. 2020. Quantification of microplastic in fillet and organs of farmed and wild salmonids – a comparison of methods for detection and quantification (NORCE Report No. 8–2020).

Goss, H., Jaskiel, J., Rotjan, R. 2018. *Thalassia testudinum* as a potential vector for incorporating microplastics into benthic marine food webs. *Marine Pollution Bulletin*, 135: 1085–1089. https://doi.org/10.1016/j.marpolbul.2018.08.024

Gouin, T. 2020. Towards improved understanding of the ingestion and trophic transfer of microplastic particles – critical review and implications for future research. *Environmental Toxicology and Chemistry*, 39: 1119–1137. https://doi.org/10.1002/etc.4718

Graham, P., Palazzo, L., Andrea de Lucia, G., et al. 2019. Microplastics uptake and egestion dynamics in Pacific oysters, *Magallana gigas* Thunberg, (1793), under controlled conditions. *Environmental Pollution*, 252: 742–748. https://doi.org/10.1016/j.envpol.2019.06.002

Gündoğdu, S., Çevik, C., Ataş, N. T. 2020. Stuffed with microplastics: microplastic occurrence in traditional stuffed mussels sold in the Turkish market. *Food Bioscience*, 37: 100715. https://doi.org/10.1016/j.fbio.2020.100715

Gündoğdu, S., Eroldoğan, O. T., Evliyaoğlu, E., et al. 2021. Fish out, plastic in: global pattern of plastics in commercial fishmeal. *Aquaculture*, 534: 736316. https://doi.org/10.1016/j.aquaculture.2020.736316

Gutow, L., Eckerlebe, A., Giménez, L., et al. 2016. Experimental evaluation of seaweeds as a vector for microplastics into marine food webs. *Environmental Science and Technology*, 50: 915–923. https://doi.org/10.1021/acs.est.5b02431

Gutow, L., Bartl, K., Saborowski, R., et al. 2019. Gastropod pedal mucus retains microplastics and promotes the uptake of particles by marine periwinkles. *Environmental Pollution*, 246: 688–696. https://doi.org/10.1016/j.envpol.2018.12.097

Hanachi, P., Karbalaei, S., Walker, T. R., et al. 2019. Abundance and properties of microplastics found in commercial fish meal and cultured common carp (*Cyprinus carpio*). *Environmental Science and Pollution Research*, 26: 23777–23787. https://doi.org/10.1007/s11356-019-05637-6

Hantoro, I., Löhr, A. J., Belleghem, F. G. A. J. V., et al. 2019. Microplastics in coastal areas and seafood: implications for food safety. *Food Additives & Contaminants: Part A*, 36: 674–711. https://doi.org/10.1080/19440049.2019.1585581

Hara, J., Frias, J., Nash, R. 2020. Quantification of microplastic ingestion by the decapod crustacean *Nephrops norvegicus* from Irish waters. *Marine Pollution Bulletin*, 152: 110905. https://doi.org/10.1016/j.marpolbul.2020.110905

Heidman, M. K., Holley, L. L., Chambers, R. M., et al. 2012. Selective feeding on nutrient-rich particles by gizzard shad *Dorosoma cepedianum* does not involve mechanical sorting. *Aquatic Biology*, 17: 129–139. https://doi.org/10.3354/ab00470

Hernandez, L. M., Xu, E. G., Larsson, H. C. E., et al. 2019. Plastic teabags release billions of microparticles and nanoparticles into tea. *Environmental Science and Technology*, 53: 12300–12310. https://doi.org/10.1021/acs.est.9b02540

James, A. G., Findlay, K. P. 1989. Effect of particle size and concentration on feeding behaviour, selectivity and rates of food ingestion by the Cape anchovy *Engraulis capensis*. *Marine Ecology Progress Series*, 50: 275–294.

Jang, M., Shim, W. J., Cho, Y., et al. 2020. A close relationship between microplastic contamination and coastal area use pattern. *Water Research*, 171, 115400. https://doi.org/10.1016/j.watres.2019.115400

Karami, A., Golieskardi, A., Ho, Y. B., et al. 2017. Microplastics in eviscerated flesh and excised organs of dried fish. *Scientific Reports*, 7: 5473. https://doi.org/10.1038/s41598-017-05828-6

Karami, A., Golieskardi, A., Choo, C. K., et al. 2018. Microplastic and mesoplastic contamination in canned sardines and sprats. *Science of the Total Environment*, 612: 1380–1386. https://doi.org/10.1016/j.scitotenv.2017.09.005

Karbalaei, S., Golieskardi, A., Watt, D. U., et al. 2020. Analysis and inorganic composition of microplastics in commercial Malaysian fish meals. *Marine Pollution Bulletin*, 150: 110687. https://doi.org/10.1016/j.marpolbul.2019.110687

Kazmiruk, T. N., Kazmiruk, V. D., Bendell, L. I. 2018. Abundance and distribution of microplastics within surface sediments of a key shellfish growing region of Canada. *PLOS ONE*, 13: e0196005. https://doi.org/10.1371/journal.pone.0196005

Kedzierski, M., Lechat, B., Sire, O., et al. 2020. Microplastic contamination of packaged meat: occurrence and associated risks. *Food Packaging and Shelf Life*, 24: 100489. https://doi.org/10.1016/j.fpsl.2020.100489

Klasios, N., De Frond, H., Miller, E., et al. 2021. Microplastics and other anthropogenic particles are prevalent in mussels from San Francisco Bay and show no correlation with PAHs. *Environmental Pollution*, 271: 116260. https://doi.org/10.1016/j.envpol.2020.116260

Koelmans, A. A., Redondo Hasselerharm, P. E., Mohamed Nor, N. H., et al. 2020. Solving the non-alignment of methods and approaches used in microplastic research in order to consistently characterize risk. *Environmental Science and Technology*, 54: 12307–12315. https://doi.org/10.1021/acs.est.0c02982

Kooi, M., Koelmans, A. A. 2019. Simplifying microplastic via continuous probability distributions for size, shape, and density. *Environmental Science and Technology Letters*, 6: 551–557. https://doi.org/10.1021/acs.estlett.9b0037

Lee, R., Lovatelli, A., Ababouch, L. 2008. Bivalve depuration: fundamental and practical aspects. *FAO Fisheries Technical Paper No. 511*. Food and Agriculture Organization of the United Nations, Rome, Italy.

Li, D., Shi, Y., Yang, L., et al. 2020. Microplastic release from the degradation of polypropylene feeding bottles during infant formula preparation. *Nature Food*, 1: 746–754. https://doi.org/10.1038/s43016-020-00171-y

Li, J., Qu, X., Su, L., et al. 2016. Microplastics in mussels along the coastal waters of China. *Environmental Pollution*, 214: 177–184. https://doi.org/10.1016/j.envpol.2016.04.012

Li, J., Green, C., Reynolds, A., et al. 2018. Microplastics in mussels sampled from coastal waters and supermarkets in the United Kingdom. *Environmental Pollution*, 241: 35–44. https://doi.org/10.1016/j.envpol.2018.05.038

Li, Q., Feng, Z., Zhang, T., et al. 2020. Microplastics in the commercial seaweed nori. *Journal of Hazardous Materials*, 388: 122060. https://doi.org/10.1016/j.jhazmat.2020.122060

Lusher A.L., Welden N.A.C. 2020 Microplastic impacts in fisheries and aquaculture. In: Rocha-Santos, T., Costa, M., Mouneyrac, C. (eds.), *Handbook of Microplastics in the Environment*. Springer, Cham. http://doi-org-443.webvpn.fjmu.edu.cn/10.1007/978-3-030-10618-8_30-1

Lusher, A. L., Mchugh, M., Thompson, R. C. 2013. Occurrence of microplastics in the gastrointestinal tract of pelagic and demersal fish from the English Channel. *Marine Pollution Bulletin*, 67(1–2): 94–99. https://doi.org/10.1016/j.marpolbul.2012.11.028

Lusher, A. L., Hollman, P. C. H., Mendoza-Hill, J. J. 2017. Microplastics in fisheries and aquaculture: status of knowledge on their occurrence and implications for aquatic organisms and food safety. FAO Fisheries and Aquaculture Technical Paper No. 615. Food and Agriculture Organization of the United Nations, Rome, Italy.

Lv, W., Yuan, Q., He, D., et al. 2020. Microplastic contamination caused by different rearing modes of Asian swamp eel (*Monopterus albus*). *Aquaculture Research* 51: 5084–5095. https://doi.org/10.1111/are.14847

McGoran, A. R., Clark, P. F., Smith, B. D., et al. 2020. High prevalence of plastic ingestion by *Eriocheir sinensis* and *Carcinus maenas* (Crustacea: Decapoda: Brachyura) in the Thames Estuary. *Environmental Pollution*, 265: 114972. https://doi.org/10.1016/j.envpol.2020.114972

Miller, M. E., Hamann, M., Kroon, F. J. 2020. Bioaccumulation and biomagnification of microplastics in marine organisms: a review and meta-analysis of current data. *PLOS ONE*, 15: e0240792. https://doi.org/10.1371/journal.pone.0240792

Mohsen, M., Wang, Q., Zhang, L., et al. 2019. Microplastic ingestion by the farmed sea cucumber *Apostichopus japonicus* in China. *Environmental Pollution* 245: 1071–1078. https://doi.org/10.1016/j.envpol.2018.11.083

Moore, R. C., Loseto, L., Noel, M., et al. 2020. Microplastics in beluga whales (*Delphinapterus leucas*) from the Eastern Beaufort Sea. *Marine Pollution Bulletin*, 150: 110723. https://doi.org/10.1016/j.marpolbul.2019.110723

Mouritsen, O. G., Rhatigan, P., Pérez-Lloréns, J. L. 2018. World cuisine of seaweeds: science meets gastronomy. *International Journal of Gastronomy and Food Science*, 14: 55–65. https://doi.org/10.1016/j.ijgfs.2018.09.002

Murano, C., Agnisola, C., Caramiello, D., et al. 2020. How sea urchins face microplastics: uptake, tissue distribution and immune system response. *Environmental Pollution*, 264: 114685. https://doi.org/10.1016/j.envpol.2020.114685

Murray, F., Cowie, P. R. 2011. Plastic contamination in the decapod crustacean *Nephrops norvegicus* (Linnaeus, 1758). *Marine Pollution Bulletin*, 62: 1207–1217. https://doi.org/10.1016/j.marpolbul.2011.03.032

Naji, A., Nuri, M., Vethaak, A. D. 2018. Microplastics contamination in molluscs from the northern part of the Persian Gulf. *Environmental Pollution*, 235: 113–120. https://doi.org/10.1016/j.envpol.2017.12.046

Nelms, S. E., Galloway, T. S., Godley, B. J., et al. 2018. Investigating microplastic trophic transfer in marine top predators. *Environmental Pollution*, 238: 999–1007. https://doi.org/10.1016/j.envpol.2018.02.016

Neto, J. G. B., Rodrigues, F. L., Ortega, I., et al. 2020. Ingestion of plastic debris by commercially important marine fish in southeast-south Brazil. *Environmental Pollution*, 267: 115508. https://doi.org/10.1016/j.envpol.2020.115508

Ory, N. C., Sobral, P., Ferreira, J. L., et al. 2017. Amberstripe scad *Decapterus muroadsi* (*Carangidae*) fish ingest blue microplastics resembling their copepod prey along the coast of Rapa Nui (Easter Island) in the South Pacific subtropical gyre. *Science of the Total Environment*, 586: 430–437. https://doi.org/10.1016/j.scitotenv.2017.01.175

Ory, N. C., Gallardo, C., Lenz, M., et al. 2018. Capture, swallowing, and egestion of microplastics by a planktivorous juvenile fish. *Environmental Pollution*, 240: 566–573. https://doi.org/10.1016/j.envpol.2018.04.093

Panti, C., Baini, M., Lusher, A., et al. 2019. Marine litter: one of the major threats for marine mammals. Outcomes from the European Cetacean Society workshop. *Environmental Pollution*, 247: 72–79. https://doi.org/10.1016/j.envpol.2019.01.029

Possatto, F. E., Barletta, M., Costa, M. F., et al. 2011. Plastic debris ingestion by marine catfish: an unexpected fisheries impact. *Marine Pollution Bulletin*, 62(5): 1098–1102. https://doi.org/10.1016/j.marpolbul.2011.01.036

Renzi, M., Guerranti, C., Blašković, A. 2018. Microplastic contents from maricultured and natural mussels. *Marine Pollution Bulletin* 131: 248–251. https://doi.org/10.1016/j.marpolbul.2018.04.035

Ribeiro, F., Okoffo, E.D., O'Brien, J.W. et al. 2020. Quantitative analysis of selected plastics in high commercial value Australian seafood by pyrolysis gas chromatography-mass spectrometry. *Environmental Science and Technology*, 4(15): 9408–9417. https://doi.org/10.1021/acs.est.0c02337

Rochman, C. M., Brookson, C., Bikker, J., et al. 2019. Rethinking microplastics as a diverse contaminant suite. *Environmental Toxicology and Chemistry*, 38: 703–711. https://doi.org/10.1002/etc.4371

Santana, C. A. Da S., Wieczorek, A. M., Browne, P. 2020. Importance of suspended particulate organic matter in the diet of *Nephrops norvegicus* (Linnaeus, 1758). *Scientific Reports*, 10: 3387. https://doi.org/10.1038/s41598-020-60367-x

Saputri, D. F. I., Daud, A., Syah, R., et al. 2020. Microplastic depuration on *Asaphis Detlorata*. *International Journal Papier Advance and Scientific Review*, 1: 37–46. https://doi.org/10.47667/ijpasr.v1i2.44

Schoof, R. A., DeNike, J. 2017. Microplastics in the context of regulation of commercial shellfish aquaculture operations. *Integrated Environmental Assessment and Management* 13: 522–527. https://doi.org/10.1002/ieam.1905

Schür, C., Rist, S., Baun, A., et al. 2019. When fluorescence is not a particle: the tissue translocation of microplastics in *Daphnia magna* seems an artifact. *Environmental Toxicology and Chemistry*, 38: 1495–1503. https://doi.org/10.1002/etc.4436

Smith, M., Love, D. C., Rochman, C. M., et al. 2018. Microplastics in seafood and the implications for human health. *Current Environmental Health Reports*, 5: 375–386. https://doi.org/10.1007/s40572-018-0206-z

Sobhani, Z., Lei, Y., Tang, Y., et al. 2020. Microplastics generated when opening plastic packaging. *Scientific Reports*, 10: 1–7. https://doi.org/10.1038/s41598-020-61146-4

Sundbæk, K. B., Koch, I. D. W., Villaro, C. G., et al. 2018. Sorption of fluorescent polystyrene microplastic particles to edible seaweed *Fucus vesiculosus*. *Journal of Applied Phycology*, 30: 2923–2927. https://doi.org/10.1007/s10811-018-1472-8

Tokhun, N., Somparn, A. 2020. Microplastic contaminations in buffet food from local Markets. *Naresuan University Journal: Science and Technology*, 28: 13–20. https://doi.org/10.14456/nujst.2020.32

Torn, K. 2020. Microplastics uptake and accumulation in the digestive system of the mud crab *Rhithropanopeus harrisii*. *Proceedings of the Estonian Academy of Sciences*, 69: 35. https://doi.org/10.3176/proc.2020.1.04

Van Cauwenberghe, L., Janssen, C. R. 2014. Microplastics in bivalves cultured for human consumption. *Environmental Pollution*, 193: 65–70. https://doi.org/10.1016/j.envpol.2014.06.010

VKM. 2019. *Microplastics: occurrence, levels and implications for environment and human health related to food. Scientific opinion of the Scientific Steering Committee of the Norwegian Scientific Committee for Food and Environment* (No. 2019:16). Norwegian Scientific Committee for Food and Environment (VKM), Oslo, Norway.

Völker, C., Kramm, J., Wagner, M. 2019. On the creation of risk: framing of microplastics risks in science and media. *Global Challenges*, 4: 1900010. https://doi.org/10.1002/gch2.201900010

Walkinshaw, C., Lindeque, P. K., Thompson, R., Tolhurst, T., Cole, M. 2020. Microplastics and seafood: lower trophic organisms at highest risk of contamination. *Ecotoxicology and Environmental Safety*, 190: 110066. https://doi.org/10.1016/j.ecoenv.2019.110066

Ward, J. E., Zhao, S., Holohan, B., et al. 2019a. Selective ingestion and egestion of plastic particles by the blue mussel (*Mytilus edulis*) and eastern oyster (*Crassostrea virginica*): implications for using bivalves as bioindicators of microplastic pollution. *Environmental Science and Technology*, 53: 8776–8784. https://doi.org/10.1021/acs.est.9b02073

Ward, J. E., Rosa, M., Shumway, S. E. 2019b. Capture, ingestion, and egestion of microplastics by suspension-feeding bivalves: a 40-year history. *Anthropocene Coasts*, 2: 39–49. https://doi.org/10.1139/anc-2018-0027

Welden, N. A. C., Cowie, P. R. 2016. Environment and gut morphology influence microplastic retention in langoustine, *Nephrops norvegicus*. *Environmental Pollution*, 214: 859–865. https://doi.org/10.1016/j.envpol.2016.03.067

Welden, N. A., Abylkhani, B., Howarth, L. M. 2018. The effects of trophic transfer and environmental factors on microplastic uptake by plaice, *Pleuronectes plastessa*, and spider crab, *Maja squinado*. *Environmental Pollution*, 239, 351–358. https://doi.org/10.1016/j.envpol.2018.03.110

Woods, M. N., Stack, M. E., Fields, D. M., et al. 2018. Microplastic fiber uptake, ingestion, and egestion rates in the blue mussel (*Mytilus edulis*). *Marine Pollution Bulletin*, 137: 638–645. https://doi.org/10.1016/j.marpolbul.2018.10.061

Zantis, L. J., Carroll, E. L., Nelms, S. E., et al. 2021. Marine mammals and microplastics: a systematic review and call for standardisation. *Environmental Pollution*, 269: 116142. https://doi.org/10.1016/j.envpol.2020.116142

Zeytin, S., Wagner, G., Mackay-Roberts, N., et al. 2020. Quantifying microplastic translocation from feed to the fillet in European sea bass *Dicentrarchus labrax*. *Marine Pollution Bulletin*, 156: 111210. https://doi.org/10.1016/j.marpolbul.2020.111210

14

Nanoplastics and the Marine Environment

The Unseen Majority?

Lia N. Corbett[1,2] *and Linda A. Amaral-Zettler*[1,2]

[1] *NIOZ – Royal Netherlands Institute for Sea Research, Den Burg, The Netherlands*
[2] *Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, Amsterdam, The Netherlands*

14.1 Introduction

In recent years, there has been an outpouring of research studies which have predominantly focused on microplastics, yet the long-term fate of microplastics (including their continual degradation in the marine environment) has only recently been deliberated. Microplastic particles in the marine environment are subjected to varied ageing and/or weathering processes during their life cycle (Figure 14.1). Degradation processes generate even smaller fragments below the micron scale, which can subsequently break down at higher rates due to their increasingly larger surface-to-volume ratio (Paul et al. 2020). Through ageing, the properties of the polymer change over time, ultimately affecting the polymer composition, the physical integrity, and the surface properties (Paul et al. 2020).

Weathering of microplastics leads to degradation through various processes, including photo-oxidation, thermal degradation, hydrolysis, mechanical/physical abrasion (including the application of shear stress forces to microplastics with crack failure, yielding fragmentation into smaller fragments), and even digestive fragmentation via egestion (Dawson et al. 2018; Enfrin et al. 2020; Mattsson et al. 2015; Paul et al. 2020). The biological degradation of plastic polymers in the marine environment is dependent on the molecular size, type of polymer, types of additives, degradation environment, and type and number of organisms in contact with the polymer (da Costa et al. 2016).

Degradation of plastic marine debris can thus change the chemical and physical characteristics of the plastic polymer, its density, and its biological impact (Mattsson et al. 2015). Plastic items larger than 5 mm have been traditionally defined as "macroplastics", while items between 1 μm and 5 mm are regarded as "microplastics" (Hartmann et al. 2019). When microscale plastic particles reach nanoscale size, their degradation products are reclassified as "nanoplastics". While no consensus on the definition of a nanoplastic yet exists, recent literature has generally adopted a nanoplastic to be a plastic particle within a size ranging from 1 to 1,000 nm (Gigault et al. 2018), with a few stricter definitions classifying nanoplastics as being plastic particles <100 nm in at least one dimension (Alimi et al. 2018; Koelmans et al. 2015).

A first, semi-quantitative proof of nanoplastics in the environment has been given by Ter Halle et al. (2017), and its formation was proven experimentally by Lambert and Wagner (2016) and Gigault et al. (2016). Yet, due to the incredibly small size of nanoplastics, assessing their fate in the aquatic environment is extremely challenging (Mintenig et al. 2018). As they generally fall below

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

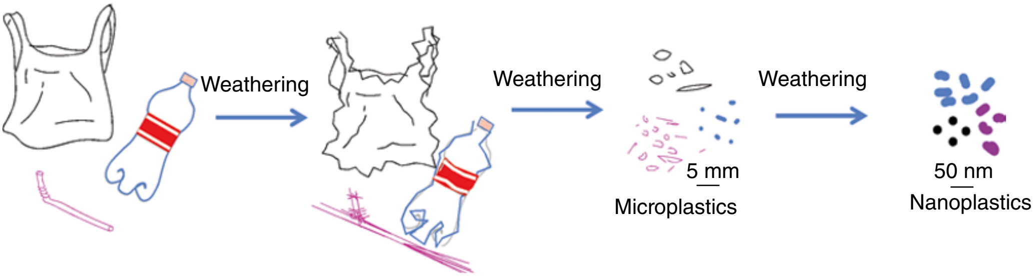


Figure 14.1 Weathering of macroplastics leads to production of secondary microplastics and ultimately secondary nanoplastics.

the detection limit of commonly available collection and identification methods, it is hypothesized that nanoplastics may account for the largest percentage of unaccounted plastic marine debris (van Sebille et al. 2015; Ter Halle et al. 2016). The existence of agglomerated plastic particles, much like suspended particulate matter, may mean that nanoplastics are ubiquitous, and either aggregated in the sediment (though nanoscale particles may be prevented from sedimentation due to collisions with water molecules and other ionic species present) or transported over long distances, albeit transport pathways of nanoplastics in aquatic systems remains poorly understood (Gigault et al. 2018). While some controversy exists as to whether nanoplastics are present in marine waters at levels sufficient to be hazardous (Gaylarde et al. 2020; and while quantitative analytical techniques to assess nanoplastic concentrations in the environment are not yet available), it is possible to extrapolate their release by fragmentation and degradation of larger plastic pieces.

In fact, evidence of nanoplastic occurrence and production has been successfully identified in laboratory settings. A few studies have attempted to produce *in vitro* degradation products of microplastics via the degradation of larger plastic pieces to better mimic natural breakdown processes. For example, the mechanical breakdown of two commonly used polystyrene (PS) items (coffee cup lids and expanded PS foam) produced plastic particles with mean diameters between 125 nm and 173 nm in size in under five minutes of mechanical treatment (Ekvall et al. 2019). Additionally, weathering of PS coffee cup lids was performed by exposing 1 cm plastic squares in a weathering chamber, complete with UV light and high temperatures (30 °C). Nanoparticle tracking analysis showed an increase in the formation of nanoplastics as small as 30 nm over time (Lambert and Wagner 2016). In another study, microplastics in advanced states of weathering that were collected from the North Atlantic gyre between 1 and 2 mm in size (determined to be composed of predominantly polyethylene) where exposed to a “homemade” photo-reactor (built to simulate solar light for degrading plastics). The results detected by a dynamic light scattering probe revealed that nanoplastics smaller than 50 nm were produced. Contrary to mechanical aging, it is speculated that photo-degradation leads to chemical changes in the polymeric chains, though this study was unable to characterize these (Gigault et al. 2016). A recent study using ^{14}C isotope tracers to investigate the degradation and mineralization of PS nanoparticles under UV radiation demonstrated the importance of water in degradation processes and the generation of leachates; irradiation in water (compared to air) did not affect the weight-average molecular weight of nanoplastics but enhanced the oxidation and mineralization of PS nanoplastics, with a significant production of small-molecule oxidative products. They determined that these hydrophilic products, after leaching into the surrounding water, continued to undergo further degradation and mineralization (though the role of water may depend on the intensity and duration of the photoreactions; Tian et al. 2019). While the generation of nanoplastics in the marine environment has not been actively demonstrated, despite their presence having been recently documented in the North Atlantic subtropical gyre (Ter Halle et al. 2017), these studies producing nanoplastics from larger plastic fragments by mimicking natural weathering behaviors are highly suggestive of nanoplastic production *in situ*.

Nanoplastics can be classified into primary and secondary nanoplastics, where primary nanoplastics are industrially produced for specific purposes (such as inclusion in cosmetics) and secondary nanoplastics result from plastic waste via degradation processes (Gaylarde et al. 2020; Paul et al. 2020). The origin of nanoplastic particles is an important consideration in nanotoxicological assays. For example, an engineered nanoplastic particle (an example of primary nanoplastics), such as a PS nanosphere, will have a surface chemistry that can be easily manipulated via chemical bond formations in a laboratory setting. Many companies utilize various additives not found in the environment for better stability of nanoplastic particles. These manufactured particles often display high sphericity, are strictly monodisperse (characterized by or as particles of approximately the same size), and exhibit stable physical and chemical properties (Alpha Nanotech 2021). Secondary nanoplastics, on the other hand, are typically the result of unintentional and incidental formation due to significant weathering of a larger plastic piece. They are polydisperse (characterized by/as particles of varied sizes) and can have an asymmetrical and heterogenous shape, and uncontrolled surface chemistries with different chemical species present (both organic and inorganic; Gigault et al. 2018). While both primary and secondary nanoplastics can form aggregates, their colloidal behavior may differ depending on the surrounding chemical and physical properties of the water column.

One issue of consensus in nanoplastics research thus far is that most studies use laboratory synthesized nanoplastics that likely do not have representative chemical makeup, density, porosity, or rugosity as compared to that of environmentally derived nanoplastics and therefore may behave significantly differently. For example, the size, surface charge, aggregation behaviors, and shape of a nanoplastic particle will often determine the degree of cellular uptake, and thus its possibility to reach targets and evoke adverse effects (Kettler et al. 2014). In fact, studies utilizing solely pristine PS beads are considered to lack environmental significance, as their properties may diverge from those encountered in environmental settings, and the use of varying methodologies, concentrations, and size ranges of utilized plastics yields often incompatible data (Koelmans et al. 2020).

More recent studies have adopted a “top-down” approach to understanding secondary nanoplastic formation by improving the representation of nanoplastic samples to mimic real environmental nano-pollutants (El Hadri et al. 2020). For example, nanoprecipitation (the generation of nanoparticles by means of precipitation from solution) generated both polyethylene (PE) and polyethylene terephthalate (PET) nanoplastics of 200–800 nm and 50–200 nm in laboratory studies (Balakrishnan et al. 2019; Rodríguez-Hernández et al. 2019). Other methods include (i) synthesizing nanoplastic particles doped with a chemically entrapped metal tracer (that can be easily detected in complex systems), (ii) nanoplastic synthesis with different surface functionalities via soap-free emulsion polymerization, (iii) laser ablation to obtain PET nanoplastics with an average dimension of 100 nm, and (iv) mechanical degradation of PS, PE, environmentally pre-degraded PS, and environmentally pre-degraded PE (El Hadri et al. 2020; Magrì et al. 2018; Mitrano et al. 2019; Pessoni et al. 2019).

Yet a massive gap in data regarding nanoplastics still exists. Most studies have been unable to quantify environmentally relevant concentrations; currently, no standardized optimized sampling, concentration, and separation methods are available, and as such, no proper nanoplastic models exist (Cai et al. 2020). Thus, it is extremely likely that a large fraction, if not the largest fraction, of marine plastic debris (in the form of nanoscale pieces) remains unknown. To adequately address environmental nanoplastic contamination, the effects of nanoplastics on ecosystem health, and potential hazards to human health, it is important to continue to characterize nanoplastics in hopes of understanding their overarching impact and fate.

Of the estimated 5–13 million metric tons of plastic waste that leaks annually into the ocean (Jambeck et al. 2015), the amount of resulting nanoplastics is presumed to be exceptionally high; however, this continuous formation of nanoscale plastic particles has been somewhat overlooked until recently (Bouwmeester et al. 2015). It is therefore evident that the comprehension of the potential impact of nanoplastics on our environment is imperative to assessing the harm on microbes, as well as up through the food chain to ourselves. Thus, understanding the behavior of nanoplastics in the marine environment is critical to understanding their potential nanotoxicological effects. Since nanoplastics are generally thought to be produced unintentionally from microscale plastic debris, it is likely that they form aggregates with other natural and/or anthropogenic materials (Gigault et al. 2018). Consequently, the colloidal behavior of nanoplastics is extremely relevant.

14.1.1 Aggregation Behavior of Nanomaterials and Nanoplastics

Our knowledge of nanoplastic behavior draws heavily from the field of nanotechnology. Nanoparticles and nanomaterials, having at least one dimension in the nanoscale (1–100 nm; Potočnik 2011), often interact with solid surfaces or other particles quite differently than that of larger, micrometer-sized particles (Lowry et al. 2012; Petosa et al. 2010). Any nanoparticle will have an exceptionally high surface-to-volume ratio. Therefore, even the simplest nanoparticle will have a distinct surface chemistry (often different from the core material itself), and that surface will be the first aspect of the nanoparticle that the environment or an organism experiences (Christian et al. 2008). The core of the nanoparticle (essentially the center) is ordinarily homogenous, whereas the surface can be functionalized with a range of small molecules, polymers, surfactants, metal ions, capping agents, and stabilizers (Christian et al. 2008; Lowry et al. 2012).

For particles less than 100 nm in size, Brownian diffusion controls the long-range forces in suspension between the individual nanoparticles, leading to collision events. When this contact occurs, it can result in either precipitation of the nanoparticles from solution, repulsion, or attachment (Christian et al. 2008; Hotze et al. 2010; Petosa et al. 2010). The stability of nanoparticles suspended in the liquid medium can be evaluated as the resultant interaction energy (the sum of van der Waals and electrical double-layer forces [EDL]), traditionally described by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory of colloidal stability, as the two surfaces approach one another (Petosa et al. 2010). Once particles collide with each other, the likelihood of attachment, or “attachment efficiency” (defined as the ratio of collisions resulting in attachment to the number of total collisions), can be controlled by both DLVO interactions and non-DLVO interactions (including steric interactions, hydration forces, and magnetic forces for iron-based materials; Alimi et al. 2018; Corsi et al. 2020; Hornyak et al. 2016; Petosa et al. 2010). However, it is important to note that the heteroaggregation between nanoparticles and particles present in the surrounding medium can often represent the interaction of two or more different particle populations, which can result in a complex combination of aggregation processes and attachment efficiencies, making theoretical and experimental determination challenging (Praetorius et al. 2020).

The increased generation of nanoparticles has resulted in the need to better understand and define their complex behaviors and impacts in the aquatic environment (Koelmans et al. 2015). The presence of engineered nanomaterials in the biosphere has increased rapidly due to continuous advances in the field of nanotechnology (Lowry et al. 2012), and the high surface-to-volume ratio of nanoparticles results in highly reactive and physiochemically diverse interactions (Nasser et al. 2020; Tallec et al. 2019).

Once in the environment, nanoparticles can undergo various processes including chemical transformation, sedimentation, and aggregation (Bundschuh et al. 2018) and may exist in the environment as free particles, homo-aggregates, or hetero-aggregates (Figure 14.2). Aggregation kinetics is an important determinant of the fate, distribution, bioavailability, and ecotoxicological potential of nanoparticles in aquatic environments (Bundschuh et al. 2018; Wang et al. 2020a).

When a nanoparticle is first introduced into a dispersion medium, the ionic strength of the dispersion medium will directly influence the Debye length and thus directly influences the particle–particle electrostatic repulsion. The increase in ionic strength will generate a decrease in the Debye length and subsequently a decrease in the electrostatic interaction. The ionic strength where aggregation starts is known as the critical coagulation concentration (CCC) and is typical for colloidal systems (Gigault et al. 2018). Similarly, the attachment efficiency is also a typical characteristic of colloidal systems and has a value between zero and one describing the probability of a collision between particles to result in attachment. If attractive forces dominate, the process is considered diffusion limited and the attachment efficiency approaches one (Alimi et al. 2018). The value of the attachment efficiency is related to the presence of an energy barrier, where a barrier height higher than the energy of the attractive forces between particles decreases the number of effective collisions (Praetorius et al. 2020). In this case, repulsive forces influence the likelihood of attachment and the process is considered reaction limited.

Colloidal barriers to aggregation are predominantly due to surface charges or steric stabilization of the colloid. In the case of steric stabilization, a long molecule is tethered to the surface of the nanoparticle, which has a high affinity for the solvent. The barrier to aggregation is therefore dependent on the relative interactions of the polymer chain with itself and with the solvent. For aggregation to occur, the solvent must be eliminated between the two particles and from around the polymer chains, which is energetically unfavorable and therefore presents a barrier to aggregation (Christian et al. 2008).

Changes in ionic concentration can also have a dramatic effect on particle stability (Christian et al. 2008). According to DLVO theory, increasing the ionic strength (IS) of a solution compresses the electrical double layer and decreases repulsive forces, resulting in a higher rate of aggregation or deposition (Alimi et al. 2018). This is especially important for manufactured nanoparticles, where engineered functionalization or incidental coatings may greatly impact nanoparticle aggregation by altering the particle surface functionalization (Alimi et al. 2018).

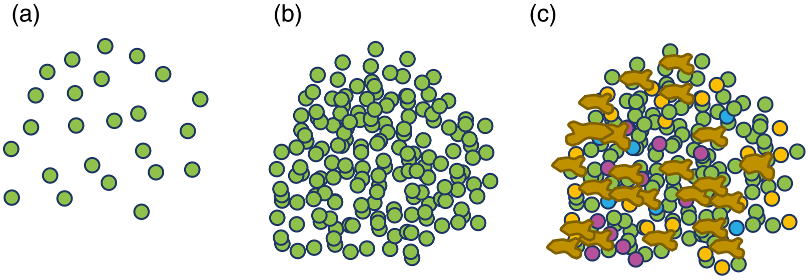


Figure 14.2 Nanoplastics may exist in the environment as (a) temporary free/unadsorbed particles, (b) homo-aggregates (clusters of a single kind of nanoplastic, occurring less frequently in the environment except when concentrations are exceptionally high), and (c) hetero-aggregates (nanoplastics adsorbed to suspended particulate matter; most probable occurrence). *Source:* Markus et al. (2016).

The reactive surfaces of nanomaterials cause them to interact with their surroundings, often binding available biomolecules to reduce their surface reactivity (Nasser et al. 2020). For example, the aggregation kinetics of carbonaceous nanoparticles (which generally follows DLVO theory), such as fullerenes, carbon nanotubes, and graphene oxide, in addition to other nanoparticles such as titanium dioxide (TiO_2), zinc oxide (ZnO), and cerium dioxide (CeO_2), are highly dependent on the solution chemistry of the water, specifically electrolytes and Natural Organic Matter (NOM; Keller et al. 2010; Li et al. 2018). NOM and other humic substances can result in a nanoscale coating of the nanomaterials, analogous to protein- and eco-corona systems (Figure 14.3), which can drastically change the aggregation, deposition, and toxic properties of the nanoparticle (Lowry et al. 2012). The hetero-aggregation between nanoparticles and biogenic particles can increase the bioavailability of nanomaterials, and these biomacromolecule-nanoparticle aggregates may offer a way of entry for nanomaterials into cells and subsequently determine the fate of the material in the organism (Lowry et al. 2012). An important consideration for several nanoparticles employed in the food, cosmetic, and medical industries (such as silver nanoparticles) is that these particles may display biocidal properties, making them less attractive to microbial colonization (Schneider 2017). This difference, combined with the polydisperse nature of plastic nanoparticles and varying surface charges, may make nanoplastics more likely to be incorporated into extracellular polymeric substances (EPSs), as the binding of biomacromolecules can coat the nanoplastic and reduce its surface energy, rendering it more stable.

Unlike engineered nanoparticles, the potential effects and interactions of nanoplastics are not yet as well understood. Nevertheless, to gain a prognostic assessment of nanoplastic behavior, nanoparticles may, to a certain extent, be used as a suitable proxy. To do so, it is important to ascertain whether nanoplastics (which are often formed due to the fragmentation and degradation of larger plastic pieces) can act as a natural analog for manufactured nanoparticles and whether the aggregation behaviors of nanoplastics are like those of other nanoparticles.

The behavior of nanoplastics (NPs) is likely driven by similar processes as nanoparticles, including interactions with macromolecules (such as adsorption of polysaccharides and organic matter), leading to the potential development of bio-coronas (within organism) or eco-coronas (in environment), physical transformations (homo- or hetero-aggregation), and biological transformations (including oxidation and redox mechanisms that may transform the surface layer of a particle; Tallec et al. 2019). The surface functionalization of a NP particle is one of the more important

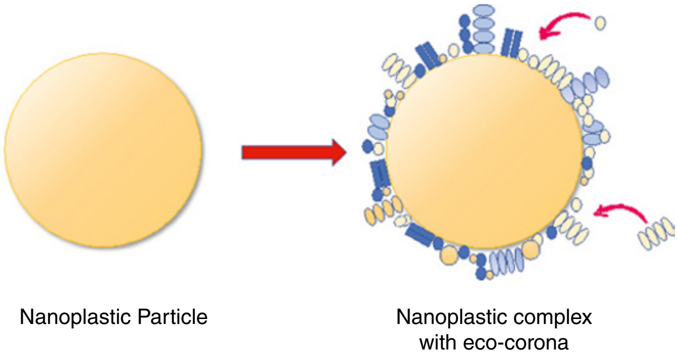


Figure 14.3 Nanoplastics develop a corona of proteins and other materials upon exposure to the environment.

factors in determining its aggregation behaviors and can of course be heavily impacted by microbial colonization.

In agreement with DLVO theory (which is generally applicable to the aggregation of nanoplastics), the aggregation rate coefficients of most NPs follow distinct reaction-controlled and diffusion-controlled regimes (Cai et al. 2018). Divalent cations destabilize NPs more aggressively than monovalent cations due to the higher capacity of charge neutralization from divalent cations (Sun et al. 2020). For polystyrene nanoplastics (PS-NPs), the attachment efficiency increases with increasing solution ionic strength until the mass transport-limited aggregation rate is reached (where the attachment efficiency is equal to one; Alimi et al. 2018). Thus, high-valence ions (such as iron chloride [$FeCl_3$]) more readily induce PS-NP aggregation than low-valence ions (Cai et al. 2018). For polystyrene latex (PSL) NPs, the presence of divalent cations (Ca^{2+} and Mg^{2+}) and dissolved organic carbon (DOC) can decrease the surface charge and increase the aggregate size in the water column (Zhang et al. 2019). The aggregation of polyethylene glycol terephthalate (PET-glycol modified) NPs also increases with increasing electrolyte concentrations (and in this case, decreasing solution pH), and attraction forces are stronger in the presence of divalent cations (Ca^{2+} and Mg^{2+}) due to the building of cross-links between the carboxyl and hydroxyl groups on different PET NPs compared to monovalent cations (Na^+ and L^+; Dong et al. 2020).

UV irradiation can play a crucial role in the aggregation processes of nanoparticles in aqueous solution. For instance, the dissolution kinetics of polymer-coated cadmium selenium/zinc sulfate CdSe/ZnS quantum dots (QDs) is driven by photo-oxidation involving the formation of superoxide radicals and affected by various environmental factors, including irradiation intensity, dissolved oxygen concentrations, temperature, the presence of humic acid, and surface coatings (Li et al. 2012). Arsenic sulfide (As_2S_3) has been shown to enhance aggregation under UV irradiation via HS· and OH· radical formation, which promotes aggregation to an intermediate species, which in turn combine into a larger aggregate through the rapid aggregation of sulfide particles (Kong et al. 2018). Polymer-stabilized silver (Ag) particles (coated with gum arabic and polyvinylpyrrolidone) have also been shown to irreversibly aggregate to different degrees based on their surface coatings once exposed to UV irradiation, with the UV content of sunlight identified as a driving force to nanoparticle aggregation (Cheng et al. 2011).

Solution chemistry coupled with UV irradiation can concurrently affect ionic strength and thus be a major factor in aggregation of nanoplastics. While the chemistry of a solution containing PO_4^{3-} may stabilize most UV-irradiated PS-NPs by inhibiting hydroxyl photogeneration, differing salts at differing concentrations can impact aggregation kinetics. Surface functional groups (such as -COOH and -NH_2) are known as auxochrome groups that have the potential to absorb light irradiation and can consequently induce degradation. UV-induced hydroxyl radicals have been shown to degrade the surface coatings of PS-NPs, leading to destabilization (with the exception in $CaCl_2$ solution due to the negative surface charge). These UV-induced hydroxyl radicals are also capable of degrading the amino groups of the amino-modified PS-NPs, decreasing the electrostatic repulsion forces among particles. Surprisingly, under UV irradiation, carboxyl-modified PS-NPs (due to their high negative surface charge and hydrophilicity) in NaCl and Na_2SO_4 solutions promote stability, though aggregation was accelerated in $CaCl_2$ due to the generation of more carboxyl groups with UV, which were found to bind with Ca^{2+} via a bridging effect (Wang et al. 2020c).

Nanoplastics can have especially strong sorption affinities for various compounds (Koelmans et al. 2015). PS-NPs can attach to metal calcium–aluminum ion flocculants in a moderately alkaline environment (pH above 5; Chen et al. 2020). Moreover, charge neutralization mechanisms were found to be responsible for the formation of hetero-aggregates with two inorganic colloids (Fe_2O_3 and alginate polysaccharide chains), with low to medium concentrations of alginate responsible for the formation of larger secondary hetero-aggregate structures (Oriekhova and Stoll 2018). The sorption of PAHs (including phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, and benzo[g,h,i]perylene) to PS-NPs was shown to be significantly higher compared to micrometer-sized PS, with PAHs being able to reach sorption sites even on small PS-NP aggregates, suggesting that the aggregate size has no significant effect on PAH sorption (Liu et al. 2016). Benzo[a]pyrene (Bap) has been studied in conjunction with PS-NPs and found to be easily and stably adsorbed to itself and the plastic surface, forming a nanocluster (with the nanocluster ultimately increasing the cellular toxicity of both compounds; Ji et al. 2020). Additionally, adsorption of PCBs (PCB 118 and PCB 126) to 70-nm PS-NPs was found to be 1–2 orders of magnitude stronger than to PS-MPs, with organic matter and salinity leading to an increase in sorption (Velzeboer et al. 2014).

Tetracycline can also favorably adsorb onto PS-NPs in neutral pH conditions in the presence of both Mg^{2+} and humic acid at a pH of 6 (but can be inhibited in Mg^{2+} alone at a pH greater than 5; Wan et al. 2019). Computational analysis using density functional theory found that the outer surface of nano-PET is nucleophilic in nature, which can allow it to increase the mass transfer and intraparticle diffusion of bisphenol A (BPA, a well-known organic compound often used as a building block of several plastics and plastic additives but also an endocrine disruptor) into the nanoplastic structure, theoretically allowing for stable complexes to form (with PET exhibiting adsorption characteristics more favorable than graphene, carbon nanotubes, activated carbon, and inorganic surfaces). While high ionic strength decreased adsorption between nano-PET and BPA, it did not completely inhibit BPA adsorption (Cortés-Arriagada 2020). A laboratory study looking at the adsorption of 40-nm PS-NPs to BPA and the antibiotic ciprofloxacin (CIP) found that UV-aged PS-NPs increased the capacity for both CIP and BPA (to a larger extent than CIP) to adsorb onto PS-NPs. Environmental conditions did not seem to have a large effect on BPA adsorption, while CIP adsorption was heavily influenced by electrostatic interactions and hydrogen bonding (Xiong et al. 2020). CIP demonstrated similar adsorption affinities to 500- and 200-nm PS-COOH NPs, with electrostatic interactions, hydrogen bonding, and hydrophobic interactions driving the adsorption process (Yilimulati et al. 2021).

Nanoplastics can also be formidable potential adsorbents of trace metals. Metal-based nanoparticles can disrupt the aggregation of different types of PS-NPs (such as unmodified-PS, PS-COOH, PS-NH_2, and PS-SO_3H). For example, CeO_2 nanoparticles can destabilize PS-NPs in NaCl and $CaCl_2$ solutions due to electrostatic neutralization and adsorption of functional groups. The increase in electrolyte concentration will progressively decrease the absolute values of the zeta potential, inducing an increase in the attachment efficiency (Li et al. 2020). Up to 97% of lead (II) (PB(II)) was found to bind to environmentally microplastic-derived (degraded via UV irradiation and mechanical degradation) nanoplastics at pH 7. The adsorption of Pb(II) was greatly influenced by pH (the increase in adsorption of Pb(II) was evidenced for pH higher than 4); an increase in pH led to an increase in the surface electronegativity in response to surface functional group deprotonation. The Freundlich adsorption constant (derived from the linear regression analysis of the Freundlich isotherm versus PB(II) concentration) of these nanoplastics with Pb(II) was similar to those of ferrihydrite, nano-geothite, and humic acid, all of which are known strong adsorbents of metals (Davranche et al. 2019). Additionally, polyethylene nanoplastics (PE-NPs) created from PE-microplastics collected in the North Atlantic gyre (dubbed PEN) were compared to reference, commercially available PE-NPs (dubbed PER) for trace metal analysis of 50 metals and metalloids. Metal analyses revealed a very high concentration of titanium (Ti), reaching 342 μg/g in PEN samples, but no Ti in PER samples. Zinc was detected in both, but much more concentrated in PEN (16 μg/g) than the PER (0.187 μg/g). Other metals such as arsenic, chromium, barium, copper, and aluminum were also found to be more concentrated in PEN compared to PER (41, 42, 48, 57, and 99 times more, respectively). These results are further indicative of the potential adsorption of environmental contaminants to plastic nanoparticles (Baudrimont et al. 2020).The high surface area of NPs may cause exceptionally strong sorption affinities for bio-macromolecules as well. Salts in solution containing and associating with macromolecules (such as sodium alginate [SA], bovine serum albumin [BSA], EPS, humic acid, and other sources of NOM) can affect NP stability (Gigault et al. 2018). The aggregation behavior of amino-modified PS (PS-NH_2) depends heavily on the concentration of NOM. In low concentrations, surface charges are neutralized, resulting in rapid aggregation, while high concentrations of NOM can reverse charges, restabilizing PS-NH_2 (Yu et al. 2019). Additionally, NOM can suppress the aggregation of unmodified PS-NPs and carboxylated PS-NPs (PS-COOH) with monovalent electrolytes (NaCl) due to steric hinderance and enhanced stability. In the presence of divalent electrolytes ($CaCl_2$), NOM can continually suppress aggregation at low concentrations but accelerate aggregation at high concentrations due to molecular bridging between Ca^{2+} and carboxyl groups in NOM (Liu et al. 2020; Yu et al. 2019). In $FeCl_3$ solutions of 0.1 mM and 1 mM concentrations (yielding a high ionic strength), NOM was found to increase PS-NP aggregation (Cai et al. 2018).

In seawater-saturated sand, the transport of PS-NPs functionalized with surface carboxyl, sulfonic, and low-density amino groups can be drastically enhanced by the presence of humic acid through the promotion of steric repulsions, while in contrast, humic acid induces high-density amino PS-NP aggregation and restricts its transport (Dong et al. 2020). Negatively charged NOM (alginate and Suwannee River humic acid [SRHA, a commonly used reference material for humic acid established by the International Humic Substances Society]) has also been shown to significantly modify the surface charge of positively charged amidine PS and decrease its zeta potential (the measure of the effective electric charge on a nanoparticle's surface, quantifying the charges (Saavedra et al. 2019; Selvamani 2019)).

For PET NPs, the addition of humic acid can significantly inhibit aggregation and promote stability (this is due to the negatively charged functional groups of HA increasing the negative surface charges of the PET NPs, which in some cases are even coated in HA molecules, providing an even greater negative charge and ultimately steric hinderance). Removing HA completely from solution (and decreasing pH) can significantly increase PET NP aggregation (Dong et al. 2020).

Salt types and ionic strength were shown to have significant effects on the stability of polyethylene nanoplastics as well. The CCC values of PE-NPs were lower in the presence of $CaCl_2$ compared to NaCl and $MgCl_2$, implying that $CaCl_2$ destabilized PE-NPs more aggressively. PE-NPs were shown to be less stable than PS-NPs in the aquatic media, though the addition of NOM improved the stability of PE-NPs via steric repulsions, implying that PE-NPs will likely be stable in natural surface waters (Shams et al. 2020).

Aggregation largely determines the fate, mobility, persistence, bioavailability, and toxicity of particles in the environment (Alimi et al. 2018; Hotze et al. 2010). The hetero-aggregation between nanomaterials and biogenic particles can increase the bioavailability of nanomaterials, and these biomacromolecule-nanoparticle aggregates may offer a way of entry for nanomaterials into cells and may determine the fate of the material in the organism (if and where particles collect inside an organism; Hotze et al. 2010; Lowry et al. 2012). In contrast to microplastics, nanoplastics have been found to enter a wide range of organs and have longer retention times (Kögel et al. 2020). Binding affinity is thus a function of both inter-particle and particle-cell wall interactions, which in turn are influenced by medium hardness and particle concentration (Nolte et al. 2017). Downsizing plastic particles from the microscale to nanoscale can lead to an evident shift in chemical properties (especially surface functional groups), and while physical factors such as water flow intensity play a dominant role in microplastic behavior (microplastics were shown to remain stable in all ionic strength solutions), chemical factors dictate the behavior of nanoplastics (Sun et al. 2020). The changes in surface functional groups can alter hydrophobicity and surface charges of nanoplastics and thus, may affect their adsorption affinities, aggregation behaviors, and may result in altered toxicity. Nanoplastics may in fact have a greater biological impact than microplastics due to their smaller dimensions and colloidal behaviors, in addition to their ability to also bind metals and other potentially toxic compounds, all of which allow them to cross biological barriers and impact cell metabolism (Gaylarde et al. 2020).

14.2 Interactions Between Nanoplastics and Marine Microbiota

Compared to engineered nanomaterials and metal nanomaterials, research on plastic nanoparticles remains in its infancy. Nanoplastics pose a credible yet uncalculated threat to marine organisms; their *modus operandi* is seemingly different from the micro-fraction and conceivably more toxic. Particle size has been identified as an important determining factor both in the extent and pathway of uptake within organisms (Oliveira et al. 2019). Considering that nanoplastics have the potential to permeate biological membranes and interact directly with organisms of all sizes, the characterization of the impacts of nanoplastics to organismal health is critical for ecosystem health. Nanoplastics can take on a new biological identity in the marine environment, often dictated by the biomolecular species on their surface (Canesi et al. 2015; Cedervall et al. 2007; Corsi et al. 2020).

The biomolecular corona is often the first point of contact between the nanoplastic particle and cells and contributes largely to the subsequent fate of a nanoplastic particle in biological systems. Differing surface functionalities and adsorbed components of the biomolecular corona can directly influence the fate of a nanoplastic particle at the molecular level, which in turn will affect the entire cell. In fact, when biological substances approach the nanoplastic surface, the formation of a bio- or eco-layer in the extracellular environment can create a novel biological identity for a nanoplastic particle (Pulido-Reyes et al. 2017).

Small disruptions to organisms at the base of the food web (including primary producers who provide materials and energy for higher trophic levels) may lead to bioaccumulation and noticeable repercussions ecosystem wide (Chae and An 2017). A handful of studies reviewed below have already begun to assess the toxicology of nanoplastic particles to marine microbiota, analyzing parameters affecting mortality and a battery of sublethal effects such as growth, reproduction, oxidative stress, photosynthesis, and cell membrane integrity.

Understanding the ecotoxicity of nanoplastics to single-celled microorganisms is crucial since microbial life is the foundation of Earth's biogeochemical cycles and ultimately our own health and well-being. For example, marine phytoplankton produce half of the oxygen in the air we breathe (Karl et al. 2003). Additionally, microbial biofilms are estimated to occupy 40–80% of the global biomass on Earth (Flemming and Wuertz 2019); therefore, the expanding habitat of the "Plastisphere" – biofilms living on the outer surface of plastic marine debris – represents an important focal point for nanoplastics' impacts (Zettler et al. 2013). EPSs (a possible target for nanoplastic adsorption) comprising of polysaccharides, proteins, lipids, nucleic acids, and extracellular DNA (eDNA; Sauer et al. 2007) are central to the formation and maintenance of the biofilm, and for many marine microbes, a biofilm is a successful strategy to colonize and survive in dynamic environments. While information is available on biofilm colonization of microplastics, this information in and of itself is only applicable to the possible colonization of nanoplastic particles, where size selection would be a determining factor for potential microbial colonizers. More likely, nanoplastic particles themselves are readily incorporated into biofilm structures, which could have community repercussions regarding toxicity. Much of our current knowledge of the impacts of nanoplastics on microbial life originates from studies employing readily available polystyrene nanoparticles, and it is not yet clear how well these are reflective of what microbes encounter in the wild.

14.2.1 Freshwater Proxies for Marine Nanoplastic Ecotoxicological Studies

Because nanoplastics have not been adequately measured in aquatic systems, only predictive evaluations are possible. Since freshwater ecosystems are often intermediates between land-based sources of pollution and the sea, freshwater models and assays may be relevant to marine ecosystems if specific differences (namely, density, biofilm formation, water chemistry, and attachment efficiencies) are considered (Koelmans et al. 2015). Similar aggregation patterns between freshwater and marine water have not been entirely quantified, though attachment efficiencies are expected to be higher in marine water due to higher ionic strengths, whereas collision frequencies will likely be lower due to the lower concentrations of natural colloids in the water column (Koelmans et al. 2015). Therefore, freshwater nanoplastics may display differing surface functionalities and exist in different concentrations than marine nanoplastics. Regarding ecotoxicology, effects experienced by freshwater organisms may ultimately differ from marine organisms, but parallels can be drawn between the types of experiments performed, and possibly even the toxicological impact.

Two separate studies looked at the relationship between freshwater toxin-producing cyanobacterium *Microcystis aeruginosa* and PS-NPs. In the first study, *M. aeruginosa* experienced varying effects after exposure to commercially purchased PS-NPs depending on the surface functionalization of the plastic particle. The synthesis of microcystin (MC) increased both under acute and long-term exposure experiments to PS-NH_2 compared to control groups, stimulating their extracellular release. For *M. aeruginosa*, an increase in MC synthesis indicates a need for the cell to protect itself from reactive oxygen species (ROS)-induced damage and enhance the fitness of bloom populations. Microcystin is a known toxin, associated with liver cancer and fatality; therefore, this foreshadows a troubling response loop, where nanoplastics might accelerate the release of MC, making it more likely for aquatic organisms to be exposed to high concentrations of MC. The results from a proteomics analysis of colonies selected from the water surface after 48 hours demonstrated that PS-NH_2 had a substantial influence on cyanobacterial protein expression, including the potential inhibition of photosynthetic activity (downregulation of photosystem II proteins such as PsbB, PsbC, and PsbD), weakening the photosynthetic electron transport chain, and reducing the carbohydrate metabolism due to downregulation. Acute exposure to low concentrations of PS-NH_2 only influenced the light reaction of photosynthesis, while high concentrations impaired both light and dark reactions. Additional observations after an acute exposure of PS-NH_2 included downregulation of lipopolysaccharide biosynthetic process-related proteins (indicating damage to cell membrane integrity). Green-fluorescent PS-NH_2 was observed to validate proteomic results and demonstrated that PS-NH_2 could penetrate the cell membrane, accumulating inside the cell via rupture of the cell membrane (Feng et al. 2020). In the second study, *M. aeruginosa* was exposed to 60-nm PS-NPs in concentrations ranging between 25 and 100 mg/L over different growth stages. The results indicated that PS-NPs caused dose-dependent inhibitory effects and increase in aggregation rates. Like the previous study, the production and release of MC were promoted with an increase in PS-NP concentration (Zheng et al. 2020).

Another freshwater cyanobacterium, *Anabaena* (involved in the carbon cycle, including global CO_2 sequestration) was exposed to 70–200 nm secondary (produced via UV irradiation and mechanical degradation of commercially purchased primary microplastic) polyhydroxy butyrate (PHB), a bio-based, biodegradable, and compostable alternative to conventional plastic polymers (traditionally considered innocuous to microbes). The growth of *Anabaena* significantly decreased by 90%, with an increase in intracellular ROS levels, severe membrane damage, decreased membrane integrity, and alteration of the cytoplasmic membrane potential causing strong depolarization of the membrane. Toxicity was confirmed to be from the PHB nanoplastics themselves rather than other abiotic degradation products released from PHB microplastics such as toxic additives (concluded after ultrafiltration removed all PHB nanoplastics and the resulting supernatant was shown to be nontoxic and not different from those of the control, which was plastic free; González-Pleiter et al. 2019). This same study also analyzed the exposure of the freshwater and soil-dwelling microalga *Chlamydomonas reinhardtii* to PHB-NPs. PHB-NPs caused a significant decrease in algal growth by 95%, an increase in intracellular ROS levels, impacted membrane integrity, and caused significant mitochondrial membrane potential depolarization. Negative effects from PHB-NPs were thus reported for both a photosynthetic cyanobacteria and a microbial eukaryote (González-Pleiter et al. 2019).

The responses of freshwater microalga *Chlorella vulgaris* were studied after exposure to commercially purchased micro- and nano-polystyrene. While control samples were recorded to have a 100% increase in chlorophyll a (Chl *a*) concentration, only a 50% increase was observed in treated samples in the exponential phase (when exposed to all PS-NP types). The 20-nm PS-NP exposed treatment achieved a reduction of >90% in Chl *a* concentration. Furthermore, morphological changes were noticed after exposure to 20-nm PS-NPs, including shrinkage and loss of spherical shape. After a 28-day incubation, a lactate dehydrogenase (LDH) assay (which measures the concentration of the LDH enzyme; increased concentrations indicate damage to the cell membrane) was performed, and LDH was found to reach a maximum value when cells were exposed to the 20-nm non-functionalized-PS-NP, followed by the 20-nm PS-COOH sample, and finally, the 50-nm PS-COOH sample (Hazeem et al. 2020). The rate of CO_2 depletion resulting from commercially acquired 20-nm amidine-PS and carboxyl-PS nanosphere adsorption was also measured in *Chlorella* sp. as a proxy for photosynthetic activity. It was found that the adsorption of both positively and negatively charged plastic beads hindered photosynthesis as a significant decrease in CO_2 depletion at and above a PS concentration of 1.8 mg/L was observed. Exposure to positively charged PS-NPs promoted a significantly higher rate of ROS production than negatively charged PS-NPs (Bhattacharya et al. 2010). Freshwater microalga *Pseudokirchneriella subcapitata* also experienced enhanced effects to 20-nm PS-NH_2, with overall higher adsorption affinity toward the positively charged nanoplastic, whereas adsorption of 110-nm PS-COOH increased as a function of medium hardness (Ca^{2+}) due to bridging occurring between the COO^- groups of the PS-COOH and Ca^{2+} (Nolte et al. 2017).

As shown above, photosynthetic organisms are essential to the functioning of aquatic ecosystems, and in freshwater, nanoplastics may induce various toxic effects on cells. These seemingly small disruptions on microalgal populations may contribute to serious impacts on higher trophic levels if initial periods of vulnerability are not followed by adaptive responses, leading to recovery (Nava and Leoni 2020). These studies demonstrate the ability of nanoplastics to affect photosynthetic systems in freshwater phototrophs, in addition to inducing increased oxidative stress and growth inhibition. To fully understand different mechanisms of detoxification employed as a response to nanoplastics, bioavailability and distribution of nanoplastics in experimental systems must shift toward a consensus to obtain accurate values of real nanoplastic concentrations that are environmentally relevant (Nava and Leoni 2020). Thus, to truly assess the impact of nanoplastics in marine ecosystems, marine-based assays are necessary.

14.3 Impact of Nanoplastics on Marine Phototrophic Microorganisms

Phototrophs (such as cyanobacteria) use light as their energy source to synthesize organic compounds and are widely distributed in marine environments. As primary producers, their presence is critical for the pelagic food chain and the overall productivity of marine systems relies on their growth. Included are diatoms, who are estimated to be responsible for approximately 40% of global primary productivity in the oceans and are recognized for producing EPS matrices – a critical foundation of the biofilm on plastic debris (González-Fernández et al. 2020), and microalgae (important in material cycling and energy transportation in the marine ecosystem, as they can assimilate nitrogen and phosphorus (among other elements) and are vital food sources for consumers in the marine environment). Though limited studies exist on the impact of nanoplastics on marine phototrophs, the topic is slowly gaining attention. The selected reviewed studies have been categorized into toxicological impact, including cytotoxicity, genotoxicity, viability, growth, and impact on photosynthetic efficiency.

14.3.1 Cytotoxicity, Genotoxicity, and Cellular Stress Responses

Nanoplastics have been shown to generate oxidative stress and initiate various cellular stress response pathways to cope with this environmental stressor in various microbial phototrophs. For example, the marine diatom *Chaetoceros neogracile* was exposed to low (0.05 mg/mL) and high (5 mg/mL) concentrations of 50 nm and 5 μm commercially purchased PS-NH_2. Both high and low exposures of *C. neogracile* to PS-NH_2 in the exponential phase demonstrated a significant decrease in esterase activity (considered as a proxy for primary metabolism) and a significant increase in intracellular ROS production. Overall, exposure to PS-NH_2 was shown to impair the major cellular and physiological parameters of *C. neogracile* more drastically during the exponential phase than during the stationary phase (González-Fernández et al. 2019). Additionally, after high PS-NH_2 exposure, *C. neogracile* experienced a decrease in glycolipids, specifically digalactosyl-diacylglycerol (DGDG) and monogalactosyl-diacylglycerol (MGDG) in exponential cultures and a reduction in the ratio between MGDG and DGDG. The overall membrane fatty acid profile increased at high PS-NH_2 exposures, indicating that PS-NH_2 exposure can lead to an impairment of long fatty acid synthesis. Chiefly, PS-NH_2 exposure led to significant changes in galactolipids and triacylglycerols at both growth phases, affecting the thylakoid membrane structure and cellular energy reserve of *C. neogracile* (González-Fernández et al. 2020).

The marine diatom *Skeletonema marinoi* was exposed to varying concentrations (1, 10, and 50 μg/mL) of 90-nm PS-COOH synthesized from commercially purchased styrene monomers as per Besseling et al. (2014) for 15 days. The results showed a concentration-dependent increase in both intracellular and extracellular ROS levels, with intracellular ROS levels significantly increasing compared to control samples for both 10- and 50-μg/mL PS-NP exposures (Bellingeri et al. 2020). The sensitivity of another marine diatom *Phaeodactylum tricornutum* to commercially purchased PS-NPs at two different sizes (50 nm and 100 nm) was studied using estimated environmentally relevant concentrations (extrapolated from previous studies on naturally derived microplastics) ranging from 0.1 to 50 mg/L. After a 24-hour exposure, an increase in oxidative stress biomarkers (ROS, O_2, and H_2O_2), damage to the photosynthetic apparatus, DNA damage, and depolarization of mitochondrial and cell membranes (from the 5 mg/L exposure) were observed (Sendra et al. 2019).

Marine cyanobacterium *Synechococcus* sp. PCC 7002 (an important primary producer in marine ecosystems with a fully sequenced genome, making it an ideal candidate for gene expression analysis) was exposed to 0.5 mg/mL of commercially purchased polyethylene microplastics and nanoplastics (ranging in size from 200 to 9,900 nm) over a 5-day and 10-day exposure period, respectively. Samples containing PE-NPs showed a clear increase in lipase/esterase production after five days of exposure, with a significant increase in esterase and hydrolase gene expression. Extracted RNA was evaluated for RNA integrity, and the yields for both micro-PE and PE-NP exposure were lower than the control samples, which indicates lowered transcription in growth-limiting or stressful conditions. Electropherograms of cultures exposed to PE-NPs displayed lower intensities of both 16S and 23S peaks compared to cultures exposed to micro-PE and control samples. This decrease (in addition to forementioned enzymatic and molecular activity modifications) is indicative of hypoxic cultures and could be the result of increased cell stress due to nanoplastic exposure (Machado et al. 2020). Cell responses of the marine red microalga *Rhodomonas baltica* to 50 nm commercially purchased polymethylmethacrylate nanoplastics (PMMA-NPs) and PMMA-COOH-NPs (at concentrations ranging from 0.5 to 100 μg/mL) caused an increase in ROS production in *R. baltica* with increasing concentration. Oxyl-radical formation (responsible for lipid oxidation) was also detected in *R. baltica* exposed to both PMMA-NP types. Hyperpolarization of the mitochondrial membrane and loss of membrane integrity were also noted with both PMMA-NP types. Mitochondrial hyperpolarization has been linked to an increase in respiration, where more oxidative phosphorylation can take place, causing a leak of electrons favoring the formation of ROS via by-product of ATP-generation (Gomes et al. 2020). Marine dinoflagellate *Karenia mikimotoi* (responsible for causing "red tide" harmful algal blooms) was exposed to commercially purchased PS-NPs of different sizes (65 nm, 100 nm, and 1 μm). Adverse effects were found to be dose-, exposure time-, and size-dependent, demonstrating an increase in oxidative stress with the decrease in particle size and increase in exposure concentration and time. Increases were detected in catalase (CAT), superoxide dismutase (SOD), and malondialdehyde (MDA) activity to all nanoplastic sizes with the greatest increase after exposure to 10 mg/L of 65-nm PS-NPs. The inhibitory rates (used as a proxy for effects on growth) after exposure to 10 mg/L were found to reach almost 100% for 65 nm, 91% for 100 nm, and 18% for 1 μm (Zhao et al. 2020).

Microbial phototrophs have developed a series of strategies to resist environmental stressors, but exposure to different plastic nanoparticles has been shown to result in oxidative toxicity in cells, including the targeting of lipids (which can be attacked directly by ROS), which ultimately affects membrane functions. Microorganisms have developed several strategies to maintain membrane integrity, but the loss in membrane integrity can decrease aspects of metabolic activity (such as esterase activity; González-Fernández et al. 2020). Both enzymatic and non-enzymatic antioxidant systems work together to protect the cell against oxidative stress and reduce ROS generation (Guan et al. 2017). The effectiveness of these systems in marine phototrophs will be an important factor in determining their adaptability to nanoplastic exposure.

14.3.2 Impacts on Photosynthetic Efficiency

For *C. neogracile* cultures in the exponential phase, the Chl *a* content decreased significantly after exposure to PS-NH_2 compared to controls (while no significant effect on Chl *a* was observed in stationary phase). After four hours of exposure at both exponential and stationary phases and at both high and low concentrations, the photosynthetic efficiency was found to decrease, whereas after 48 hours of exposure, a decrease was observed only in the exponential phase at high concentrations of exposure (González-Fernández et al. 2019). Similarly, *C. neogracile* was studied at two growth phases using the same low and high concentrations of 50-nm PS-NH_2 for effects relating to pigment and lipid compositions. For specimens in the exponential phase, a decrease of 75% in the quantity of pigments composing the fucoxanthin-chlorophyll protein (FCP) complex (chlorophyll *c* [Chl *c2*], Chl *a*, the sub-products of Chl *a* [allo Chl *a* and epi Chl *a*], and fucoxanthin [Fx]) was observed at high concentrations of exposure, in addition to a decrease in β-carotene (β-car) and phaeophytin (Phx) pigments (González-Fernández et al. 2020).

After a 72-hour exposure to 50- and 100-nm PS-NPs, the inhibition of chlorophyll content was observed for *P. tricornutum*. The smaller PS-NP size (50 nm) induced greater effects after a 24-hour exposure, while the larger PS-NP size (100 nm) induced greater effects at and after 72-hours of exposure (though compared to the smaller PS-NP particles, the larger size showed more stability overall; Sendra et al. 2019).

Green microalga *Platymonas helgolandica* was exposed to 70-nm PS-NPs and experienced a decrease in photosynthetic pigments. Exposure to 200 μg/L concentrations decreased the Chl *a* and carotene content, while exposure to both 200 and 2000 μg/L concentrations decreased the chlorophyll b (Chl *b*) content compared to the control groups (Wang et al. 2020b).

The exposure of *R. baltica* to both PMMA-NPs and PMMA-COOH-NPs caused an overproduction in pigment, namely, Chl *a*, Chl *b*, carotenoids, xanthophyll, and peridinin. Photosystem II (PSII) performance decreased with exposure; both nanoplastic types yielded an increase in the oxygen evolution complex (OEC) and a reduction in the relative electron transfer rate (ETR). OEC is a sensitive component in the electron transport chain and its alteration can be directly correlated to a reduction in electron transfer between photosystems. Consequently, the inhibition of PSII–PSI electron transport can affect all biochemical processes linked to photosynthesis (Gomes et al. 2020).

The ability of nanoplastics to significantly impact photosynthetic machinery is troubling: the reduction in photosynthetic efficiency has been linked to alterations in the electron transport chain that determines the production of ROS (Sendra et al. 2019) and affects the cell's metabolic capacity. Photosynthetic pigments are targeted by nanoplastics; microalgae, for example, adapt to alterations in light availability by modifying pigment composition to optimize photosynthesis, as changes in photosynthetic pigment levels are typically a quick response to stressful conditions (González-Fernández et al. 2020). This can result in either the overproduction of pigments due to an increase in energy demand by the organism, or reduction in pigment production due to a decrease in photosynthetic efficiency, highlighting the susceptibility of the organism to nanoplastic exposure.

14.3.3 Viability and Growth

For *C. neogracile* exposed to 50-nm PS-NH_2, the growth rate decreased by 49, 57, and 62% compared to controls after 48, 72, and 98 hours of exposure, respectively (González-Fernández et al. 2019). After a 48-hour exposure to both PS-NP sizes, growth data for *P. tricornutum* showed a significant inhibitory response compared to controls, with an increase in the percentage of non-viable cells since the first hours of exposure, and after a 72-hour exposure, the inhibition of population growth was observed (Sendra et al. 2019). A marine *Chlorella* sp. was exposed to 200 nm commercially acquired aminated, carboxylated, and unmodified PS-NPs (pristine and pre-treated in EPS to form eco-corona incorporated PS-NPs). Cell viability was heavily impacted, with PS-COOH causing a 45% reduction in viability and 50% increase in ROS, followed by PS-NH_2 (35% reduction in viability and 35% increase in ROS), and finally unmodified PS-NPs (30% reduction in viability and 25% increase in ROS; Natarajan et al. 2020). Diatom *Thalassiosira weissflogii* (exposed to reference PE-NPs and PE-NPs generated from PE collected in the North Atlantic gyre) showed a decrease in algal concentration after 10 hours of exposure to reference PE-NPs (a trend that did not reoccur for longer exposures), while growth was inhibited at a concentration of 1000 μg/L (the highest concentration tested) for the gyre-derived PE-NPs (Baudrimont et al. 2020).

Furthermore, microalgal species *Tetraselmis chuii*, *Nanochloropsis gaditana*, *Isochrysis galbana*, and diatom *T. weissflogii* were exposed to 40-nm PMMA-NPs (prepared by microemulsion polymerization of methyl methacrylate [MMA] with SDS as a stabilizer). *T. weissflogii* and *T. chuii* were the most sensitive and least sensitive, respectively. Growth inhibition was experienced by all species after 96 hours. *T. weissflogii* was significantly affected at concentrations equal to or higher than 18.8 mg/L. The growth rates of *T. chuii* and *N. gaditana* were significantly reduced at concentrations higher than 150 mg/L (Venâncio et al. 2019).

Microalga *P. helgolandica* experienced significant growth suppression within the first four days of exposure to PS-NPs in a dose-dependent manner. The cell density of *P. helgolandica* in the 2,000 μg/L exposure group compared to the control group (exposed to no NPs) was approximately 41.4%, 42.6 %, 55.6 %, and 70.1% less after the first, second, third, and fourth days, respectively. Additionally, the heterocyst frequency of microalgae exposed to 2,000 μg/L nanoplastics was significantly higher than that in the control groups, while exposure to 200 μg/L led to a smaller, yet noticeable increase (Wang et al. 2020b).

The decline in cell viability and growth rate is the principal toxicity indicator (Natarajan et al. 2020). ROS generation can correspond to a decrease in cell viability, and nanoplastic exposure has been shown to induce significant inhibitory responses on growth. While these studies demonstrate a decline in cell viability and growth after exposure to different nanoplastic types, it remains important to consider the exposure concentration when ultimately determining toxicity responses, as these studies used concentrations ranging from μg/mL and μg/L to mg/mL and mg/L.

14.3.4 Intracellular and External Aggregation

When exposed to 5 mg/mL of commercially purchased PS-NPs, *Synechococcus* sp. remained viable in all cases but saw high occurrences of aggregation with PS-NPs, and these aggregates were larger and sedimented more rapidly than either the control sample or the freshwater cyanobacterium sample. This is indicative that *Synechococcus* excrete EPS after exposure to PS-NPs to create large aggregates, causing the NPs to sink (de Oliveira et al. 2020).

Additionally, confocal imagery of *P. tricornutum* cells exposed to PS-NPs showed internalization of PS-NPs and adsorption of PS-NPs to the cell surface (Sendra et al. 2019). The results of PMMA-NP and PMMA-COOH-NP exposure to *R. baltica* showed that PMMA formed microscale aggregates, causing an overall higher impact on physiological parameters than PMMA-COOH-NPs, apart from growth, where PMMA-COOH-NPs significantly decreased the cell number at concentrations higher than 25 ug/mL (Gomes et al. 2020).

SEM imaging revealed the direct contact between *K. mikimotoi* cells and PS-NPs, yielding hetero-aggregates and damage to the cell wall and membrane. Both the 65 nm and 100 nm sizes attached to the transverse, posterior, and/or longitudinal flagella, increasing the difficulty of motion for the cells and leading to loss of cellular integrity and leakage/outflow induction of the cytoplasm owing to ruptures of the cell wall and cell membrane (Zhao et al. 2020).

P. helgolandica exposed to 200 μg/L and 2,000 μg/L of 70-nm PS-NPs exhibited aggregation clusters on the cellular surface, leading to fragmentation, loss of membrane integrity, and cell wall deformation. In comparison, the control groups exhibited an intact cellular structure with high plumpness, complete shape, and smooth surfaces (Wang et al. 2020b). Green microalga *Dunaliella tertiolecta* was exposed to varying concentrations (0.5, 1, 5, 10, 25, and 50 μg/mL) of 40-nm PS-COOH and 50-nm PS-NH_2; PS-COOH was shown to form microscale aggregates in the media as well as adsorb on microalgae, while PS-NH2 formed nanoscale aggregates (127 nm) in the media and inhibited algal growth (Bergami et al. 2017).

The adsorption of nanoplastic particles onto cell membranes and cell walls can prove to be detrimental to microbial organisms. Aggregation clusters can lead to excess fragmentation and loss of membrane integrity, while adsorbed particles can hinder photosynthesis through the reduction in light intensity and promote ROS production (Koelmans et al. 2015). Internalization of nanoplastic particles can in turn lead to intracellular aggregates, which can inhibit various biological systems and damage organelle morphology.

14.3.5 Additional Effects

S. marinoi cells reduced their chain length, with exposed samples showing a high percentage of single-cell and two-cell length chains (accounting for 95% and 84% of the 10 and 50 μg/L exposures, respectively), compared to the control samples showing only 36% of single-cell and two-cell chains, and 46% of four- and eight-cell chains. TEM analysis showed adhesion of PS-NPs onto the surface of the cell, with significant localization in the terminal fultoportula processes (TFFPs), which are elongated structures responsible for chain formation and maintenance (chain formation in *S. marinoi* has an adaptive function in reducing grazing mortality; Bellingeri et al. 2020; Bjærke et al. 2015).

Marine *Chlorella* sp. saw changes in eco-corona formation dependent on the surface functionality of PS-NPs. While cells treated with PS-NPs in the absence of EPS experienced declines in cell viability (with the highest effects measured for PS-COOH), an increase in cell viability was observed with increasing ageing period in a medium containing EPS, presumably due to enhanced eco-corona formation over the PS-NPs. Specimens exposed to the EPS-containing medium demonstrated a significant lessening in oxidative stress and cytotoxic impact due to eco-corona formation. The results also demonstrated that negatively charged PS-NPs have a higher binding affinity for EPS constituents than positively charged PS-NPs (Natarajan et al. 2020).

P. tricornutum was further investigated to determine the impact of commercially purchased 60-nm PS-COOH nanoplastics interacting with EPS, a major fraction of NOM. The EPS was found to facilitate the formation of eco-coronas, which in turn was found to alter the biological interactions with and toxicity to *P. tricornutum* by changing the bioavailability of the PS-NP. The results demonstrated that EPS significantly reduced PS-COOH aggregation in seawater, and an important fraction of EPS remained adsorbed onto PS-COOH upon incubation, leading to the formation of an eco-corona (Grassi et al. 2020).

EPS can provide an additional protective layer for microbial communities and in certain cases might even alleviate toxicity by reducing the concentration of free nanoplastic particles in the culture medium and inhibit cell internalization of plastic nanoparticles (Pulido-Reyes et al. 2017).

These studies demonstrate that nanoplastics can profoundly alter the metabolic functions of phototrophic organisms in a multitude of ways, including growth inhibition, induction of oxidative stress, decrease in photosynthetic efficiency, formation of aggregates, DNA damage, and more, depending on the exposure concentration, exposure time, and particle size. As primary producers, marine phototrophic microorganisms provide material and energy for higher trophic levels and are at the base of biomass production of oceanic waters (Grassi et al. 2020). Harmful effects sustained by marine phototrophic microorganisms can rebound to higher trophic levels, and due to their small size and abundance in the water column, they are likely to encounter nanoplastic colloids. As primary producers, they may constitute the main pathway for the trophic transfer of contaminants (including nanoplastics), yet our understanding of the impact nanoplastics have on these organisms remains scarce; therefore, further studies are highly necessary to fully comprehend how nanoplastics affect marine primary producers (Grassi et al. 2020).

14.4 Impact of Nanoplastics on Marine Heterotrophic Microorganisms

Though phototrophic microorganisms are vitally important to primary production in the marine environment, heterotrophs (organisms that rely on organic material and remineralize nutrients [Dodds and Whiles 2010]) may also associate with nanoplastics in the marine environment, and trophic transfer is thus also possible. Heterotrophic bacteria are known to recycle waste and contaminants in marine environments and therefore have a high ecological importance. Heterotrophic microorganisms are highly connected with various ecosystem components and thus are also suitable targets for nano-ecotoxicological research.

14.4.1 Cytotoxicity, Cellular Stress Responses, and Viability

When exposed to 50-nm commercially purchased PS nanobeads, the marine heterotrophic bacterium *Halomonas alkaliphilia* (gram-negative bacteria with an important role in nitrogen cycling of marine environments) experienced a range of toxicological effects. At a concentration of 80 mg/L, PS-NPs (but not PS-microplastics) influenced growth responses (cell viabilities increased, attributed to hormetic responses [biphasic response to exposure] of the cell, which in itself is considered a defensive and adaptive response to stress), chemical composition (FTIR analyses showed carbohydrate, polysaccharide, and amide adsorption bands all shifted toward higher wave numbers compared to control groups and microplastic treatments, suggesting alteration of the bacterial chemical composition related to the size of plastic), and ammonia conversion efficiencies (nanoplastic exposure yielded an increased in NH_4^+–N conversion efficiencies). Both PS-NH_2 and unmodified-PS-NP treatments (but not PS-microplastics) induced ROS generation (the PS-NH_2 treatment was significantly higher than the unmodified PS-NP treatment; Sun et al. 2018).

The bacterium *Shewanella oneidensis* MR-1 (a facultative anaerobe capable of living in a wide range of ecological niches, including variable salt concentrations and temperatures) also experienced sub-lethal effects after exposure to 160-nm PS-NPs (synthesized as described by Mitrano et al. [2019]). Riboflavin alteration occurred in the presence of PS-NPs (a significant increase in riboflavin secretion occurred with all doses up to and including 150 mg/L concentrations, with a significant decrease at the highest concentration of 300 mg/L) in both aerobic and anaerobic conditions. No alteration was observed with exposure to TiO_2 nanoparticles, thus confirming that the response was the result of a particular polymer. *S. oneidensis* is known to excrete riboflavin and other flavin mediators for several bacterial functions, though the function of this flavin response is still being investigated (Fringer et al. 2020). Benthic marine microbial foraminifera *Ammonia parkinsoniana* was exposed to 1 mg/L concentrations of commercially purchased 42-nm PS-NP. The mitochondria of specimens treated with PS-NPs were swollen and degraded compared to control specimens, and ROS production was induced for all exposed specimens. Specimens treated with PS-NPs showed an enhanced accumulation of neutral lipids occurring as lipid droplets. Lipid droplets (containing primarily neutral lipids such as esterified cholesterol and triglycerides) have been hypothesized to sequester contaminants to protect the cell (Ciacci et al. 2019).

Rotifers (classified as "micro-animals" rather than microbes) exhibit a generally low feeding selectivity as filter feeders and therefore might be especially susceptible to nanoplastic ingestion. Marine rotifer *Brachionus plicatilis* was exposed to laboratory-synthesized 40-nm polymethylmethacrylate (PMMA-NPs) nanoplastics for 48 hours, and the results demonstrated that the survival of the rotifer was greatly affected. Based on size category distinctions for *B. plicatilis* (SS [100–160 μm], S [140–220 μm], and L [190–320 μm]), type L rotifers displayed a significant decrease in survival at concentrations higher than 9.38 mg/L, while types S and SS were only affected at 75 mg/L exposure concentrations. This could mean that larger rotifers are more susceptible to nanoplastic toxicity, as their filtration ability is dependent on size and higher ability to incorporate particles due to a higher foraging activity (Venâncio et al. 2019). *B. plicatilis* was also exposed to 40-nm PS-COOH and 50-nm PS-NH_2 (both commercially purchased). PS-COOH exposure did not cause mortality to the rotifer, whereas PS-NH_2 caused mortality at a concentration greater than or equal to 2.5 μg/mL (Manfra et al. 2017). The LC_{50} of PS-NH_2 in the study of Manfra et al. was 6.62 mg/L, whereas the LC_{50} in the study of Venâncio et al. was >13.3 mg/L, suggesting that PMMA-NPs are less toxic than PS-NH_2 for *B. plicatilis*. Contrary to mortality caused by PS-NH_2, the exposure of *B. plicatilis* to 100-nm unmodified PS-NPs (commercially acquired) showed no significant effects on mortality for rotifers exposed to all concentrations (0.001–10 mg/L) and exposure times (24 and 48 hours), though swimming behavior and speed were impaired after exposure to all concentrations (Gambardella et al. 2018).

Another marine rotifer, *Brachionus koreanus*, was exposed to the synergistic effects of 50, 500, and 6,000 nm non-functionalized PS-NPs (commercially purchased) and two model organic pollutants: 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) and triclosan (TCS). The rotifers were exposed to 10 μg/mL of fluorescently labelled PS-NPs to monitor ingestion and plastic accumulation rate. A parallel experiment exposed rotifers to 50-nm PS-NPs at different concentrations (0, 0.1, 1, 10, and 20 μg/mL) to monitor ROS and conduct MDA assays (to measure the final product of lipid peroxidation) and to quantify MXR (multixenobiotic resistance that acts as a first line of defense in response to xenobiotics) activity measurements to assess the synergistic effects of POPs and PS-NPs. The results indicated that the smaller, nanoscale PS sizes demonstrated a stronger accumulation in the cells compared to the microbeads, which can be indicative of oxidative stress-induced damages on lipid membranes. ROS and MDA levels displayed a concentration-dependent increase up to 10 μg/mL exposure, indicating that nanoplastics generate oxidative stress and induces oxidative damage on lipid components. MXR activity was partially inhibited by PS-NP pre-exposure, which yielded an enhanced toxicity to BDE-47 and TCS (with population growth and reproduction rates showing a further decrease in the pre-exposure group than the chemical only exposure control; Jeong et al. 2018).

14.4.2 Aggregation and Impacts on Community Composition and Biofilm Formation

Flash-red conjugated PS-NPs (fluorescently labelled) were documented in *A. parkinsoniana* after a 24-hour exposure at a concentration of 1 mg/L in all chambers (Ciacci et al. 2019). *H. alkaliphilia* experienced adherence of positively charged beads (PS-NH_2) onto its cell surface via electrostatic activity (Sun et al. 2018). PS-NH_2 showed nano-aggregate formation in *B. plicatilis*, while PS-COOH showed micro-aggregate formation (Manfra et al. 2017).

In a study of a panel of heterotrophic marine bacteria, including *Marinobacter adhaerens*, *Oceanobacter kriegii*, *Marinobacter algicola*, *Cobetia marina*, *Marinobacter hydrocarbonoclasticus*, *Pseudoalteromonas carrageenovora*, and *Phaeobacter inhibens*, the presence of carboxylated PS-NPs had little impact on cell-cell aggregation, with only the 200-ppm concentration significantly increasing aggregation of *P. carrageenovora* and *C. marina*, whereas amidine PS-NP exposure increased aggregation of all bacterial species. Additionally, lower concentrations of carboxylated PS-NPs had no impact on the amount of biofilm formed; however, 200-ppm exposure significantly increased biofilm formation for *M. adhearens*, *M. algicola*, *C. marina*, and *O. krieggi*, and confocal laser scanning microscopy of the biofilms revealed that nanoparticles were integrated into the biofilm itself. For amidine PS-NPs, a similar effect was observed, except at 200-ppm exposure, biofilm formation significantly decreased for *M. hydrocarbonoclasticus*, *P. inhibins*, *P. carrageenova*, *M. algicola*, and *C. marina*. The results of this study indicate that mild exposure to PS-NPs will likely not have a significant impact on the formation of marine bacterial biofilms, though surface functionalities and concentration can ultimately impact biofilm formation (Okshevsky et al. 2020).

The heterotrophic microbial composition and diversity of *Mytilus galloprovincialis* (assessed through 16S rRNA gene amplification and sequencing) varied after exposure to commercially acquired PS-NPs. Control specimens of *M. galloprovincialis* hemolymph were dominated by *Shewanella*, *Vibrio*, and *Mycoplasma*, with these three genera accounting for >60% of abundance. Exposure to PS-NH_2 resulted in an evident shift in hemolymph microbial composition, demonstrating an increase for *Vibrio* (39.2%) and *Psychrobium* (17.2%), with these two genera thus accounting for 56% of relative abundance, while other genera such as *Shewanella* (8.6%) and *Mycoplasma* (3%) decreased. Though relative abundances changed, the overall membership of the representative core community members (consisting of *Vibrio*, *Shewanella*, *Psychrobium*, *Pseudoalteromonas*, *Colwellia,* and *Aureispira*) remained stable and constant regardless of PS-NH_2 exposure (Auguste et al. 2020).

Furthermore, after exposure to PS-NPs, an increase in EPS was observed for *H. alkaliphilia* (suggested to be a potential protective mechanism to nanoplastic exposure; Sun et al. 2018). In *S. oneidensis*, PS-NPs associated indirectly with the bacterial EPS and directly with the bacterial membrane (binding them so strongly that the associated PS-NPs remained attached after a series of cell-washing steps; Fringer et al. 2020). A study by Summers et al. (2018) demonstrated *in vitro* that 50-nm and 500-nm PS-NPs readily formed agglomerates in seawater with mucilaginous material, revealed to be glycoprotein in composition (isolated from *Halomonas* sp. TGOS-10). Marine bacterial EPS was determined to be a key agent in the agglomeration of plastic nanoparticles, with a higher number of agglomerates formed as a function of increasing EPS concentration (Summers et al. 2018). Several factors impact the capacity of biofilms to retain nanoparticles, including the amount of biofilm, bacterial strains, particle size, surface functionalities, media composition, and concentrations of nanoparticles (Deschênes and Ells 2020).

These studies demonstrate the importance of nanoplastic particle size on toxicity; it is often a crucial factor in determining aggregate formation, cytotoxicity, and growth effects, as smaller nanoplastics can permeate membranes with greater ease. In cases where mortality is not an endpoint, various sublethal effects have been shown. Furthermore, surface functionality continues to be an important factor, as unmodified and negatively charged nanoplastics are often less toxic than positively charged nanoplastics and more readily incorporated into EPS (at least for multiple studies using PS as the polymer of choice). The biotoxicity of nanoplastics is affected by a combination of various parameters, including chemical composition, size heterogeneity, composition of surface materials, colloidal stability, and morphology.

14.5 Ecosystem Implications

Nanoplastics are extremely small and therefore capable of interacting at the cellular level, resulting in another dimension of toxicological concern. These toxicological effects on marine fauna are further complicated by the ability of nanoplastics to adsorb onto eco-coronas, or to adsorb a wide range of additional molecules to themselves. Current studies have demonstrated that the primary toxic effects of nanoplastics on organisms are affected by the surface chemical properties and particle size of nanoplastics, though other factors, such as exposure concentration, can also play a role.

Marine nanoplastics have recently been detected in natural aquatic ecosystems, including polymers of PE, PS, PVC, and PET sampled from the North Atlantic subtropical gyre (Ter Halle et al. 2017). Yet, there is relatively little information available on the abundance and distribution of nanoplastic particles, and the ecological relevance of laboratory observations is likely to be low since they cannot fully reflect the complexity of aquatic environments (Nava and Leoni 2020). For example, large concentrations of nanoplastics have sometimes been used in bench studies to test the effects on nanoplastics within short periods of time, and often these test concentrations cannot or do not occur naturally in the environment.

Therefore, it is still premature to assign exposure-specific trends to specific taxa, but establishing environmentally relevant concentrations of nanoplastics, expanding nanoplastic polymer types used in ecotoxicology assays, targeting organisms that regularly interact with marine plastic debris, and generating secondary nanoplastics from microplastics collected from the environment are the crucial next steps in generating relevant and widely applicable data. Until these challenges are adequately addressed, they will continue to hinder the risk assessment of nanoplastics in the environment.

If it truly is the case that these tiny plastic nanoparticles can be transferred along the food chain to higher trophic level organisms, they may ultimately find their way into the human food chain. Table 14.1 summarizes various toxicological effects of nanoplastics on select multicellular marine organisms relevant to the seafood industry. Since humans are the ultimate consumer in the aquatic food web, the introduction of nanoplastics seems plausible with the continual consumption of plastic-containing aquatic products.

14.6 Potential Effects of Nanoplastics on Humans

Due to a lack of *in vivo* studies on nanoplastic toxicology and human health, most understanding of the effects of nanoplastics on human health originates from *in vitro* studies and extrapolations from non-plastic nanotoxicology research (Kihara et al. 2020). To ascertain the exact effects of plastic nanoparticles in human physiological systems, a significant increase in *in vitro* studies of relevant mammalian model cell cultures, accurate quantification of environmental nanoplastic concentrations, and a standardized methodology of sampling procedures and analytical techniques are required (Teles et al. 2020; Zarus et al. 2020). Nonetheless, understanding routes of contamination/exposure, uptake kinetics, and estimations of toxicological impact from non-plastic nanoparticle studies can aid in unraveling the potential toxicological effects imposed by bioactive nanoplastics.

Potentially adverse effects from nanoplastics may result from a combination of toxicity induced by the plastic polymer itself, the chemical composition of the nanoplastic (i.e., leaching of additives), or the ability of nanoplastics to adsorb, concentrate, and release environmental molecules/toxins/pollutants into organisms (Revel et al. 2018). Three major exposure pathways to nanoplastics have been proposed: inhalation (primarily impacting the lungs), ingestion (primarily impacting the gastrointestinal [GI] tract), and dermal (via absorption by the skin; Kihara et al. 2020; Lehner et al. 2019).

Inhalation is likely relevant in occupational settings, where bulk plastics undergo mechanical and milling stress and may involve nanoplastic-containing aerosols (Kihara et al. 2020; Lehner et al. 2019). Due to the large alveolar surface area of the lung (~145 m^2) and the very thin tissue barrier of >1 μm, nanosized particles have the potential to penetrate the capillary blood system and distribute throughout the body (Gehr et al. 1978). This is a cause for concern given that once plastic

Table 14.1 Toxicological effects of different nanoplastic polymers on various marine organisms relevant to the seafood industry.

Species	Common name	Plastic polymer	Size	Concentration	Effects	Routes of exposure	Global production estimates (capture and aquaculture)	Study
Crassostrea virginica	Eastern oyster	PS	100 nm	1.3×10^4 particles/mL	Aggregates enhanced the uptake of PS-NPs; ↑ retention times, suggesting that they were transported to the digestive gland	Aqueous exposure	~118 000 tons (2016; aquaculture only)	Ward and Kach (2009)
Crassostrea gigas	Pacific oyster	PS-COOH; PS-NH_2	100 nm	0.1, 1, 10, 100 µg/mL	Aggregates attached to the cell; ROS levels ↑ with PS-COOH	Aqueous exposure of gametes	~573 000 tons (2016; Aquaculture only)	González-Fernández et al. (2018)
Mytilus edulis	Blue mussel	PS	30 nm	0, 100, 200, 300 µg/mL	Particles adsorbed to gills; ↓ filtering activity; production of pseudo-feces	Aqueous exposure	~260 000 tons (2016)	Wegner et al. (2012)
Mytilus galloprovincialis	Mediterranean mussel	PS-NH_2	50 nm	1, 5, 50 µg/mL	Immune parameters affected; induced pre-apoptotic processes; ↑ in extracellular ROS and NO (nitric oxide) production	Aqueous exposure	~105 000 tons (2016; aquaculture only)	Canesi et al. (2015)
Euphausia superba (juvenile)	Antarctic krill	PS-COOH; PS-NH_2	50 nm	2.5 µg/mL	PS-COOH formed agglomerates; ↑ in exuviae production; ↓ swimming activity (PS-NH_2 exposure); Fecal pellet structure changes	Aqueous exposure/ ingestion	~273 000 tons (2016; catch only)	Bergami et al. (2020)
Litopenaeus vannamei	Whiteleg shrimp	PS	44 nm	50 µg/mL	↑ in the activity of GST and SOD in the hepatopancreas; changes in essential amino acids; gut microbiome characteristics initially affected but microorganisms adapted to the prolonged exposure	Dietary exposure	>4 155 000 tons (2016; aquaculture only)	Chae et al. (2019)
Larimichthys crocea	Large yellow croaker	PS	100 nm	1.8189×10^{13} items/mL	↓ digestive enzyme activities; change in gut bacterial phyla proportion; ↑ of pathogenic bacteria; lysosomal activity and specific growth rate (SGR) ↓; total mortality of juvenile fish ↑	Aqueous exposure	~269 000 tons (2016)	Gu et al. (2020)
Sparus aurata	Gilthead sea bream	PMMA	40 nm	0.001, 0.01, 0.1, 1, 10 mg/L	Up-regulation of mRNA levels of key genes associated with the lipid metabolism; ↑ in cholesterol and triglycerides in plasma; ↑in erythrocytic nuclear abnormalities (ENAs)	Aqueous exposure	>195 000 tons (2016)	Brandts et al. (2021)
Dicentrarchus abrax	European seabass	PMMA	45 nm	0.02;0.2; 2 mg/L	Changes in molecular signaling pathways related to the lipid metabolism; ↓ in esterase activity levels in plasma and ↓ in levels of alkaline phosphatases in skin mucus	Aqueous exposure	~191 000 tons (2016; aquaculture only)	Brandts et al. (2018)

Source: Global production estimate data obtained from FAO.org.

nanoparticles have entered the human body and overcome primary tissue barriers, transport through the bloodstream can carry them to secondary organs. It has been shown *in vitro* that carboxylated polystyrene nanoparticles can undergo a "cellular hitchhiking" mechanism by penetrating into red blood cells as a result of van der Waals, electrostatic forces, hydrogen bonding, and hydrophobic forces between the PS and red blood cells, leading to significant prolongation of circulation compared to free plastic nanoparticles of the same diameter (99.9% of unbound particles were rapidly eliminated in 2 minutes, compared to over 12 hours with RBC-bound PS-NPs (Chambers et al. 2004)). Furthermore, nanoplastics can potentially avoid rapid clearance by the liver and spleen and increase its circulation time (Lehner et al. 2019).

Contact with the skin is predicted to occur using personal care products that contain nanoplastics or contaminated water or air, but currently a lack of experimental evidence exists to confirm this as a major hazard. The skin provides the body with a protective barrier against external influences (primarily the *stratum corneum*), and due to the hydrophobic properties of many plastic nanoparticles, significant dermal uptake is not expected, though entry routes via hair follicles and injured skin areas have not been explored (Lehner et al. 2019).

Oral ingestion (likely through drinking water and food matrices) is therefore likely to represent the main route of entry/exposure route for humans (Lehner et al. 2019). While plastic piping is widely utilized in drinking water distribution lines (due to their superior performance in terms of portability, corrosion resistance, cost, and service life), data are not yet available as to whether this directly leads to nanoplastic contamination in water (Xu et al. 2019). Thus, the presence of nanoplastics in the food chain and marine products may serve as one of the most important routes of entry for humans.

Nanoplastic uptake and accumulation as well as trophic transfer of nanoplastics within aquatic organisms have been somewhat demonstrated under experimental conditions, for example, in freshwater systems, ~55 nm fluorescently labelled PS-NPs adhered to the surface of algae, were present in the digestive organs of the higher trophic level species, even induced histopathological changes in fish livers, and were present in the yolk sac of hatched juveniles (Chae et al. 2018). Yet, it has not been experimentally confirmed that nanoplastic uptake from dietary contamination results in human exposure (Lehner et al. 2019). Considering that the global production of seafood is approaching 155 million tons per year (with fish accounting for over 100 million tons per year) and over 4.3 billion people rely on fish for 15% of their average per capita intake of animal protein (approximately 33 calories per capita per day), ingestion of nanoplastic-contaminated food is of growing concern (Fisheries 2012; Ritchie and Roser 2019). PS-NPs have been successfully detected in complex food matrices (fish fillet samples) with asymmetric flow field fractionation coupled with multi-angle light scattering following enzymatic digestion, without affecting the main characteristics of the nanoplastic and successfully degrading the food matrix. Unfortunately, the results could not be replicated for PE-NPs, further highlighting the importance of continued research efforts to quantify and detect nanoplastics in the human food chain (Correia and Loeschner 2018). Improving detection methods could yield significant insight into trophic transfer, which can lead to biological accumulation, where the next trophic level will have higher concentrations of plastic nanoparticles (Bouwmeester et al. 2015).

Nanoplastic translocation across the gut could occur due in part to the ability of plastic nanoparticles to penetrate cells and the gut epithelium (Revel et al. 2018). The GI tract has an average surface area of 200 m^2 and therefore represents the primary exposure site for plastic particle uptake (Lehner et al. 2019). Oral ingestion is followed by various steps that ultimately influence the possible interactions of the nanoplastic particle, including contact with digestive fluids, contact with intestinal cells, uptake/transport in the intestine, or even excretion. While on route to the intestinal epithelium, plastic nanoparticles will pass through several different compartments of the gastrointestinal tract, and these interactions may affect the physicochemical properties and surface parameters of the nanoplastic (Paul et al. 2020). The intestinal tissue will try to function as a biological barrier, preventing systemic distribution of harmful substances as best as possible (the human excretory system should be able to remove up to 90% of ingested microplastics and nanoplastics [Campanale et al. 2020]). If adopting the more conservative definition of nanoplastics (less than or equal to 100 nm), their behavior will likely act in a size-dependent manner. Larger nanoplastics may remain in the lumen (where the potential exists to cause local irritation of the intestinal tissue or release of adsorbed particles into the lumen), whereas smaller nanoplastics may cross the epithelium through either paracellular routes (tight junctions between intestinal epithelial cells) and be taken up into enterocytes of the intestinal epithelium or active endocytosis (Bouwmeester et al. 2015; Paul et al. 2020). Particles that are not translocated may also influence and perturbate the structure and composition of the gut microbiome (stressed organisms may demonstrate a greater diversity or turnover of microbial species compared to healthy organisms), but studies have yet to comprehensively describe this effect for nanoplastics (Teles et al. 2020).

If nanoplastic particles can circumvent biological barriers, including mucosal barriers, (particularly relevant for particles smaller than 100 nm that may be misidentified as physiological molecules by these barriers and make use of inherent entry mechanisms to cross them, including pinocytosis and vesicular phagocytic processes), they may have a greater opportunity to enter the bloodstream and circulate (Kihara et al. 2020; Revel et al. 2018). This translocation is both size and surface charge dependent (Bouwmeester et al. 2015).

The uptake of plastic nanoparticles will be undoubtedly influenced by their interactions with surrounding biological components, such as proteins, phospholipids, or carbohydrates, due to their size, surface functionalities, and ionic charges (Lehner et al. 2019). The adsorption of these biomacromolecules can result in the formation of a shell, or “protein corona”, around the nanoplastic particle consisting of various biological constituents; thus, the interactions between organs and tissues in the human system will likely occur with protein-coated rather than bare-plastic nanoparticles, which may in turn influence the incorporation of the nanoplastic by altering the characteristics and surface charges (for example, negatively charged nanoplastics may be internalized by endocytosis, whereas positively charged nanoplastics may be carried by micropinocytosis; Lehner et al. 2019; Waring et al. 2018). The formation of these complexes with biomacromolecules creates additional contributing factors and further complicates the establishment of causal relationships between nanoplastics and human toxicology, as both the chemical identity of the protein corona and the intrinsic properties of the nanoplastic itself can factor into the determination of biochemical processes (Kihara et al. 2020).

The formation of a protein corona can be competitive, and thus the complex will form two distinctive structures: a “hard” corona, where proteins rapidly and strongly adhere to the nanoplastic surface (for human plasma systems, these are generally human serum albumin [has], apolipoproteins, and IgG), and a “soft” corona, where proteins are loosely bound atop and can take many hours to equilibrate due to high sensitivity from the external environment composition (Beddoes et al. 2015; Kihara et al. 2020). Plastic nanoparticle size can also influence the formation of soft versus hard coronas: smaller nanoplastics have been shown to have stronger attractions to HSA and formed hard corona complexes compared to larger nanoplastics that formed soft corona complexes at pH 5, and these hard corona complexes were more likely to form larger aggregates with one another (Kihara et al. 2019).

The presence of a protein corona is not necessarily deleterious; variations in protein types, the biological identity of the corona (i.e., the physicochemical properties of the complex formed around the corona), the morphology of the corona complex, and the structure of participating proteins (from secondary to quaternary) will all contribute to determining the fate of the protein-nanoplastic complex (Kihara et al. 2020). On one hand, the protein corona may result in a loss of or alteration to the functionality of the protein, where those tightly bound to the corona may undergo partial unfolding of their secondary structure; fully hydrophobic plastics favor and even enhance alpha-helical structures, while non-hydrophobic plastics are prone to change alpha-helical structures into a beta-loop-like conformation on the surface of the corresponding plastic nanoparticle (Hollóczki 2020). Protein coronas may also extend the lifetime of the nanoplastic within the biological system (Kihara et al. 2020). On the other hand, the addition of proteins and small molecules to the nanoplastic surface may sterically hinder the targeting ligands, reducing their capacity, and increase the nanoparticle size by up to several nanometers, affecting its ability for uptake through barriers (Beddoes et al. 2015).

Although very limited information on the human toxicity of nanoplastics is available, the potential risks of engineered nanoparticles may facilitate the understanding of potential effects, though not all studies can be readily extrapolated to nanoplastics. Since ionic toxicity can be excluded for nanoplastics, only chemically inert nanoparticles should be considered relevant for understanding the potential of nanoplastics toxicity: gold (Au) and TiO_2 nanoparticles approach this definition of inertness (Bouwmeester et al. 2015).

TiO_2 nanoparticles have been shown to cross the follicle-associated epithelium (FAE; through the *in vitro* use of a human epithelial colorectal adenocarcinoma cell [Caco-2] and lymphoblast-like Raji-B coculture) and further accumulate in human intestine microfold cells (M-cells) and mucus-secreting cells. Though TiO_2 nanoparticles did not cause overt cytotoxicity or apoptosis, they were shown to induce epithelium impairment (by inducing deregulation of genes encoding proteins involved in epithelial structure maintenance) and may possibly persist in gut cells, where they may cause chronic damage (Brun et al. 2014). Caco-2 cells were also utilized *in vitro* to test Au nanoparticle (AuNP) toxicity and were found to be absorbed by intestinal epithelium cells. The results indicated that in terms of total particle mass, the smaller the particle size, the lower the total amount of AuNPs accumulated in the epithelial cells. Conversely, in terms of total particle number, the smaller the particle size, the greater the total accumulation of AuNPs within the epithelial cells. Cytotoxic effects were measured after accumulation of AuNPs, with AuNPs progressively spreading throughout the epithelium cells and eventually accumulating within different cellular organelles, including endosomes, lysosomes, Golgi apparatus, mitochondria, and nucleus. Depolarization of the mitochondrial membrane (where a decrease in mitochondrial membrane potential is an indicator of cell death) was reported, with larger AuNPs yielding overall higher toxicity due to the formation of aggregates (Yao et al. 2015). Additionally, the transcriptome profile of Caco-2 cells has been shown to change upon exposure to AuNPs, with smaller AuNPs leading to a stronger effect on gene expression. Genes associated with RNA/zinc ion/transition metal binding decreased, while genes associated with cadmium/copper ion binding and glutathione metabolism increased, along with nuclear factor E2-related factor 2 (Nrf2) responsive genes (a redox and xenobiotics sensitive transcriptional factor involved in the proper expression of proteins utilized in cellular adaptation to oxidative stress; Bajak et al. 2015). These studies indicate that the nanoparticle size is extremely important in determining the types of effects experienced by epithelial cells: while a range of particle size can permeate the epithelial membrane, larger particles are most likely to form aggregates and impair cell functionality, whereas smaller particles may be responsible for genotoxic effects. Combining the results of these kinds of studies with *in vitro* studies using plastic nanoparticles on human cell lines may prove to be the best method in understanding the potential toxicological impacts of nanoplastics on humans.

While the toxicity of TiO_2 and Au nanoparticles is relatively well studied, the pathophysiological consequences of acute and chronic nanoplastic exposure in human systems remains unclear (Yong et al. 2020). We do know that certain plastics (e.g., PS) may release monomers that are directly toxic to cells (styrene; Saido et al. 2014). *in vitro* studies using human cells lines exposed to plastic nanoparticles could offer insight on potential toxicological effects, especially those targeting cell lines associated with the GI tract and the circulatory system.

Nanoplastics are expected to reach the human GI tract through the consumption of contaminated food products and, in the case of marine examples, contaminated seafood (Yong et al. 2020). Ingested nanoplastics would therefore likely encounter the intestinal epithelium, where potential translocation could occur, bringing along hazardous adsorbed compounds. A recent study looked at the relationship between PET nanoplastics (as independent and complex-bound with one of three common contaminants: glyphosate [a widely used herbicide], levofloxacin [an antibiotic], and Hg^{2+} [mercury metal ions, considered to be a highly hazardous chemical to humans]) and heterogenous Caco-2 cells to determine short- and long-term effects (Magrì et al. 2021). Short-term assays evaluated cell viability and detected no evidence of alterations with either NP or NP-contaminant complexes nor were oxidative events triggered. The study further investigated potential long-term effects using metabolomics to collect mechanistic information induced by small variations of the basal cellular metabolism. Metabolomic analysis targeted anabolic glycolysis with production of lactic acid, with control (untreated) samples displaying a high lactate/glucose ratio, indicating that most of the consumed glucose is converted into lactate. In all treated samples, the consumption of glucose was significantly higher (indicating the cells may be modifying their metabolism in the presence of contaminants), while the glucose/lactate ratio strongly decreased (suggesting that glucose was being redirected toward alternative metabolic processes). Additionally, an increase in the lactate/alanine ratio indicated a higher reductive and lower oxidative state of the cells in response to oxidative stress; both these results suggest cellular effort to compensate for increased oxidative stress not distinguishable at a macroscopic level. Overall, all NP-contaminant complexes demonstrated higher glucose consumption than NP-only treatments. This study highlighted the importance of combining alternative methodologies with standard biological assays to fully assess the complex relationship between plastic nanoparticles and the human system, as no short-term toxicological effects were measured, but potential long-term effects may exist, similar to AuNPs described in Bajak et al. (2015).

In another study looking at translocation with epithelial cells, three *in vitro* intestinal cell models were employed with increasing complexity: a monoculture (Caco-2), a co-culture with mucus secreting HT29-MTX cells (where negatively charged nanoplastics may experience electrostatic repulsion and positively charged nanoplastics may undergo mucus entrapment), and a tri-culture with M-cells. These cells were exposed to two sizes (50 and 100 nm) of unmodified and positively and negatively modified (two types of negatively charged 50 nm) PS-NPs. The results demonstrated that the presence of mucus significantly reduced the translocation of neutral 50-nm PS-NPs but increased the translocation of at least one type of negative 50-nm PS-NP. Translocation was clearly affected by size, with 100-nm PS-NPs reaching up to 0.8 % translocation and 50-nm PS-NPs reaching up to 7.8%. The study also analyzed the attached protein content and found that the neutral and negatively charged 100-nm PS-NPs had the highest protein content, followed by the neutral and negatively charged 50-nm PS-NPs; however, almost no proteins were detected on the 50-nm and 100-nm positively charged PS-NPs. The neutral and negatively charged 50-nm PS-NPs with the largest number of adsorbed proteins translocated to the highest extent, indicating that a protein corona-nanoplastic complex is more likely to interact with epithelial cells versus a nanoplastic particle itself (Walczak et al. 2015b).

A similar study exposed two different co-culture models (differentiated Caco-2/HT29 intestinal cells and Caco-2/HT29 + Raji-B cells) to pristine (50–100 nm) and fluorescent (40–90 nm) PS-NPs for 24 hours. The results indicated that exposure to PS-NPs did not induce any apparent toxicity to either cell group nor were the cells' barrier integrity and permeability affected. Despite the absence of toxicity, the uptake of PS-NP was detected in both cell groups with the fluorescently labelled PS-NPs. Ultimately, while the PS-NPs were able to enter and cross the epithelial barrier of the digestive system, they did not exert apparent hazardous effects (Domenech et al. 2020).

The gastrointestinal digestion of the protein coronas of 50-nm positive and negative PS-NPs was studied *in vitro* using a co-culture of Caco-2 and HT29-MTX cells. Digested and pristine PS-NPs differed in translocation rates, with the *in vitro* gastrointestinal digestion significantly increasing the translocation rates of all PS-NPs, except for the unmodified ones. Upon *in vitro* digestion, translocation was 4-fold higher for the positively charged PS-NPs. Digestion was shown to significantly reduce the amount of protein in the corona for three of the four types of PS-NPs used and affected the composition of the protein corona by decreasing the presence of higher molecular weight proteins and shifting the protein content to low molecular weight proteins. *in vitro* gastrointestinal digestion was shown to significantly affect the protein corona and significantly increase the *in vitro* translocation of differently charged PS-NPs, with overall surface functionalities ultimately affecting their uptake potency (Walczak et al. 2015a).

If nanoplastics can translocate into the circulatory system, blood cells may be affected. Whole blood samples from different donors were exposed *ex vivo* to different concentrations of pristine (50–100 nm) and fluorescent (40–90 nm) PS-NPs. No toxicity was detected in the overall white blood cell population, though these cells demonstrated a high capacity to uptake PS-NPs. However, differences were seen in different lineages: limited uptake in lymphocytes, high uptake in monocytes, and intermediate uptake in polymorphonuclear (PMN) cells. PMN and monocytes experienced a significant increase in the levels of DNA damage, but not in lymphocytes. However, these results were dose-dependent (DNA damage was shown for cells exposed to 100 μg/mL) and thus may not be environmentally realistic (Ballesteros et al. 2020). In another study, three different human leukocytic cell lines (Raji-B, TK6 [lymphoblasts], and THP-1 [monocytes]) were exposed to 50-nm PS-NPs. The monocytic THP-1 cells had the highest level of particle internalization (even at low exposure concentrations, this cell line had the highest ability to internalize particles), but no adverse effects were observed (indicating that this cell line seems to be more resistant), while Raji-B and TK6 had lesser PS-NP uptake but underwent mild toxicity, ROS production, and negative genotoxic effects (in concentrations at or above 200 μg/mL). Despite this, the overall effects were mild and only detected at very high concentrations that are not expected to be relevant from an environmental point of view. Furthermore, no associations between cell uptake and toxicity were observed, supporting previously published studies reporting the lack of toxicity of pristine PS-NPs (Rubio et al. 2020).

These studies highlight the ability of nanoplastics to translocate in the GI tract and potentially even reach the circulatory system, but this translocation event is not always deleterious, yielding minimal to no short-term effects on cell viability. Protein corona formation seems to be a common and expected event, with differing surface functionalities influencing the protein content. Thus, the ability of nanoplastics to form protein coronas and translocate does not necessarily exert a health hazard, though more research is needed to determine long-term, chronic effects.

Nanoplastics may induce minor cytotoxic and genotoxic effects on the human cell lines most likely to be exposed to nanoplastic particles, but this field of research remains in its infancy. The human system is extremely complex, as are the behaviors of plastic nanoparticles. For example, it is not known to what extent nanoplastics can be further degraded after ingestion (under acidic conditions found in the gut or inside cells in digestive organelles such as the lysosome) nor the extent at which nanoplastics promote the uptake of chemical additives and the subsequent leaching of these additives (Lehner et al. 2019). While current research seems to indicate that worries of acute toxicity or long-term effects that could significantly enhance cell mortality are somewhat unfounded, very little is known about how environmental nanoplastics may affect human health (Yong et al. 2020), which may carry different additives and adsorb different types of environmental pollutants during their long life in the environment (Lehner et al. 2019). Reported studies rely heavily on model engineered PS-NPs, but other polymers such as PE, PP, and PET are the main polymer material present in the natural environment; additionally, environmental nanoplastics appear in various shapes and sizes, while model PS remains monodisperse (Lehner et al. 2019). The inconsistent use of units, exposure media, and plastic polymer type/origin make it difficult to combine exposure and effect data to truly characterize and manage risk, while current bioaccumulation studies may need to be modified to account for colloidal chemistry and the relationship between plastic nanomaterial and dynamic systems (Handy et al. 2012; Lehner et al. 2019). Reliable analytical methods for identification and quantification of nanoplastics in food are lacking, and the detection of nanoplastics in food poses a serious challenge because the resolution and contrast between nanoplastics and the surrounding food matrix are very low, all of which severely hamper current research efforts (EFSA Panel on Contaminants in the Food Chain 2016).

14.7 Outlook and Future Considerations

While the analysis of microplastics is established for particles as small as 1 μm, sub-micrometerscale and nanoscale plastic particles face a methodological gap (Schwaferts et al. 2019). Table 14.2 attempts to summarize a few of the most widely utilized detection methodologies in nanoplastic literature. Another important consideration of laboratory work is sample pre-treatment and establishment of appropriate separation steps to isolate nanoplastics (such as ultrafiltration, ultracentrifugation, evaporation, and flow field fractionation; Wang et al. 2020a). These methodological challenges associated with separation and analysis of nanoplastics are one of the greatest challenges to progressing our understanding of this field.

Despite the use of various analytical tools and instrumentation, no standardized methodology exists that can be readily applied to secondary nanoplastics. Most toxicological studies are reported against unrealistic environmental conditions, though the ability to determine environmental concentrations remains unknown (Barbosa et al. 2020). This is therefore a key limitation to developing standardized testing, as the complexity of marine water and realistic nanoplastic concentrations are not reflected in test media. The most frequently used nanoplastic polymer in reviewed literature remains PS; however, this is not consistent with the global plastic demand: PE, PP, and PVC have annual plastic productions of 29.7, 19.3, and 10%, respectively, while PS only accounts for 6% (Wang et al. 2020a).

Development of sensitive and selective analytical techniques is required to detect and retain environmental nanoplastics both as single particles and in bulk/adsorbed form (and accurately identify their chemical composition to provide confirmation of nanoplastics in the target system). These methods must be selective toward multiple types of plastic polymers found in a variety of environmental matrices (sediment, water, biota), while ensuring that applied conditions for removing these matrices do not alter the plastic particles of interest (Jakubowicz et al. 2020; Wagner and Reemtsma 2019).

Table 14.2 Examples of select available methods for nanoplastic detection.

Method classification	Analysis methods	Detection range	Description	Example studies (nanoplastics)	Pitfalls of technique
Particle sizes/ distribution; light scattering	Dynamic light scattering (DLS)	1 nm to ~3 μm	Provides a measure of the size of nanoparticles from the scattered light in a colloidal suspension polymeric solution	Oriekhova and Stoll (2018)	Unable to chemically identify NPs
	Laser diffraction (LD)	10 nm to 10 mm	Utilizes diffraction patterns of a laser passed through an object	Sun et al. (2020)	Unable to chemically identify NPs
	Nanoparticle tracking analysis (NTA)	30 nm to 2 μm	Uses scattering of laser light to provide information on hydrodynamic diameters of individual particles in the low nanometer to low micrometer size range	Lambert and Wagner (2016); Ekvall et al. (2019)	Unable to chemically identify NPs
	Electrophoretic light scattering (ELS)	1 nm to 3 μm	Measures the fluctuation of laser intensity generated by particle movement in an electric field	Heinlaan et al. (2020)	Unable to chemically identify NPs
	Multiangle laser scattering (MALS)	10 nm to 1 μm	Uses the scattering of laser light applied at different angles to determine the particle size; requires monodisperse samples, thus often applied in-line with size fractionation techniques, such as AF4	Gigault et al. (2016); Correia and Loeschner (2018); Monikh et al. (2019)	Unable to chemically identify NPs
Particle sizes/ distribution; separation	Asymmetrical flow field flow fractionation (AF4)	1 nm to 1 μm	Separation of analytes according to their diffusive properties, which are directly proportional to their hydrodynamic size, by applying a crossflow through an ultrafiltration membrane	Monikh et al. (2019); Gigault et al. (2017); Mintenig et al. (2018)	Unable to chemically identify NPs
Imaging analysis; microscopy	Scanning electron microscopy (SEM)	<1 nm and up	Utilizes high-energy electrons to provide information on the material/particle surface	Oriekhova and Stoll (2018); Gniadek and Dąbrowska (2019)	Quantification difficult
	Transmission electron microscopy (TEM)	<1 nm and up	Utilizes high-energy electrons to provide information regarding the interior of the analyzed sample/particle	Ekvall et al. (2019)	Use may be hindered in different matrices; quantification difficult

(*Continued*)

Table 14.2 (Continued)

Method classification	Analysis methods	Detection range	Description	Example studies (nanoplastics)	Pitfalls of technique
	Atomic force microscopy (AFM)	<1 nm to 1 µm	Scanning probe microscopy-based procedure (can be coupled with pyramidal tips) to assess surface topography in addition to nanoscale deformation and adhesion of individual NPs	Zimmermann et al. (2020); Dazzi et al. (2012)	Artifacts possible due to particle movement
Imaging analysis; spectrometry	Energy-dispersive X-ray spectrometry (EDS)	nm range	Utilizes detectors to discern plastic particles from natural organic and inorganic particles in sample	Gniadek and Dąbrowska (2019)	Elemental information not sufficient
	UV–VIS spectrophotometer	190 nm to 900 nm	Measures light absorbance across UV and visible light ranges; used to quantify analytes in a sample based on absorption characteristics	Zhang et al. (2019); Chen et al. (2020)	Information on size not provided
Chemical characterization; spectroscopy	Pyrolysis gas chromatography mass spectrometry (Py-GC-MS)	<1 nm to >20 µm	Analytical technique that thermally degrades a sample via pyrolysis into small molecular fragments for subsequent separation/identification using GC-MS	Zhou et al. (2018); Mintenig et al. (2018)	Dry sample needed; difficult to use with certain polymers; preconcentration necessary
	Raman micro-spectroscopy (RM)	> 100 nm	Light scattering technique where a molecule scatters incident light from a high intensity laser; high spatial resolution	Sobhani et al. (2020); Gillibert et al. (2019); Lv et al. (2020)	Diffraction limit of the laser spot hinders imaging of smaller nanoparticles
	Fourier-transform infrared spectroscopy (FT-IR)	10 µm + (bulk analysis)	Identifies the functional groups present in organic/inorganic compounds by measuring their absorption of infrared radiation over a range of wavelengths; quick analysis time; works well for bulk analyses (Berna 2017). Best coupled with other techniques for NP analysis	Ekvall et al. (2019)	Only for bulk analysis

Source: Information in this table was adapted in part from Jakibowicz et al. (2020), Wang et al. (2020), and Schwaferts et al. (2019).

The current literature on the toxicological impacts of nanoplastics remains unclear on the actual toxicological impact and environmental fate given a true, natural system. To properly assess the environmental risk of nanoplastics, studies must be conducted on relevant microorganisms previously documented to associate with marine plastic debris. Furthermore, it is important for toxicity studies to distinguish between nanoplastic-specific toxicity versus toxicity of water-soluble additives and adsorbed particle additives, as these have been previously demonstrated to generate false positive results of acute toxicity in bacteria, freshwater microalgae, and a crustacean (Heinlaan et al. 2020). Additionally, the importance of a corona complex cannot be understated: studies should not only derive nanoplastics from environmentally sourced microplastics, but these nanoplastics may exist in bound form, rendering them more stable, as a corona coating can reduce the surface energy of a nanoplastic (Nasser et al. 2020), which may even serve to reduce the toxicity experienced by various microorganisms. On the other hand, agglomeration of nanoplastics on the cell surface and biofilm surfaces may impact buoyancy in the water column and affect cellular membrane structure and integrity. With all these considerations, there may not yet exist an all-encompassing takeaway for nanoplastic toxicology.

The degradation of larger plastic polymers in marine environments may yield nanoscale particles. Assuming nanoplastics occur in the marine environment (and are not degraded into molecular components), as it stands, nanoplastics have such varying and unique shapes and chemical compositions that it remains difficult to predict their behaviors in marine systems, including their ability to aggregate, sediment, accumulate, and transfer through the trophic chain. Nanoplastics may theoretically constitute a higher particle number but very low mass in a sample, which further highlights the importance of hetero-aggregates at the nanometer scale (Jakubowicz et al. 2020). Nanoplastics in the marine environment represent a frontier area of research, and continued research efforts will undoubtedly help shape our understanding of its impacts in the short and longer term.

References

Alimi, O. S., Budraz, J. F., Hernandez, L. M., et al. (2018). Microplastics and nanoplastics in aquatic environments: aggregation, deposition, and enhanced contaminant transport. *Environmental Science & Technology*, 52(4): 1704–1724.

Alpha Nanotech. (2021). *Analytical-Grade Colloidal Polystyrene Nanospheres*. Available from https://www.alphananotechne.com/polystyrene-nanoparticles (accessed December 1, 2020).

Auguste, M., Lasa, A., Balbi, T., et al. (2020). Impact of nanoplastics on hemolymph immune parameters and microbiota composition in *Mytilus galloprovincialis*. *Marine Environmental Research*, 159(11): 105017.

Bajak, E., Fabbri, M., Ponti, J., et al. (2015). Changes in Caco-2 cells transcriptome profiles upon exposure to gold nanoparticles. *Toxicology Letters*, 233: 187–199.

Balakrishnan, G., Déniel, M., Nicolai, T., et al. (2019). Towards more realistic reference microplastics and nanoplastics: preparation of polyethylene micro/nanoparticles with a biosurfactant. *Environmental Science: Nano*, 6: 315–324.

Ballesteros, S., Domenech, J., Barguilla, I., et al. (2020). Genotoxic and immunomodulatory effects in human white blood cells after *ex vivo* exposure to polystyrene nanoplastics. *Environmental Science: Nano*, 7: 3431–3446.

Barbosa, F., Adeyemi, J. A., Bocato, M. Z., et al. (2020). A critical viewpoint on current issues, limitations, and future research needs on micro- and nanoplastic studies: from the detection to the toxicological assessment. *Environmental Research*, 182: 109089.

Baudrimont, M., Arini, A., Guégan, C., et al. (2020). Ecotoxicity of polyethylene nanoplastics from the North Atlantic oceanic gyre on freshwater and marine organisms (microalgae and filter-feeding bivalves). *Environmental Science and Pollution Research*, 27: 3746–3755.

Beddoes, C. M., Case, C. P., Briscoe, W. H. (2015). Understanding nanoparticle cellular entry: a physicochemical perspective. *Advances in Colloid and Interface Science*, 218: 48–68.

Bellingeri, A., Casabianca, S., Capellacci, S., et al. (2020). Impact of polystyrene nanoparticles on marine diatom *Skeletonema marinoi* chain assemblages and consequences on their ecological role in marine ecosystems. *Environmental Pollution*, 262: 114268.

Bergami, E., Pugnalini, S., Vannuccini, M. L., et al. (2017). Long-term toxicity of surface-charged polystyrene nanoplastics to marine planktonic species Dunaliella tertiolecta and Artemia franciscana. *Aquatic Toxicology*, 189: 159–169.

Bergami, E., Manno, C., Cappello, S., et al. (2020). Nanoplastics affect moulting and faecal pellet sinking in Antarctic krill (*Euphausia superba*) juveniles. *Environment International*, 143: 105999.

Besseling, E., Wang, B., Lürling, M., et al. (2014). Nanoplastic affects growth of *S. obliquus* and reproduction of *D. magna*. *Environmental Science & Technology*, 48(20): 12336–12343.

Bhattacharya, P., Lin, S., Turner, J. P., et al. (2010). Physical adsorption of charged plastic nanoparticles affects algal photosynthesis. *The Journal of Physical Chemistry C*, 114: 16556–16561.

Bjærke, O., Jonsson, P. R., Alam, A., et al. (2015). Is chain length in phytoplankton regulated to evade predation? *Journal of Plankton Research*, 37(6): 1110–1119.

Bouwmeester, H., Hollman, P. C. H., Peters, R. J. B. (2015). Potential health impact of environmentally released micro-and nanoplastics in the human food production chain: experiences from nanotoxicology. *Environmental Science & Technology*, 49: 8932–8947.

Brandts, I., Barría, C., Martins, M. A., et al. (2021). Waterborne exposure of gilthead seabream (*Sparus aurata*) to polymethylmethacrylate nanoplastics causes effects at cellular and molecular levels. *Journal of Hazardous Materials*, 403: 123590.

Brandts, I., Teles, M., Tvarijonaviciute, A., et al. (2018). Effects of polymethylmethacrylate nanoplastics on *Dicentrarchus labrax. Genomics*, 110(6): 435–441.

Brun, E., Barreau, F., Veronesi, G., et al. (2014). Titanium dioxide nanoparticle impact and translocation through ex vivo, in vivo and in vitro gut epithelia. *Particle and Fibre Toxicology*, 11: 1–16.

Bundschuh, M., Filser, J., Lüderwald, S., et al. (2018). Nanoparticles in the environment: where do we come from, where do we go to? *Environmental Sciences Europe*, 30: 1–17.

Cai, H., Xu, E. G., Du, F., et al. (2020). Analysis of environmental nanoplastics: progress and challenges. *Chemical Engineering Journal*, 410: 128208.

Cai, L., Hu, L., Shi, H., et al. (2018). Effects of inorganic ions and natural organic matter on the aggregation of nanoplastics. *Chemosphere*, 197: 142–151.

Campanale, C., Massarelli, C., Savino, I., et al. (2020). A detailed review study on potential effects of microplastics and additives of concern on human health. *International Journal of Environmental Research and Public Health*, 17(4): 1212.

Canesi, L., Ciacci, C., Bergami, E., et al. (2015). Evidence for immunomodulation and apoptotic processes induced by cationic polystyrene nanoparticles in the hemocytes of the marine bivalve Mytilus. *Marine Environmental Research*, 111: 34–40.

Cedervall, T., Lynch, I., Lindman, S., et al. (2007). Understanding the nanoparticle–protein corona using methods to quantify exchange rates and affinities of proteins for nanoparticles. *Proceedings of the National Academy of Sciences*, 104: 2050–2055.

Chae, Y., An, Y.-J. (2017). Effects of micro-and nanoplastics on aquatic ecosystems: current research trends and perspectives. *Marine Pollution Bulletin*, 124(2): 624–632.

Chae, Y., Kim, D., Kim, S. W., et al. (2018). Trophic transfer and individual impact of nano-sized polystyrene in a four-species freshwater food chain. *Scientific Reports*, 8: 1–11.

Chae, Y., Kim, D., Choi, M.-J., et al. (2019). Impact of nano-sized plastic on the nutritional value and gut microbiota of whiteleg shrimp *Litopenaeus vannamei* via dietary exposure. *Environment International*, 130: 104848.

Chen, Z., Liu, J., Chen, C., et al. (2020). Sedimentation of nanoplastics from water with Ca/Al dual flocculants: characterization, interface reaction, effects of pH and ion ratios. *Chemosphere*, 252: 126450.

Chambers, E., Mitragotri, S. (2004). Prolonged circulation of large polymeric nanoparticles by non-covalent adsorption on erythrocytes. *Journal of Controlled Release*, 100: 111–119.

Cheng, Y., Yin, L., Lin, S., et al. (2011). Toxicity reduction of polymer-stabilized silver nanoparticles by sunlight. *The Journal of Physical Chemistry C*, 115: 4425–4432.

Christian, P., Von der Kammer, F., Baalousha, M., et al. (2008). Nanoparticles: structure, properties, preparation and behaviour in environmental media. *Ecotoxicology*, 17: 326–343.

Ciacci, C., Grimmelpont, M. V., Corsi, I., et al. (2019). Nanoparticle-biological interactions in a marine benthic foraminifer. *Scientific Reports*, 9: 1–10.

Correia, M., Loeschner, K. (2018). Detection of nanoplastics in food by asymmetric flow field-flow fractionation coupled to multi-angle light scattering: possibilities, challenges and analytical limitations. *Analytical and Bioanalytical Chemistry*, 410: 5603–5615.

Corsi, I., Bergami, E., Grassi, G. (2020). Behavior and bio-interactions of anthropogenic particles in marine environment for a more realistic ecological risk assessment. *Frontiers in Environmental Science*, 8: 60.

Cortés-Arriagada, D. (2020). Elucidating the co-transport of bisphenol A with polyethylene terephthalate (PET) nanoplastics: a theoretical study of the adsorption mechanism. *Environmental Pollution*, 270: 116192.

da Costa, J. P., Santos, P. S., Duarte, A. C., et al. (2016). (Nano) plastics in the environment–sources, fates and effects. *Science of the Total Environment*, 566–567: 15–26.

Davranche, M., Veclin, C., Pierson-Wickmann, A.-C., et al. (2019). Are nanoplastics able to bind significant amount of metals? The lead example. *Environmental Pollution*, 249: 940–948.

Dawson, A. L., Kawaguchi, S., King, C. K., et al. (2018). Turning microplastics into nanoplastics through digestive fragmentation by Antarctic krill. *Nature Communications*, 9: 1–8.

Dazzi, A., Prater, C. B., Hu, Q., et al. (2012). AFM–IR: combining atomic force microscopy and infrared spectroscopy for nanoscale chemical characterization. *Applied Spectroscopy*, 66: 1365–1384.

de Oliveira, T. T. S., Andreu, I., Machado, M. C., et al. (2020). Interaction of cyanobacteria with nanometer and micron sized polystyrene particles in marine and fresh water. *Langmuir*, 36: 3963–3969.

Deschênes, L., Ells, T. (2020). Bacteria-nanoparticle interactions in the context of nanofouling. *Advances in Colloid and Interface Science*, 277: 102106.

Dodds, W., Whiles, M. (2010). Chapter 17 – Nutrient use and remineralization. In: Niskern, D. (Ed.), *Freshwater Ecology*. Library of Congress, Washington, pp. 437–467.

Domenech, J., Hernández, A., Rubio, L., et al. (2020). Interactions of polystyrene nanoplastics with *in vitro* models of the human intestinal barrier. *Archives of Toxicology*, 94: 2997–3012.

Dong, S., Cai, W., Xia, J., et al. (2020). Aggregation kinetics of fragmental PET nanoplastics in aqueous environment: complex roles of electrolytes, pH and humic acid. *Environmental Pollution*, 268: 115828.

EFSA Panel on Contaminants in the Food Chain. (2016). Presence of microplastics and nanoplastics in food, with particular focus on seafood. *Efsa Journal*, 14: e04501.

Ekvall, M. T., Lundqvist, M., Kelpsiene, E., et al. (2019). Nanoplastics formed during the mechanical breakdown of daily-use polystyrene products. *Nanoscale Advances*, 1: 1055–1061.

El Hadri, H., Gigault, J., Maxit, B., et al. (2020). Nanoplastic from mechanically degraded primary and secondary microplastics for environmental assessments. *NanoImpact*, 17: 100206.

Enfrin, M., Lee, J., Gibert, Y., et al. (2020). Release of hazardous nanoplastic contaminants due to microplastics fragmentation under shear stress forces. *Journal of Hazardous Materials*, 384: 121393.

Feng, L.-J., Sun, X.-D., Zhu, F.-P., et al. (2020). Nanoplastics promote microcystin synthesis and release from cyanobacterial *Microcystis aeruginosa*. *Environmental Science & Technology*, 54: 3386–3394.

Fisheries, F. (2012). *The State of World Fisheries and Aquaculture*. Rome: Aquaculture Department, pp. 1–153.

Flemming, H.-C., Wuertz, S. (2019). Bacteria and archaea on Earth and their abundance in biofilms. *Nature Reviews Microbiology*, 17: 247–260.

Food and Agriculture Organization of the United Nations. (2021). *Cultured Aquatic Species Information Programme*. Available from https://www.fao.org/fishery/culturedspecies/en (accessed January 23, 2021).

Fringer, V. S., Fawcett, L. P., Mitrano, D. M., et al. (2020). Impacts of nanoplastics on the viability and riboflavin secretion in the model bacteria *Shewanella oneidensis*. *Frontiers in Environmental Science*, 8: 1–11.

Gambardella, C., Morgana, S., Bramini, M., et al. (2018). Ecotoxicological effects of polystyrene microbeads in a battery of marine organisms belonging to different trophic levels. *Marine Environmental Research*, 141: 313–321.

Gaylarde, C. C., Neto, J. A. B., da Fonseca, E. M. (2020). Nanoplastics in aquatic systems – are they more hazardous than microplastics? *Environmental Pollution*, 272: 115950.

Gehr, P., Bachofen, M., Weibel, E. R. (1978). The normal human lung: ultrastructure and morphometric estimation of diffusion capacity. *Respiration Ecology*, 32: 121–140.

Gigault, J., Pedrono, B., Maxit, B., et al. (2016). Marine plastic litter: the unanalyzed nano-fraction. *Environmental Science: Nano*, 3: 346–350.

Gigault, J., El Hadri, H., Reynaud, S., et al. (2017). Asymmetrical flow field flow fractionation methods to characterize submicron particles: application to carbon-based aggregates and nanoplastics. *Analytical and Bioanalytical Chemistry*, 409: 6761–6769.

Gigault, J., Ter Halle, A., Baudrimont, M., et al. (2018). Current opinion: What is a nanoplastic? *Environmental Pollution*, 235: 1030–1034.

Gillibert, R., Balakrishnan, G., Deshoules, Q., et al. (2019). Raman tweezers for small microplastics and nanoplastics identification in seawater. *Environmental Science & Technology*, 53: 9003–9013.

Gniadek, M., Dąbrowska, A. (2019). The marine nano-and microplastics characterisation by SEM-EDX: the potential of the method in comparison with various physical and chemical approaches. *Marine Pollution Bulletin*, 148: 210–216.

Gomes, T., Almeida, A. C., Georgantzopoulou, A. (2020). Characterization of cell responses in *Rhodomonas baltica* exposed to PMMA nanoplastics. *Science of the Total Environment*, 726: 138547.

González-Fernández, C., Le Grand, F., Bideau, A., et al. (2020). Nanoplastics exposure modulate lipid and pigment compositions in diatoms. *Environmental Pollution* 262: 114274.

González-Fernández, C., Tallec, K., Le Goïc, N., et al. (2018). Cellular responses of Pacific oyster (*Crassostrea gigas*) gametes exposed in vitro to polystyrene nanoparticles. *Chemosphere*, 208: 764–772.

González-Fernández, C., Toullec, J., Lambert, C., et al. (2019). Do transparent exopolymeric particles (TEP) affect the toxicity of nanoplastics on *Chaetoceros neogracile*? *Environmental Pollution*, 250: 873–882.

González-Pleiter, M., Tamayo-Belda, M., Pulido-Reyes, G., et al. (2019). Secondary nanoplastics released from a biodegradable microplastic severely impact freshwater environments. *Environmental Science: Nano*, 6: 1382–1392.

Grassi, G., Gabellieri, E., Cioni, P., et al. (2020). Interplay between extracellular polymeric substances (EPS) from a marine diatom and model nanoplastic through eco-corona formation. *Science of The Total Environment*, 725: 138457.

Gu, H., Wang, S., Wang, X., et al. (2020). Nanoplastics impair the intestinal health of the juvenile large yellow croaker *Larimichthys crocea*. *Journal of Hazardous Materials*, 397: 122773.

Guan, N., Li, J., Shin, H.-D., et al. (2017). Microbial response to environmental stresses: from fundamental mechanisms to practical applications. *Applied Microbiology and Biotechnology*, 101: 3991–4008.

Handy, R. D., Cornelis, G., Fernandes, T., et al. (2012). Ecotoxicity test methods for engineered nanomaterials: practical experiences and recommendations from the bench. *Environmental Toxicology and Chemistry*, 31: 15–31.

Hartmann, N. B., Hüffer, T., Thompson, R. C., et al. (2019). Are we speaking the same language? Recommendations for a definition and categorization framework for plastic debris. *Environmental Science & Technology*, 53: 1039–1047.

Hazeem, L. J., Yesilay, G., Bououdina, M., et al. (2020). Investigation of the toxic effects of different polystyrene micro-and nanoplastics on microalgae *Chlorella vulgaris* by analysis of cell viability, pigment content, oxidative stress and ultrastructural changes. *Marine Pollution Bulletin*, 156: 111278.

Heinlaan, M., Kasemets, K., Aruoja, V., et al. (2020). Hazard evaluation of polystyrene nanoplastic with nine bioassays did not show particle-specific acute toxicity. *Science of the Total Environment*, 707: 136073.

Hollóczki, O. (2020). Evidence for protein misfolding in the presence of nanoplastics. *International Journal of Quantum Chemistry*, 121(3): e26372.

Hornyak, G. L., Rao, A. K. (2016). Fundamentals of Nanoscience (and Nanotechnology). *Nanoscience in Dermatology. Academic Press*, pp. 15–29.

Hotze, E. M., Phenrat, T., Lowry, G. V. (2010). Nanoparticle aggregation: challenges to understanding transport and reactivity in the environment. *Journal of Environmental Quality*, 39: 1909–1924.

Jakubowicz, I., Enebro, J., Yarahmadi, N. (2020). Challenges in the search for nanoplastics in the environment—A critical review from the polymer science perspective. *Polymer Testing*, 93: 106953.

Jambeck, J. R., Geyer, R., Wilcox, C., et al. (2015). Plastic waste inputs from land into the ocean. *Science*, 347: 768–771.

Jeong, C.-B., Kang, H.-M., Lee, Y. H., et al. (2018). Nanoplastic ingestion enhances toxicity of persistent organic pollutants (POPs) in the monogonont rotifer *Brachionus koreanus* via multixenobiotic resistance (MXR) disruption. *Environmental Science & Technology*, 52: 11411–11418.

Ji, Y., Wang, Y., Shen, D., et al. (2020). Revisiting cellular toxicity of Benzo [a] pyrene from the view of nanoclusters: size-and nanoplastics adsorption-dependent bioavailability. *Nanoscale*, 13: 1016–1028.

Karl, D. M., Laws, E. A., Morris, P., et al. (2003). Metabolic balance of the open sea. *Nature*, 426: 32.

Keller, A. A., Wang, H., Zhou, D., et al. (2010). Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices. *Environmental Science & Technology*, 44: 1962–1967.

Kettler, K., Veltman, K., van de Meent, D., et al. (2014). Cellular uptake of nanoparticles as determined by particle properties, experimental conditions, and cell type. *Environmental Toxicology and Chemistry*, 33: 481–492.

Kihara, S., Köper, I., Mata, J. P., et al. (2020). Reviewing nanoplastic toxicology: it's an interface problem. *Advances in Colloid and Interface Science*, 295: 102337.

Kihara, S., van der Heijden, N. J., Seal, C. K., et al. (2019). Soft and hard interactions between polystyrene nanoplastics and human serum albumin protein corona. *Bioconjugate Chemistry*, 30: 1067–1076.

Koelmans, A. A., Besseling, E., Shim, W. J. (2015). Nanoplastics in the aquatic environment. critical review. In Bergmann, M., Gutow, L., Klages, M. (Eds.), *Marine Anthropogenic Litter*. Cham: Springer, pp. 325–340.

Koelmans, A. A., Redondo-Hasselerharm, P. E., Mohamed Nor, N. H., et al. (2020). Solving the nonalignment of methods and approaches used in microplastic research to consistently characterize risk. *Environmental Science & Technology*, 54: 12307–12315.

Kögel, T., Bjorøy, Ø., Toto, B., et al. (2020). Micro- and nanoplastic toxicity on aquatic life: determining factors. *Science of the Total Environment*, 709: 136050.

Kong, L., Peng, X., Hu, X., et al. (2018). UV-light-induced aggregation of arsenic and metal sulfide particles in acidic wastewater: the role of free radicals. *Environmental Science & Technology*, 52: 10719–10727.

Lambert, S., Wagner, M. (2016). Characterisation of nanoplastics during the degradation of polystyrene. *Chemosphere*, 145: 265–268.

Lehner, R., Weder, C., Petri-Fink, A., et al. (2019). Emergence of nanoplastic in the environment and possible impact on human health. *Environmental Science & Technology*, 53: 1748–1765.

Li, S., Liu, H., Gao, R., et al. (2018). Aggregation kinetics of microplastics in aquatic environment: complex roles of electrolytes, pH, and natural organic matter. *Environmental Pollution*, 237: 126–132.

Li, X., He, E., Xia, B., et al. (2020). Impact of CeO_2 nanoparticles on the aggregation kinetics and stability of polystyrene nanoplastics: importance of surface functionalization and solution chemistry. *Water Research*, 186: 116324.

Li, Y., Zhang, W., Li, K., et al. (2012). Oxidative dissolution of polymer-coated CdSe/ZnS quantum dots under UV irradiation: mechanisms and kinetics. *Environmental Pollution*, 164: 259–266.

Liu, L., Fokkink, R., Koelmans, A. A. (2016). Sorption of polycyclic aromatic hydrocarbons to polystyrene nanoplastic. *Environmental Toxicology and Chemistry*, 35: 1650–1655.

Liu, Y., Huang, Z., Zhou, J., et al. (2020). Influence of environmental and biological macromolecules on aggregation kinetics of nanoplastics in aquatic systems. *Water Research*, 186: 116316.

Lowry, G. V., Gregory, K. B., Apte, S. C., et al. (2012). Transformations of nanomaterials in the environment. *Environmental Science & Technology*, 46: 6893–6899.

Lv, L., He, L., Jiang, S., et al. (2020). In situ surface-enhanced Raman spectroscopy for detecting microplastics and nanoplastics in aquatic environments. *Science of The Total Environment*, 728: 138449.

Machado, M. C., Vimbela, G. V., Silva-Oliveira, T. T., et al. (2020). The response of *Synechococcus* sp. PCC 7002 to micro-/nano polyethylene particles-Investigation of a key anthropogenic stressor. *PLoS One*, 15: e0232745.

Magrì, D., Sanchez-Moreno, P., Caputo, G., et al. (2018). Laser ablation as a versatile tool to mimic polyethylene terephthalate nanoplastic pollutants: characterization and toxicology assessment. *ACS Nano*, 12: 7690–7700.

Magrì, D., Veronesi, M., Sánchez-Moreno, P., et al. (2021). PET nanoplastics interactions with water contaminants and their impact on human cells. *Environmental Pollution*, 271: 116262.

Manfra, L., Rotini, A., Bergami, E., et al. (2017). Comparative ecotoxicity of polystyrene nanoparticles in natural seawater and reconstituted seawater using the rotifer Brachionus plicatilis. *Ecotoxicology and Environmental Safety*, 145: 557–563.

Mattsson, K., Hansson, L., Cedervall, T. (2015). Nano-plastics in the aquatic environment. *Environmental science. Processes & Impacts*, 17: 1712–1721.

Mintenig, S., Bäuerlein, P. S., Koelmans, A., et al. (2018). Closing the gap between small and smaller: towards a framework to analyse nano-and microplastics in aqueous environmental samples. *Environmental Science: Nano*, 5: 1640–1649.

Mitrano, D. M., Beltzung, A., Frehland, S., et al. (2019). Synthesis of metal-doped nanoplastics and their utility to investigate fate and behaviour in complex environmental systems. *Nature Nanotechnology*, 14: 362–368.

Monikh, F. A., Grundschober, N., Romeijn, S., et al. (2019). Development of methods for extraction and analytical characterization of carbon-based nanomaterials (nanoplastics and carbon nanotubes) in biological and environmental matrices by asymmetrical flow field-flow fractionation. *Environmental Pollution*, 255: 113304.

Nasser, F., Constantinou, J., Lynch, I. (2020). Nanomaterials in the environment acquire an “eco-corona” impacting their toxicity to *Daphnia magna*—a call for updating toxicity testing policies. *Proteomics*, 20: 1800412.

Natarajan, L., Omer, S., Jetly, N., et al. (2020). Eco-corona formation lessens the toxic effects of polystyrene nanoplastics towards marine microalgae *Chlorella* sp. *Environmental Research*, 188: 109842.

Nava, V., Leoni, B. (2020). A critical review of interactions between microplastics, microalgae and aquatic ecosystem function. *Water Research*, 188: 116476.

Nolte, T. M., Hartmann, N. B., Kleijn, J. M., e al. (2017). The toxicity of plastic nanoparticles to green algae as influenced by surface modification, medium hardness and cellular adsorption. *Aquatic Toxicology*, 183: 11–20.

Okshevsky, M., Gautier, E., Farner, J. M., et al. (2020). Biofilm formation by marine bacteria is impacted by concentration and surface functionalization of polystyrene nanoparticles in a species-specific manner. *Environmental Microbiology Reports*, 12: 203–213.

Oliveira, M., Almeida, M., Miguel, I. (2019). A micro(nano)plastic boomerang tale: a never ending story? *TrAC Trends in Analytical Chemistry*, 112: 196–200.

Oriekhova, O., Stoll, S. (2018). Heteroaggregation of nanoplastic particles in the presence of inorganic colloids and natural organic matter. *Environmental Science: Nano*, 5: 792–799.

Paul, M. B., Stock, V., Cara-Carmona, J., et al. (2020). Micro-and nanoplastics–current state of knowledge with the focus on oral uptake and toxicity. *Nanoscale Advances*, 2: 4350–4367.

Pessoni, L., Veclin, C., El Hadri, H., et al. (2019). Soap-and metal-free polystyrene latex particles as a nanoplastic model. *Environmental Science: Nano*, 6: 2253–2258.

Petosa, A. R., Jaisi, D. P., Quevedo, I. R., et al. (2010). Aggregation and deposition of engineered nanomaterials in aquatic environments: role of physicochemical interactions. *Environmental Science & Technology*, 44: 6532–6549.

Potočnik, J. (2011). Commission recommendation of 18 October 2011 on the definition of nanomaterial. *Official Journal of the European Union*, L 275/38-L 275/40.

Praetorius, A., Badetti, E., Brunelli, A., et al. (2020). Strategies for determining heteroaggregation attachment efficiencies of engineered nanoparticles in aquatic environments. *Environmental Science: Nano*, 7: 351–367.

Pulido-Reyes, G., Leganes, F., Fernández-Piñas, F., et al. (2017). Bio-nano interface and environment: a critical review. *Environmental Toxicology and Chemistry*, 36: 3181–3193.

Revel, M., Châtel, A., Mouneyrac, C. (2018). Micro(nano)plastics: a threat to human health? *Current Opinion in Environmental Science & Health*, 1: 17–23.

Ritchie, H., Roser, M. (2019). *Seafood Production*. Our World in Data. https://ourworldindata.org/biodiversity.

Rodríguez-Hernández, A. G., Muñoz-Tabares, J. A., Aguilar-Guzmán, J. C., et al. (2019). A novel and simple method for polyethylene terephthalate (PET) nanoparticle production. *Environmental Science: Nano*, 6: 2031–2036.

Rubio, L., Barguilla, I., Domenech, J., et al. (2020). Biological effects, including oxidative stress and genotoxic damage, of polystyrene nanoparticles in different human hematopoietic cell lines. *Journal of Hazardous Materials*, 398: 122900.

Saavedra, J., Stoll, S., Slaveykova, V. I. (2019). Influence of nanoplastic surface charge on eco-corona formation, aggregation and toxicity to freshwater zooplankton. *Environmental Pollution*, 252: 715–722.

Saido, K., Koizumi, K., Sato, H., et al. (2014). New analytical method for the determination of styrene oligomers formed from polystyrene decomposition and its application at the coastlines of the North-West Pacific Ocean. *Science of the Total Environment*, 473: 490–495.

Sauer, K., Rickard, A. H., Davies, D. G. (2007). *Biofilms and biocomplexity. Microbes*, 2: 347–353.

Schneider, G. (2017). Antimicrobial silver nanoparticles – regulatory situation in the European Union. *Materialstoday: Proceedings*, 4: S200–S207.

Schwaferts, C., Niessner, R., Elsner, M., et al. (2019). Methods for the analysis of submicrometer- and nanoplastic particles in the environment. *TrAC Trends in Analytical Chemistry*, 112: 52–65.

Shams, M., Alam, I., Chowdhury, I. (2020). Aggregation and stability of nanoscale plastics in aquatic environment. *Water Research*, 171: 115401.

Selvamani, V. (2019). Stability studies on nanomaterials used in drugs. In: Mohapatra, S. S., Ranjan, S., Dasgupta, N., et al. (Eds.), *Characterization and Biology of Nanomaterials for Drug Delivery*. Amsterdam: Elsevier, pp. 425–444.

Sendra, M., Staffieri, E., Yeste, M. P., et al. (2019). Are the primary characteristics of polystyrene nanoplastics responsible for toxicity and ad/absorption in the marine diatom *Phaeodactylum tricornutum*? *Environmental Pollution*, 249: 610–619.

Sobhani, Z., Zhang, X., Gibson, C., et al. (2020). Identification and visualisation of microplastics/nanoplastics by Raman imaging (i): Down to 100 nm. *Water Research*, 174: 115658.

Summers, S., Henry, T., Gutierrez, T. (2018). Agglomeration of nano-and microplastic particles in seawater by autochthonous and de novo-produced sources of exopolymeric substances. *Marine Pollution Bulletin*, 130: 258–267.

Sun, H., Jiao, R., Wang, D. (2020). The difference of aggregation mechanism between microplastics and nanoplastics: role of Brownian motion and structural layer force. *Environmental Pollution*, 268: 115942.

Sun, X., Chen, B., Li, Q., et al. (2018). Toxicities of polystyrene nano-and microplastics toward marine bacterium *Halomonas alkaliphila*. *Science of the Total Environment*, 642: 1378–1385.

Tallec, K., Blard, O., González-Fernández, C., et al. (2019). Surface functionalization determines behavior of nanoplastic solutions in model aquatic environments. *Chemosphere*, 225: 639–646.

Teles, M., Balasch, J. C., Oliveira, M., et al. (2020). Insights into nanoplastics effects on human health. *Science Bulletin*, 65: 1966–1969.

Ter Halle, A., Jeanneau, L., Martignac, M., et al. (2017). Nanoplastic in the North Atlantic subtropical gyre. *Environmental Science & Technology*, 51: 13689–13697.

Ter Halle, A., Ladirat, L., Gendre, X., et al. (2016). Understanding the fragmentation pattern of marine plastic debris. *Environmental Science & Technology*, 50: 5668–5675.

Tian, L., Chen, Q., Jiang, W., et al. (2019). A Carbon-14 radiotracer-based study on the phototransformation of polystyrene nanoplastics in water versus in air. *Environmental Science: Nano*, 6: 2907–2917.

van Sebille, E., Wilcox, C., Lebreton, L., et al. (2015). A global inventory of small floating plastic debris. *Environmental Research Letters*, 10: 124006.

Velzeboer, I., Kwadijk, C., Koelmans, A. (2014). Strong sorption of PCBs to nanoplastics, microplastics, carbon nanotubes, and fullerenes. *Environmental Science & Technology*, 48: 4869–4876.

Venâncio, C., Ferreira, I., Martins, M. A., et al. (2019). The effects of nanoplastics on marine plankton: a case study with polymethylmethacrylate. *Ecotoxicology and Environmental Safety*, 184: 109632.

Wagner, S., Reemtsma, T. (2019). Things we know and don't know about nanoplastic in the environment. *Nature Nanotechnology*, 14: 300–301.

Walczak, A. P., Kramer, E., Hendriksen, P. J., et al. (2015a). *in vitro* gastrointestinal digestion increases the translocation of polystyrene nanoparticles in an *in vitro* intestinal co-culture model. *Nanotoxicology*, 9: 886–894.

Walczak, A. P., Kramer, E., Hendriksen, P. J., et al. (2015b). Translocation of differently sized and charged polystyrene nanoparticles in *in vitro* intestinal cell models of increasing complexity. *Nanotoxicology*, 9: 453–461.

Wan, T., Lu, S., Cheng, W., et al. (2019). A spectroscopic and theoretical investigation of interaction mechanisms of tetracycline and polystyrene nanospheres under different conditions. *Environmental Pollution*, 249: 398–405.

Wang, L., Wu, W.-M., Bolan, N. S., et al. (2020a). Environmental fate, toxicity and risk management strategies of nanoplastics in the environment: current status and future perspectives. *Journal of Hazardous Materials*, 401: 123415.

Wang, S., Liu, M., Wang, J., et al. (2020b). Polystyrene nanoplastics cause growth inhibition, morphological damage and physiological disturbance in the marine microalga Platymonas helgolandica. *Marine Pollution Bulletin*, 158: 111403.

Wang, X., Li, Y., Zhao, J., et al. (2020c). UV-induced aggregation of polystyrene nanoplastics: effects of radicals, surface functional groups and electrolyte. *Environmental Science: Nano*, 7: 3941–3926.

Ward, J. E., Kach, D. J. (2009). Marine aggregates facilitate ingestion of nanoparticles by suspension-feeding bivalves. *Marine Environmental Research*, 68: 137–142.

Waring, R. H., Harris, R. M., Mitchell, S. C. (2018). Plastic contamination of the food chain: a threat to human health? *Maturitas*, 115: 64–68.

Wegner, A., Besseling, E., Foekema, E. M., et al. (2012). Effects of nanopolystyrene on the feeding behavior of the blue mussel (*Mytilus edulis* L.). *Environmental Toxicology and Chemistry*, 31: 2490–2497.

Xiong, Y., Zhao, J., Li, L., et al. (2020). Interfacial interaction between micro/nanoplastics and typical PPCPs and nanoplastics removal via electrosorption from an aqueous solution. *Water Research*, 184: 116100.

Xu, Y., He, Q., Liu, C., et al. (2019). Are micro-or nanoplastics leached from drinking water distribution systems? *Environmental Science & Technology*, 53: 9339–9340.

Yao, M., He, L., Mcclements, D. J., et al. (2015). Uptake of gold nanoparticles by intestinal epithelial cells: impact of particle size on their absorption, accumulation, and toxicity. *Journal of Agricultural and Food Chemistry*, 63: 8044–8049.

Yilimulati, M., Wang, L., Ma, X., et al. (2021). Adsorption of ciprofloxacin to functionalized nano-sized polystyrene plastic: kinetics, thermochemistry and toxicity. *Science of The Total Environment*, 750: 142370.

Yong, C. Q. Y., Valiyaveetill, S., Tang, B. L. (2020). Toxicity of microplastics and nanoplastics in mammalian systems. *International Journal of Environmental Research and Public Health*, 17: 1509.

Yu, S., Shen, M., Li, S., et al. (2019). Aggregation kinetics of different surface-modified polystyrene nanoparticles in monovalent and divalent electrolytes. *Environmental Pollution*, 255: 113302.

Zarus, G. M., Muianga, C., Hunter, C., et al. (2020). A review of data for quantifying human exposures to micro and nanoplastics and potential health risks. *Science of The Total Environment*, 756: 144010.

Zettler, E. R., Mincer, T. J., Amaral-Zettler, L. A. (2013). Life in the "plastisphere": microbial communities on plastic marine debris. *Environmental Science & Technology*, 47: 7137–7146.

Zhang, F., Wang, Z., Wang, S., et al. (2019). Aquatic behavior and toxicity of polystyrene nanoplastic particles with different functional groups: complex roles of pH, dissolved organic carbon and divalent cations. *Chemosphere*, 228: 195–203.

Zhao, T., Tan, L., Zhu, X., et al. (2020). Size-dependent oxidative stress effect of nano/micro-scaled polystyrene on *Karenia mikimotoi*. *Marine Pollution Bulletin*, 154: 111074.

Zhou, X.-X., Hao, L.-T., Wang, H.-Y.-Z., et al. (2018). Cloud-point extraction combined with thermal degradation for nanoplastic analysis using pyrolysis gas chromatography–mass spectrometry. *Analytical Chemistry*, 91: 1785–1790.

Zheng, X., Yuan, Y., Li, Y., et al. (2020). Polystyrene nanoplastics affect growth and microcystin production of *Microcystis aeruginosa*. *Environmental Science and Pollution Research*, 28(11): 1–10.

Zimmermann, S. R., Mead, J. L., von Kleist-Retzow, F. T. (2020). Probing friction and adhesion of individual nanoplastic particles. *The Journal of Physical Chemistry C*, 124: 24145–24155.

15

Human Behavior and Marine Plastic Pollution

S. Nuojua[1], *D. Cracknell*[1], *and S. Pahl*[1,2]

[1] *University of Plymouth, Plymouth, UK*
[2] *University of Vienna, Vienna, Austria*

15.1 Introduction: Human Behavior and Marine Plastic Pollution

This chapter summarizes the *human dimension* in plastic pollution, with a particular focus on human behavior and its determinants. Section 15.1 introduces the topic in the context of increased public interest in and concern about plastic pollution and explains how human behavior is relevant in the overall system of plastic flow. Section 15.2 briefly reviews antecedents of behavior such as risk perception, motivation and social norms. Section 15.3 presents the early results of a scoping review of recent behavior change interventions. We close by discussing the international dimension of behavior research and highlighting some limitations and research gaps.

15.1.1 Media and Problem Awareness

Ocean pollution has been a pressing agenda in public and scientific fora for decades. Yet, it appears that public and media interest has only relatively recently reached a high point (SAPEA 2019). To illustrate, one example for plastic pollution reaching extensive public audiences was the broadcasting of the BBC documentary series *Blue Planet II* in December 2017 (Thompson 2019). The documentary demonstrated how plastic pollution harms oceanic wildlife, and it asserted that a radical change is required in how plastics are managed and valued in society. The concurrent surge in public awareness, also thereafter termed the "Blue Planet effect" (Hunt 2017) was further amplified by social sharing of emotional messaging and pleas: Distressing images of charismatic animals being tangled in or otherwise affected by plastic were distributed widely within various social media channels. Often these images were circulated in an attempt to engender an emotional or moral response, which can be an effective technique for inspiring change (Barberá-Tomás et al. 2019). The Blue Planet effect is thought to have been a key contributor to policy change, such as the ban on a variety of single-use plastic items in the United Kingdom (Schnurr et al. 2018).

However, such a rise in public awareness does not guarantee that people's attitudes have changed to a meaningful extent, or that this awareness has translated into behavior change (see Section 15.3.4.1). Changing plastics use in society requires actions that go beyond informing the public or evoking an emotional response. Additional motivational and contextual antecedents of environmental behavior need to be addressed in order to effect substantial and long-lasting change.

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

Moreover, taking a systems perspective helps understand how plastic flows through economic sectors and society to the ocean (Jambeck et al. 2015).

15.1.2 Complexities of the Human–Plastics Interaction

The human element can be found at all stages within the plastics system (Pahl et al. 2017). From plastic being manufactured to its post-consumer phase, human decisions at the individual or collective scales contribute to the flow and fate of plastics. The various human operators, such as manufacturers and consumers, can have differing motivations for using (or not using) plastic: Financial, practical, and environmental considerations are possible reasons for why plastic is chosen over alternative materials. These choices are to some extent dictated by policy makers, economic, legal and technical factors, and other regulations and constraints. Therefore, assigning responsibility for plastic pollution to a singular entity or focusing on single types of items or materials is only a starting point, given the complexity and interlinked nature of the plastics system. Rather, a solutions-oriented holistic approach where opportunities for intervention are identified on various levels and sectors within the system can achieve substantial pollution reduction. Such an ambitious global agreement or framework is being suggested by the ad hoc open-ended expert group on marine litter and microplastics (AHEG-4 summary document, 2020, Point 22g), taken forward to the 2022 United Nations Environment Assembly (UNEA- 5). From the behavioral viewpoint, change opportunities lie particularly in the consumer and waste management sectors in both the public and private domain. Purchasing, reusing, recycling, and littering are some of the behaviors that are often targeted in behavioral change interventions (see Section 15.3). Efforts to change these behaviors are necessary and relevant, and, in contrast to policy or infrastructural change, behavior change can happen relatively rapidly (SAPEA 2019). Section 15.2 provides an overview of determinants of behavior in the environment and marine plastic litter context.

15.2 Human Behavior

15.2.1 Antecedents of Behavior: Lessons from Environmental Psychology

Why individuals behave the way they do in the environmental context is a key question of interest in environmental psychology. Generally agreed-upon antecedents of environmental behavior include, but are not limited to, motivational, contextual and habitual factors, knowledge, and perceptions of risk (e.g. Pahl and Wyles, 2016; Steg et al. 2014). Motivation refers to the direction of effort (which behavior is selected from available options) as well as its intensity (how much effort is expended). In the environmental context, primary motives such as a pro-environmental lifestyle can be suppressed by competing motives or barriers, such as desire for comfort or convenience (Kollmuss and Agyeman 2002). One's personal attitudes toward the environment and its pressing issues, as well as fundamental values and the prevailing social norm are considered important determinants of environmental motivations and behavior. One way of changing behavior to be more sustainable is by modifying key antecedents of behavior; therefore, we provide this brief review. We focus on psychological and contextual antecedents here rather than sociodemographic factors due to space constraints.

1) Knowledge

Scholars in environmental psychology have repeatedly asserted that increasing knowledge is not in itself, and on its own, an effective strategy for fostering behavior change (Abrahamse and Steg 2013; Carmi et al. 2015; Schultz 1999). However, relevant knowledge can trigger or support any goal-directed action. For example, knowledge about environmental consequences of behavior, or “connecting the dots,” can motivate behavior to occur for environmental reasons. Also, practical, “how-to” knowledge has an important function in triggering successful behavior change, for example for sorting waste and recycling (see Section 15.3). Similarly, provision of information may induce behavior change when the information is carefully tailored to a specific group, for example in combination with personally relevant feedback (Abrahamse et al. 2007). Information campaigns are more effective when there is collective support from the community: For example, the “Think before you flush” campaign, designed to reduce waterborne disposal of sanitary products in the UK (reviewed in Ashley et al. 2005), turned out effective in smaller communities characterized by high community identity.

2) Risk Perception

What the public and wider society make of the risks associated with plastic pollution plays a role in how they react to it. As noted by Syberg et al. (2018), these risk perceptions have shifted dramatically over the last decades. Before the turn of the millennium, plastic pollution was viewed as a distant and abstract threat: For example, the so-called Plastic Gyre in the North Pacific was already in the public discourse, but it was perceived as far removed from human civilization. Furthermore, the public had little knowledge of the harmful impacts of plastic pollution on ecosystems. Psychological distance (Liberman and Trope 2008) may be a useful concept for explaining why hazards that are distant along multiple dimensions are not perceived as particularly high-risk. For example, the Plastic Gyre is both geographically remote to most people, as well as temporally, as the accumulation of debris has occurred over decades and therefore cannot be linked to specific human populations or behaviors. Therefore, in the late twentieth century, plastic pollution was not yet associated with considerable environmental risk and global concern.

However, these days people report seeing plastic pollution or marine litter on a regular basis (Hartley et al. 2018; Henderson and Green 2020; European and UK respondents). Macroplastic pollution is highly visible, and the public can readily make the connection between plastics use and marine pollution. Furthermore, there is now ample evidence for how plastic pollution, and more recently microplastics affect marine wildlife (e.g., Anbumani and Kakkar 2018; Steer and Thompson 2020). Increasing availability and dissemination of information on such impacts is making the risks of plastic pollution more tangible (Syberg et al. 2018). As a result, public risk perception is now more reflective of (scientific) reality, and various actors within the plastics system have become more receptive and accepting of mitigating actions. The now less elusive nature of plastic pollution makes it a focal concern.

How risk perceptions are formed can be investigated by analyzing people’s mental models and opinion construction: Anderson et al. (2016) ran a series of focus group interviews with environmentalists, students, and beauticians, in order to capture their understandings of microplastics used in cosmetics (microbeads). The interviewees’ responses were prompted with a demonstration of the quantities of microbeads filtered from different personal care products. The respondents expressed worry and revulsion, and they concluded that microbeads were an unnatural and unnecessary addition to these everyday products. This study demonstrates that the “yuck factor,” an instinctive emotional reaction and repulsion (Schmidt 2008), is present in responses to microplastics. The yuck factor is especially relevant to hazards that are considered artificial and unnatural, and as such it can shape risk perceptions considerably.

3) Attitudinal Orientations and Values

Often the reason that people give to justify a pro-environmental lifestyle is that they care for the environment. Environmental attitudes, such as concern, have been traditionally thought of as critical predictors of pro-environmental behavior (Huddart Kennedy et al. 2015; Kaiser et al. 1999).

For example, findings from the Europe-wide MARLISCO survey showed that concern for marine litter (which is mostly plastic) significantly predicted intentions to take action to reduce it (Hartley et al. 2018). Yet, recent research asserts that from a consumer's point of view plastic is much more than an environmental concern: Rhein and Schmid (2020) used qualitative inquiry to assess attitudes toward plastic packaging. They found that while many recognize that plastic packaging can harm the environment, consumers also value plastic for its positive properties such as durability and hygiene, and may be therefore more inclined to ensure appropriate disposal and value recovery. Therefore, the authors suggest that concern may motivate mitigating behaviors, but customized strategies that acknowledge different consumer profiles are needed in efforts to reduce plastic pollution.

Furthermore, attitude toward the natural environment in general can guide action. Nature connectedness, defined as the subjective sense of connection with the natural world, has been shown to be associated with pro-environmental behavior (e.g., Martin et al. 2020). Similarly, affinity toward the marine environment, or ocean connectedness, has been linked with more sustainable packaging preferences (Nuojua et al., 2022). A similar yet distinguished concept from nature connectedness is biospheric value orientation: Values are higher-order beliefs that guide behavior across contexts, and a biospheric value orientation refers to a tendency to assess events and experiences on account of their impact on the natural world (Stern and Dietz 1994). Biospheric values have been shown to motivate a range of environmental behaviors (Nguyen et al. 2016; Van der Werff et al. 2013). In addition, altruistic values (valuing the wellbeing of others in the society) are predictive of pro-environmental behavior, too (Steg et al. 2014). Prakash et al. (2019) showed that young consumers who hold altruistic values are more likely to purchase products in eco-friendly packaging. While values are considered stable across contexts and therefore difficult to change, connectedness to nature may be promoted in several ways. For example, taking part in coastal activities that are perceived as particularly meaningful, such as beach cleans (Wyles et al. 2017), or fostering ocean literacy (Guest et al. 2015) can help promote connection to nature.

4) Social Norm

The social norm, meaning one's understanding of what other people do or approve of, can shape environmental behavior substantially (Klöckner 2013; Nigbur et al. 2010). There is a strong consensus that waste disposal and littering behaviors are guided by social norms (Schultz et al. 2013). For example, locations that are already littered attract more litter, and recycling messages often urge people to recycle because others in the community do so too (Thomas and Sharp 2013). De Groot et al. (2013) found normative messaging to be even more effective than environmental messaging in reducing plastic bag use in a supermarket. Social norms on plastics use are likely to have shifted as a result of a change in public engagement and policy in recent years. Yet, normative messages tend to be more persuasive when they target close-knit communities, as people hold the opinions of their valued others in higher regard than those of the wider society (Borg et al. 2020).

5) Contextual Factors

Nevertheless, being environmentally oriented, having the appropriate normative support or being highly educated does not always lead to pro-environmental behavior. Behavior is often habitual, and habits tend to be grounded on the prevailing context. For example, littering is more likely to occur when there is poor availability of bins, or when the receptacles are not clearly marked (Schultz et al. 2013). Similarly, inappropriate flushing of sanitary products is often attributed to contextual restrictions such as inconvenient location of the sanitary disposal bin and handwashing basin (Hawkins et al. 2019). Consumer behavior can also be limited by product range and price. On the other hand, today's consumers have the option to be selective in their purchasing, as there are various alternatives to plastic in the market. Furthermore, consumer preferences have shifted toward more "natural" and organic products, which has contributed toward a reduction in plastic use in some of its applications (Wagner and Lambert 2018). In addition to "true" contextual factors such as inadequate infrastructure, the perceived context can similarly hinder pro-environmental behavior (Box 15.1). For example, consumers in Germany rated price as the main contextual barrier to buying eco-conscious fashion (Wiederhold and Martinez 2018), even though in a qualitative inquiry consumers acknowledged that the price barrier is often a matter of perception (McNeill and Moore 2015). As this brief overview of context factors suggests, psychological and contextual antecedents need to be considered together in any attempts to change behavior.

Box 15.1 Methods in human behavior research.

Environmental psychology research uses rigorous quantitative and qualitative analyses to study human actions and perceptions in the environmental context. Quantitative approaches are often used to explain behavior or its psychological determinants, with the application of statistical analyses that require large study samples. For example, Hartley et al. (2018) surveyed 1133 members of the public in order to obtain a cross-sectional assessment of attitudes and behaviors in relation to marine litter, as well as relationships between these concepts. In survey-based research the survey items and scales have to be designed carefully, so that they capture the essence of the variable of interest in a reliable manner. For example, survey questions need to be worded in a nonbiased, clear manner. Survey research often relies on self-report data, which may be considered a methodological shortcoming due to the potential social desirability effects (Van de Mortel 2008). That is, people may want to present themselves in a positive light when filling in surveys, although the effect of this bias is not considered substantial in environmental research (Milfont 2009; Vesely and Klöckner 2020). Furthermore, recording behavior directly may require considerable resources and is therefore often impractical. With adequate resources in a fitting context the behaviors of the public can be observed as they unfold: Schultz et al. (2013) conducted systematic observations of littering behavior in nearly 10 000 individuals across 130 locations in the United States.

In addition to quantitative methods, qualitative enquiry is often used in psychology research. Qualitative methods aim to uncover more in-depth or nuanced understandings of the studied phenomena. For example, Henderson and Green (2020) conducted a focus group study to elicit how members of the public engage with and conceptualize emerging information about macro- and microplastic pollution. Plastic pollution research has also seen applications of mixed methodology which involves both quantitative and qualitative approaches: McNicholas and Cotton (2019) applied an inductive Q-method inquiry to determine areas of agreement and disagreement across stakeholder groups on plastic pollution management solutions. Such an approach enables application of quantitative techniques without the requirement of a large sample size, making it an attractive methodological alternative. However, more traditional mixed methods approaches combine large-scale surveys with qualitative elements in order to capture a comprehensive account of the behaviors or perceptions of interest. For example, Phelan et al. (2020) conducted a survey to assess knowledge and behaviors in relation to plastic waste, as well as focus group discussions to develop solutions to plastic pollution in Indonesian coastal communities.

See Pahl and Wyles (2016) for a more extensive summary of human research methods in the plastic context.

Having summarized the main determinants of human behavior, Section 15.3 presents the early results of a scoping review of recent academic literature on behavior change interventions (2015–2020) designed to reduce plastic consumption and waste in four specific sectors: business and retail, tourism and leisure, schools and education, and community.

15.3 Scoping Review of Behavior Change Interventions 2015–2020

We complemented the selective review of factors linked to behavior in Section 15.2 with a scoping review to explore the range and nature of interventions intended to address plastic pollution. This type of approach to evidence synthesis was deemed most appropriate as the purpose of the review was to identify types of emerging evidence available, as well as to clarify key factors related to recent behavior change approaches in the context of plastic pollution (Munn et al. 2018; see Arksey and O'Malley 2005; Joanna Briggs Institute 2015, for further details on scoping review methodology).

Behavior change interventions in four key sectors were considered: business and retail (e.g. shops, cafés, and advertising); tourism and leisure; schools and education, and community more broadly. These sectors were identified as key target areas for efforts to induce transformational change in how plastics are used and managed in our current Preventing Plastic Pollution project. Searches for relevant academic literature were conducted in three generic databases (Web of Science, Scopus, PsychINFO) as well as sector-specific databases (e.g. Business Source Complete), using relevant keywords and their variants (e.g. plastic, behavior change, intervention), together with sector-specific terms (e.g. consumer, business; tourism, leisure; school, education; public, communities). Searches were limited to peer-reviewed articles, written in English, and published between 2015 and autumn 2020. Using a snowball technique, the list of included studies was extended by searching for relevant forward and backward citations from the located journal articles.

Results of searches were collated, reviewed, and included in the scoping review, regardless of the results showing successful change or not. Articles that were regarded as unsuitable for the purposes and scope of the review and duplicates were excluded. The most common reasons for these exclusions were absence of an intervention design and lack of assessment of intervention effectiveness. The search process resulted in a final total of 47 papers out of 377 records after the initial search: 10 in the business and retail category; 6 for tourism and leisure; 12 in schools and education; and 19 in community), incorporating over 60 individual studies. In the following sections we present a qualitative summary of the findings from these behavior change studies for each sector separately, illustrated by key findings from the articles rather than all articles exhaustively.

15.3.1 Business and Retail (10 Articles)

The scoping review revealed that regulatory approaches, such as introducing a charge for single-use plastic carrier bags (e.g. Thomas et al. 2016) or banning their use altogether (e.g. Macintosh et al. 2020), are common in the business and retail sector and came up in searches for behavior change. However, the main focus of this chapter is traditional behavior change interventions that use the principles reviewed in Section 15.2. We found that these types of studies were often combined with regulation, so this is what we focus on in the remainder.

The majority of interventions undertaken in business and retail centered on investigating the impact of information (message) provision and, importantly, how this information was framed in order to best encourage pro-environmental behaviors. Several of these studies linked directly with the aforementioned regulatory approaches. For instance, Muralidharan and Sheehan (2016) investigated how and why advertising messages, either framing a single-use carrier bag charge as a "gain" (avoiding the fee) or a "loss" (paying a tax), impacted shoppers' behavior when considering whether or not to bring their own reusable bags to the supermarket. Their study, administered as an online survey, suggested that a penalty framed as a "loss" was more effective at encouraging shoppers to bring their own reusable bags, than a message framed as a "gain." They suggest that the terms "tax" and "fee" were perceived differently, with people perceiving that having to pay a tax was more restrictive to their freedom of choice than avoiding a fee, and was therefore perceived as more of a loss, even though both the tax and fee were avoidable.

Later work by Muralidharan and Sheehan (2018) also focused on advertising messaging. Across two studies, they evaluated the role of "guilt" on generating favorable attitudes and behaviors toward compliance with a carrier bag charge, and investigated how the framing of advertisements, either focusing on "egoistic" (making a monetary saving) or "biospheric" (looking after the environment) values influenced compliance. They found that environmental concern in females was higher when they felt more guilt regarding compliance. Furthermore, the type of advertising message influenced levels of guilt, with females exposed to the savings advertisement having higher level of guilt than those exposed to the environment advertisement. In summary, they suggest that, although females in the savings advertisement condition tended to express stronger concern for the environment, their concern appeared to be motivated by avoiding the carrier bag charge. The study's authors suggest that appealing to egoistic concerns may be more effective than environmental concerns when seeking to encourage compliance with such regulatory interventions. However, other work on environmental behaviour questions whether egoistic concerns are the best way of motivating behaviour (Bolderdijk et al. 2013).

Poortinga and Whitaker (2018) also investigated the impact of message framing, alongside other easy to implement measures aimed at encouraging the use of reusable coffee cups. Environmental messaging (e.g. posters) highlighted the number of coffee cups ending up in landfill and asked customers to bring their own cup. This was displayed in 12 university and business site cafés. Additionally, eight sites sold reusable cups and, at four sites, reusable coffee cups were distributed free to customers at the start of the intervention. Four of the sites introduced a financial incentive, either a discount for customers using a reusable cup or a charge for using a disposable cup. These simple measures – environmental messaging and readily available alternatives – increased the use of reusable coffee cups. Furthermore, although a discount for bringing one's own coffee up did not significantly affect reusable coffee cup sales, placing a charge on disposable coffee cups did increase the use of reusable coffee cups. These findings support Muralidharan and Sheehan's (2016) work suggesting that a loss (a charge/fee) may be more effective than a gain (a discount) when seeking to encourage pro-environmental behaviors.

Loschelder et al. (2019) also explored the impact of messaging on disposable coffee cup use. Across field and laboratory studies, they found that their use of "dynamic norm" messaging, broadly "More and more customers are switching from the to-go-cup to a sustainable alternative. Be part of this movement and chose a reusable mug", had a stronger influence on the increased use of reusable mugs compared to other types of "norm" messaging or no message at all. Grebitus et al.'s (2020) work focused on investigating bottled water choices by comparing people's choices after receiving, or not receiving, an environmental message. They found that when exposed to an environmental message, people were more likely to choose sustainable packaging for bottled water and were also more willing to pay for sustainable packaging.

Thongplew and Kotlakome (2019) also sought to reduce single-use plastic consumption by introducing a suite of interventions at beverage locations (e.g., cafés, convenience stores), in Ubon

Ratchathani University, Thailand. They sought to reduce the purchase of bottled water by providing free drinking water from dispensers and by supplying free reusable bottles. They also offered a discount for consumers who brought their own cup to use for other café beverages. Finally, in order to monitor consumers' behaviors, participants were encouraged to download an "app" that provided environmental information on the impacts of plastic bottles and cups. The "app" also enabled participants to record the number of plastic bottles and cups they avoided using, and their monetary savings. It is important to note that, culturally, Thai people generally do not drink tap water and rely heavily on bottled water; therefore, few consumers owned or used reusable bottles before the intervention. The project was launched as part of the university's "Green Club" and focus group feedback suggested that this "social" aspect – being part of a group making change together – was important. Additional feedback from the focus group included comments that the water dispensers were convenient (although some concerns were raised about hygiene) and reusable bottles were practical (although some issues were raised relating to bottle weight and design). Although more explicit signage about the discount availability and amount was deemed necessary, a price reduction was viewed as an additional incentive and benefit, rather than a main motivating factor. Furthermore, participants were not in favor of an increased discount as they thought this may increase the overall beverage cost. Overall, the "app" was not thought to be particularly useful and was rarely used after download. Finally, although the interventions increased the number of reusable plastic bottles and cups used, feedback suggested that these sustainable actions would be limited to the university setting: consumers did not consider using the reusable bottles in other settings. Ofstad et al. (2017) also noted that although university staff and students at a Norwegian university reported increased recycling following the implementation of a new recycling scheme on campus, their sustainable actions did not extend to increased recycling at home.

Several other studies have focused on sustainable packaging and the waste management of single-use plastics. Klaiman et al. (2016) explored the impact of information from a video on consumers' preferences and willingness to pay for different types of common beverage packaging. The video information significantly and positively affected consumer preferences and demand for packaging recyclability. Furthermore, willingness to pay for recyclable material was highest for plastic packaging compared to other types of packaging, such as glass, carton or aluminum. Interestingly, although further work by Klaiman et al. (2017) also revealed how providing information could influence preferences for packaging material, it did not significantly affect recycling behavior.

Product labeling is another form of information provision. "Certification schemes," private regulations initiated by nongovernmental organizations or companies, aim to convey responsible production practices (Misund et al. 2020), thus enabling consumers to make more informed choices about their purchases. Misund et al. (2020) explored consumers‘ willingness to pay for products certified as microplastic-free, across three European countries: Norway, Germany and Portugal. Although participants generally preferred products (e.g., salmon, toothpaste, bottled water) that were certified as microplastic-free, they were rarely willing to select these items if there was a price premium attached. Interestingly, there were cross-country differences, with Portugal being the most willing to pay a price premium and Norway the least willing.

Asking people to make a commitment to undertake their stated pro-environmental action(s) appears another effective way to encourage behavior change. Rubens et al. (2015) asked supermarket shoppers to commit to stop using free plastic bags by signing a poster. Observations of participating shoppers revealed that those who had made this public and personal commitment were less likely to take the free plastic bags than shoppers in other conditions (e.g., no commitment made).

15.3.2 Tourism and Leisure (6 Articles)

Information provision and message framing can also be effective in a tourism and leisure context. Grazzini et al. (2018) investigated whether a message framed as a loss (to the environment, e.g., in terms of additional environmental resources used) or a gain (e.g. less resources used, better for wildlife, etc.) was more effective at influencing hotel guests' recycling behaviors. These loss- and gain-framed messaged were paired with either a "concrete" message about *how* to recycle or an "abstract" message explaining *why* it was important to recycle. Overall, they found that any type of message encouraging recycling was more effective at promoting recycling than no message at all. However, guests' recycling behaviors were significantly greater when exposed to a loss-, rather than gain-, framed message. Furthermore, matching a loss-framed message with a concrete message about how to recycle was particularly effective, due to greater perceived self-efficacy.

Dolnicar et al. (2019) sought to investigate whether sharing a hotel's monetary savings with guests would encourage more sustainable behaviors. Their intervention, encouraging guests to opt out of a room clean, was framed in one of three ways: to reduce their environmental impact; to reduce the hotel's costs, which would be shared with them in the form of a free drink; or a combination of both approaches. They found that encouraging hotels guests to voluntarily opt out of a room clean in return for a free drink was the most effective way to reduce the number of daily room cleans. Appeals based on a combination of environmental and financial benefits were also effective; appealing to guests to opt out of a room clean for environmental reasons alone was the least effective approach. Although not directly related to plastic consumption or waste management, it may be possible to apply this approach in such contexts.

Information and messaging can come in numerous forms, and can be delivered in a variety of ways, including media campaigns, posters and information leaflets, television documentaries, and personal interactions. Although filling a knowledge deficit gap does not necessarily result in actual behavior change, there are some instance in which provision of previously unknown information can be of use. For instance, Sisson et al. (2020) surveyed over 200 students about their awareness and likely use of a reusable cup program, that reduces the need for single-use plastics at live events (r.Cup – www.rcup.com). They found that nearly 95% of students were not previously aware of the program, but, after exposure to the infographic, over 80% reported that they were likely to use the program in the future.

Mellish et al. (2019) chose to deliver their information in the form of an educational talk on Zoos Victoria's education program, "When Balloons Fly". The talk focused on the threats of balloons to wildlife and encouraged visitors to use a wildlife-friendly alternative (bubbles) instead. Following the talk, visitors were invited to make a pledge (either in a pledge book or on a pledge board) to use bubbles instead of balloons at their next outdoor event. The study evaluated visitors' knowledge, attitudes, and behaviors (intended and actual), relating to the use of balloons over a six-month period. Mellish and colleagues found that visitors had a better understanding of the threats of balloons immediately after their visit and reported that they were more likely to replace balloons with bubbles in the future. Follow-up surveys suggested that fewer balloons had been purchased and used by visitors, and that visitors had also encouraged others not to use balloons. The authors of this study also noted that when visitors received a pre-talk survey, which included take-home information, visitors had more positive attitudes and were significantly less likely to use balloons. They suggest that the pre-survey may have "primed" visitors, thus promoting better engagement with the conservation-education material.

Zelenika et al. (2018) investigated ways of reducing contamination across waste streams at a public event, testing three different types of intervention: bin tops with signage; bin tops with signage plus 3D items; and staffed bins. Staffing the bins with volunteers who verbally instructed visitors on where to put their waste resulted in the least contamination of recycling bins. Hottle et al. (2015) also tested the effect of staffing waste and recycling bins at a series of three baseball games and found that staffing the bins resulted in the lowest contamination rates, further highlighting this as an effective intervention.

Willis et al. (2019) sought to reduce single-use plastic bottle litter by introducing free filtered water refill stations at key littering "hotspots" along the Brisbane River. Although they found some evidence of reduced littering, they suggested that the intervention may have been more effective if implemented in areas where consumers purchase bottled water, rather than in locations where they dispose of their empty bottles.

15.3.3 Schools and Education (12 Articles)

All of the behavior change interventions included (13 interventions, 12 papers) were educational in nature. Three of these interventions, all conducted in Hong Kong (Chow et al. 2017; So et al. 2016; Yeung et al. 2017), involved comparisons of different teaching approaches centered around knowledge about the waste hierarchy as well as classification and sorting of plastic waste. Chow et al. (2017) used direct teaching, hands-on and simulation game-based approaches with primary school pupils in Hong Kong. The direct teaching approach involved teacher-centered information provision about plastic waste and its management, while in the hands-on teaching group pupils engaged in observation of their surroundings and experimental activities as "scientists." The simulation game-based approach entailed teacher-led role-play where the pupils acted as citizens of a "plastic city" and learned to connect their daily activities to environmental problems. While none of these approaches were effective in changing recycling and waste management intentions, all of them were successful in increasing the pupils' knowledge about plastic waste and the waste hierarchy.

Yeung et al. (2017) found similar teaching approaches to be more effective in older students at a Hong Kong university. They compared the simulation game-based approach to guided inquiry involving on-campus observation tasks, experiments and data collection via interviews and internet searches. While both approaches equally increased knowledge on plastic waste and behavioral intentions relevant to reducing, reusing and recycling, only the gaming simulation approach successfully increased pro-environmental attitudes toward waste management. The gaming simulation involved real-life dilemmas, such as realizing financial gains and enhanced social status at the expense of the environment, and once the participants had reflected afterward on the decisions they made in the game, they expressed remorse over their actions. Therefore, according to Yeung et al. (2017), the activity likely caused the students to critically re-evaluate their values concerning the environment. Furthermore, it is likely that the "tragedy of the commons" element in this type of learning activity holds more relevance and potential for attitude change in the older demographic, as opposed to school pupils (such as in Chow et al. 2017). Although children have been shown to demonstrate strategies to overcome such common-pool resource dilemmas (Koomen and Herrmann 2018), they may be less likely to engage in critical re-evaluation of values as a result.

An additional four studies (Hartley et al. 2015, 2018; Hsiao et al. 2016; Mapotse et al. 2017) reported success in changing at least some plastic-related behaviors. For example, Hartley et al. (2015, 2018) studied the impacts of two educational interventions in promoting litter-reducing behaviors in schoolchildren. The first one (Hartley et al. 2015) involved activities including artwork, demonstrations and mini-experiments, to educate UK pupils on marine plastic pollution. Hartley et al. (2018) used a two-minute video contest to get pupils across 12 locations in Europe to engage with the issue of marine litter as well as potential solutions. Both interventions increased knowledge as well as concern regarding marine litter in the partaking children. More importantly, both interventions were successful in promoting self-reported behaviors such as picking up litter, buying goods with less packaging and encouraging family and friends to take action at follow-up. These findings were particularly encouraging, because as pointed out by Hartley et al. (2015), simply increasing concern and worry about an environmental issue can make children feel powerless, but when paired with evidence that the children have also engaged in actions to reduce the problem, such interventions are valuable means of helping make a positive change.

Furthermore, according to more qualitative observations, interventions by Hsiao et al. (2016) and Mapotse et al. (2017) were successful in changing behavior: Hsiao et al. (2016) applied a qualitative methodology, as the pupils were only five years old. Their intervention involved teaching activities based around eight picture books, two of which introduced the pupils to the impacts of and solutions to litter, including recycling and reuse. According to the educators' "environmental concept checklist" interviews, pupils had learned to bring their own tissues when leaving the house, avoid buying excessively packaged goods, as well as bring their own shopping bags. In addition, the educators reported that following the picture book intervention, no plastic soymilk cups were left unrecycled; however there was no reduction in use of plastic bags in the school. Furthermore, Mapotse et al. (2017) observed an increase in litter bin use following a series of "pupils as researchers" activities, including a litter-pick in the school yard, in a South African school. These examples illustrate alternative ways in which behavior change can be assessed and evaluated, through interviews and observations, and even in groups of pupils who are not yet literate (Hsiao et al. 2016).

In addition, out of three holistic educational interventions that involved field trips to collect plastic debris from coastal areas (Locritani et al. 2019; Owens et al. 2018; Torres et al. 2019), only Locritani et al. (2019) report success in changing some plastic-relevant behaviors. In their "work-related learning internship," Italian pupils aged 16–17 monitored marine litter, examined it using microscopes and engaged in discussions on potential solutions. Following the intervention, pupils reported increased levels of picking up litter and encouraging others to reduce litter, but their litter disposal or consumer behavior did not change. Furthermore, Owens et al. (2018) did not assess plastic-related behaviors directly, but their undergraduate seminar module on marine debris and policy was successful in increasing other environmental behaviors. However, these behaviors also increased in the control group (laboratory-based environmental class), and pro-environmental attitudes only changed in the control group. Finally, Torres et al. (2019) implemented a similar learning module in middle- and high-school students in the USA, but willingness to change personal behaviors to reduce marine litter was only assessed in a small sub-group ($n = 31$) of participants. Around half of these students reported that they were very likely to take litter-reducing action after partaking in the learning module. These approaches are examples of valuable citizen science activities that may further knowledge regarding the types and quantities of marine litter, as well as raise awareness about the issue. As suggested by Torres et al. (2019), it is imperative that such holistic educational interventions connect the issue of marine litter to specific actions that can address the core causes of litter, in order to effect behavior change.

Two out of the 12 interventions (Hartley et al. 2018; Hoang et al. 2016) did not include a measure of environmental behavior, whether observed, self-reported or intended behavior. For example, Hartley et al. (2018) assessed the impact of an online training course on European educators' perceived confidence, skills and competence in relation to teaching about marine litter. The training course was successful in increasing these perceptions, but it did not make educators (who were already concerned) more concerned about marine litter. The educators also manifested positive intentions to integrate what they had learned into their teaching. This kind of "higher-order" evaluation of intentions to embed plastic pollution related content in teaching activities can be employed when there are no means of directly reaching the target group (here: schoolchildren) or when teaching about plastic pollution cannot be enforced, only recommended. Second, Hoang et al. (2016) evaluated a brief 30-minute environmental activity, including a waste separation game and teaching about elementary concepts of waste management, in three Vietnamese elementary schools. They did not measure behavior, but they found that pupils' knowledge on plastic bags, as well as on food waste collection and treatment systems, improved significantly post-intervention. Furthermore, their study was the only one out of the reviewed studies to have incorporated a follow-up measure: Their findings showed that the gains in knowledge were maintained two months after the intervention. While such brief educational sessions are not likely to cause immediate quantifiable changes in environmental behavior, they can nonetheless help guide pro-environmental behaviors that are dependent on knowledge (such as waste sorting, see Section 15.2.1.1).

Finally, outside the schools context and open to any participants, Tabuenca, Kalz and Löhr (2019), investigated the impact of a "massive open online course" (MOOC) on marine litter, developed and organized by the Open University of the Netherlands and the United Nations Environment Programme (UNEP). Of particular interest was the influence of the course on participants' "environmental activism". Results revealed that participants who completed a post-MOOC questionnaire believed themselves to be a "slightly more active person" in helping to tackle marine litter, than those who completed a pre-MOOC questionnaire. Although this finding was statistically significant, there was, however, no significant difference between pre- and post-MOOC questionnaire means relating to whether participants thought the course would help them with actions that would combat marine litter.

15.3.4 Community (19 Articles)

Out of the four categories, we found most studies in the broader community category, so we subdivided these into reducing and recycling behaviors in this section. This approximately reflects the split in the studies found.

1) Reducing Plastic Consumption

People gain information from, and are influenced by, a variety of sources, including family members, peers, their community, professional bodies, NGOs, and government agencies (see also social norms in Section 15.1). The media, as mentioned in Section 15.1.1, is another source of information that can be influential, especially when a "celebrity" figure is involved. The "Blue Planet II" documentary series, presented by naturalist and broadcaster Sir David Attenborough, has been credited with changing consumer behavior by raising awareness of the issue of plastic pollution (Dunn et al. 2020). Evidence of reduced plastic consumption by those who viewed the documentary, however, appears limited, prompting Dunn et al. (2020) to investigate further. Following randomized control trials, using revealed preferences toward plastic or paper packaging as a measure of plastic consumption, it was concluded that viewing a single episode of Blue Planet II was unlikely to change behaviors, although it did positively influence environmental knowledge. The authors suggest, however, that Blue Planet II documentaries increased media attention of marine plastic pollution overall and encouraged discussions, including at policy level, which may ultimately effect wider societal change.

In addition to broader values (see Section 2.1.3.2), religious beliefs may also influence pro-environmental behavior. For instance, in Islam, nature is to be respected and damage to the environment is forbidden; this has led some to suggest that a return to religious traditions may help deal with environmental crises (Siyavooshi et al. 2019). With this in mind, Siyavooshi et al. (2019)

aimed to investigate the effectiveness of using Islamic values and environmental knowledge on willingness to purchase environmentally friendly containers as alternatives to plastic containers. Attendees at a large religious assembly received either brochures containing environmental messages or religious messages about environmental protection; the control group received no information brochure. Both environmental and religious messages increased willingness to purchase environmentally friendly alternatives, compared with the control group, with religious messages increasing willingness the most.

Heidbreder and Schmitt (2020) used Christian Lent as a "window of opportunity" for encouraging behavior change. Lent, the 40-day period leading to Easter in the Christian calendar, is often used by people to reform their habits, usually by "giving up" something that they enjoy, such as chocolate. Heidbreder and Schmitt's study aimed to reduce plastic consumption by encouraging three groups of students to undertake a plastic "fast" for Lent. One group of students undertook the challenge with no additional information, whereas the other two groups answered reflective questions, and were giving information about either the *problems* of plastic (to strengthen moral norms) or *actions* (to strengthen perceived behavioral control). All three groups reduced their plastic consumption, but the provision of information did not enhance the reduction effects.

Heidbreder et al. (2020) used an established campaign, "Plastic Free July", as their "window of opportunity" to effect behavior change. Pre-campaign, all participants were challenged to reduce their plastic consumption; around half of participants received information about how to reduce their plastic consumption, the others received no information. Following this intervention, and in contrast to the study above, those who had received information on ways to reduce their plastic consumption used slightly, but significantly, less plastic than those who had received no "how-to" information.

2) Improving Recycling Practices

Almost half of the interventions aimed at encouraging behavior change in communities focused on improving waste management practices of the general public. Overall, studies tested a range of interventions aimed at increasing recycling rates and reducing recycling bin contamination. The location of the recycling and waste bins was found to be an important contextual factor in increasing recycling: the closer and more convenient the bins were, the greater the recycling rate (e.g. DiGiacomo et al. 2018; Miller et al. 2016). Furthermore, placing recycling and waste bins together, rather than apart, also improved recycling rates and accuracy (Leeabai et al. 2019). Interestingly, removing waste bins from classrooms and offices, and positioning them further away, but next to recycling bins, still increased actual (Fritz et al. 2017) or self-reported recycling behaviors (Ofstad et al. 2017), in a university setting.

Recycling bin signage can also impact recycling rates. Deciding whether to use images (photographs), icons, or words may be the first point of consideration when considering signage design. Wu et al. (2018) found that using images significantly improved the speed and accuracy of "virtual" sorting of different litter items, compared with using words alone. There was also a trend that icons were better than words, although not statistically significant. Standardizing the spatial configuration of waste categories (e.g. consistently from left to right: waste, paper, recycling, compost), rather than displaying categories in a random order, also resulted in more efficient sorting. Displaying images of permitted items only was more effective than displaying both permitted and nonpermitted items, but only when icons were used; there were no such differences when pictures were used. Placing actual items (e.g. plastic bottle, disposable coffee cup) as examples or visual prompts, however, appears to have minimal or no effect on recycling rates (Miller et al. 2016; Zelenika et al. 2018).

Cheung et al. (2018) found that coupling a new eight-compartment recycling bin with an information and instruction poster significantly improved the separation and cleanliness of recycled plastics, compared with other recycling options (eight-compartment bins without a poster, or single-compartment bins with or without a poster). Weekly feedback posters, showing improvements or declines in recycling compared with previous weeks, improved recycling further.

Meng and Trudel (2017) used icons in their study in the form of negatively valenced emoticons (red "frowny" faces). When placed on waste bins (vs no emoticon) as "point-of-decision" prompt, students' recycling increased from 46 to 62%, even though the recycling bin was located three feet further from their path than the waste bin. Photographs of cute animals have also been found to be effective at increasing recycling rates. In an online survey, Wang et al. (2017) found that, for some people, viewing a poster of a cute animal, rather than a noncute animal, increased their recycling intentions. A follow-up study in the field investigated the effect of "active" (e.g. active cute animal running toward the viewer, with "Recycle NOW!") vs "passive" (e.g. stationary cute animal, with "Recycle please") messaging, and found that active messaging was more effective at encouraging recycling than passive messaging (Wang et al. 2017). Furthermore, the effect was sustained over the eight-week experimental period. Although not everyone responds to cute animals in the same way, cuteness has been used in prosocial appeals (e.g. advertising campaigns for wildlife organizations), as it is thought to trigger an instinct to nurture and protect (Wang et al. 2017).

Another way to encourage recycling was explored by Winterich et al. (2019) who studied whether "product transformation salience" (recyclables being turned into new products) increased recycling. In a series of six studies, recycling messages that showed recyclable materials (e.g., plastic bottles, aluminum cans) being turned into a new product were more effective in encouraging recycling than a message to recycle alone.

Although the above findings provide a range of simple yet effective ways in which recycling rates can be optimized, there are instances in which the packaging itself can hinder recycling efforts. For instance, despite the interest in replacing petroleum-based plastics with bio-plastics (from biomass), consumers' familiarity with these items, particularly their end-of-life disposal options, is poor (Taufik et al. 2020). While petroleum-based plastic can generally be recycled, options for bio-plastics vary: some can be recycled, others cannot; and some bio-plastics are compostable. Although recyclable bio-plastics can be recycled in much in the same way as their petroleum-based counterparts, composable bio-plastics usually require the biodegradation process to occur in an industrial composting facility (Taufik et al. 2020). Although consumers perceive compostable bio-plastics to be more environmentally friendly than petroleum-based plastics, only around 37% of consumers disposed of it correctly (in organic waste). In contrast, correct disposal rates of recyclable bio-based and petroleum-based plastics into the recycling waste bins were much higher (around 80 and 90%, respectively; Taufik et al. 2020). Authors of this study suggest that increasing consumers' familiarity with bio-based products could help improve the correct end-of-life disposal of these products.

Overall, the above studies focus on ways to optimize existing recycling practices, focusing on clearer product recycling information, improved signage and prompts, or optimal placement of bins. However, for some countries, even establishing an effective solid waste selective collection (recycling) system can be problematic: in low-middle income countries, predominately those in the Global South, a "lack of awareness, infrastructure, administrative support and knowledge about recycling are the main barriers for its operation, reducing the possibility of successes" (Ferronato et al. 2020). A project undertaken in a Bolivian university found that adding new recycling bins for plastic and paper waste, introducing information banners above the bins, and implementing a series of information events and activities (e.g., free, voluntary seminars and waste management courses), resulted in modest, yet promising, adoption of the new waste management system, which could be further improved with continued information campaigns to raise awareness and knowledge of environmental issues (Ferronato et al. 2020).

In Thailand, numerous universities have already implemented programs aimed at encouraging the reduction, reuse and recycling (3Rs) of waste on campus (Tangwanichagapong et al. 2016). In 2014, in order to become a "green campus," the Asian Institute of Technology implemented several initiatives, largely voluntary or incentive-driven, to tackle waste: these initiatives included the installation of packaging-waste segregation bins, a plastic bin reduction campaign, and a "cash-for-trash" program (Tangwanichagapong et al. 2016). Survey feedback from 12% of the campus population revealed significant differences between those who had actively participated in the 3Rs initiatives and those who had not. Active participants had a better knowledge and understanding of the waste management hierarchy, and were more likely to believe in recycling for better waste management; they were also more supportive of a plastic bag charge and more likely to avoid using plastic bags. Although there was no difference in self-reported waste disposal behaviors, the cash-for-trash program was more effective at reducing the amount of recyclable packaging in the solid waste stream, than the recyclable packaging-waste separation project. It was concluded that incentive-driven initiatives were more effective at reducing waste to landfills and encouraging behavior change, than voluntary approaches (Tangwanichagapong et al. 2016).

Although initiatives, such as installing bin schemes, can increase recycling and reduce the quantity of waste sent for disposal, there is, generally, less focus on measuring actual or self-reported behaviors, or on reducing consumption (Torres-Pereda et al. 2020). This may be especially true for countries in the Global South: Torres-Pereda et al. (2020) point out that while Global North countries have had some success in reducing and recycling waste, evidence of effective waste management initiatives for their country of study, Mexico, is limited. Torres-Perada et al. (2020) assessed the impact of an Environmental Education Intervention (EEI) aimed at reducing waste generation, and encouraging more sustainable behaviors, among members of a national institution. The EEI included a wide range of approaches such as information campaigns (e.g., about the 3Rs and disposable materials, such as plastic bottles); community engagement activities (e.g. a recycling challenge, craft activities, waste management workshops and focus groups); installation of bins and water fountains; and a reusable cup discount scheme. Results of these interventions revealed a reduction in the generation and use of single-use disposable and nonecological materials, such as plastic bottles and polystyrene containers. Furthermore, there was some evidence of "spillover" of pro-environmental behaviors into the home.

15.4 Plastic Pollution and Behavior in the Global South

As seen in Section 15.3, a number of behavioral studies on plastic pollution in the Global South have emerged in recent years. This is a necessary development as published behavioral research has traditionally targeted Global North communities, and thus findings from these studies may lack relevance to other nations or cultures (Henrich et al. 2010). Although the basics of (environmental) behavior are considered consistent across cultural and geographic groups (Fang et al. 2017), there are important international differences. Firstly, social and public pressure to engage in pollution-reducing practices may be lacking in some contexts. For instance, Strydom (2018) found that the majority of urban South Africans reported a lack of social support from their friends, neighbors and municipalities for recycling. However, social norms and conventions regarding environmental behavior are to some extent dictated by existing values (Aoyagi-Usui et al. 2003;

Harris 2006) and could change very rapidly. For example, Garcia et al. (2019) noted that religion, especially in Muslim communities, could be an important consideration in efforts to tackle plastic pollution, as Islamic values encourage sustainable reuse and condemn polluting the environment. Moreover, some countries in the Global South (and beyond) have experienced significant economic growth only recently, and thereby postmaterialist values are likely manifested differently in these countries in comparison to the Global North (Oreg and Katz-Gerro 2006). Such developments in value orientations are relevant for consumption practices, including purchasing and disposal of plastic. Gender is an additional factor. For example, and in line with other environmental literature, Zambrano-Monserrate et al. (2020) showed that those Ecuadorian families where the head of the household was a woman, was highly educated or took part in social organizations, were more likely to use alternatives to plastic bags when shopping.

Simmons and Fielding (2019) conducted a study on the psychological predictors of sustainable waste management practices in Indonesian coastal communities. Unlike in Western samples where social norm is frequently a key predictor of environmental behavior, in this Indonesian sample it was not. Instead, a positive attitude toward appropriate waste disposal as well as a sense of confidence in one's ability to dispose of waste properly predicted sustainable waste management intentions. Furthermore, those who showed stronger intentions of responsible waste management also thought that marine ecosystems were changing for the better. This finding was contrary to the researchers' expectations, as traditionally perceptions that the environment is degrading work toward motivating pro-environmental behavior (e.g. Keshavarz and Karami 2016).

In a similar vein, a study on office workers in Thailand found that believing in one's ability to change waste management behaviors to be more sustainable predicted a range of waste reducing, reusing and recycling behaviors (Janmaimool 2017). However, perceiving environmental pollutants caused by waste as a severe threat did not influence people's self-reported green purchasing or waste avoidance behaviors, only disposal and recycling. The author suggests that in the studied population, green purchasing practices are likely governed by competing factors such as general environmental awareness and income level. That is, these consumers do not readily make the connection between what they buy and how severe they perceive the state of waste pollution to be.

The examples here illustrate that perceiving a sense of control in how one manages waste is amongst the key variables predicting sustainable waste management behaviors (Graham-Rowe et al. 2015; Pakpour et al. 2014). Often these perceptions of control reflect the contextual confines of behavior, such as properties of the waste infrastructure and management system: When the system works, the public are confident in using it and feel in control. Similarly, they may feel more confident about changing their behavior when the context permits such change. In many low-income countries in the Global South, adequate waste infrastructure is lacking, and the recovery of recyclable waste relies on an informal and unregulated recycling sector (Gall et al. 2020). Therefore, determinants of sustainable waste management behavior, as well as effective techniques for changing these behaviors, may look different in the Global South in comparison to Global North communities.

Similar to the Global North where the marine plastic pollution crisis has mobilized communities to take action, such as engage in clean-ups, opportunities may arise in the Global South. For example, across the African and South-American context, responses to plastic pollution may help develop environmental stewardship (Jambeck et al. 2018), create jobs, especially for women (Gutberlet et al. 2017), as well as encourage creativity and innovation (Schmaltz et al. 2020) – especially in communities that are cohesive and close to the natural environment, which oftentimes provides their livelihood, and that have strong values and the ability to change rapidly given support and empowerment.

15.5 Research Gaps and Limitations

15.5.1 Scoping Review

Clearly, literature on behavior change in the context of plastic pollution is growing. This is a welcome development, which extends earlier work that focused on perceptions, attitudes and, in some cases, behaviors, at a single point in time, a snapshot approach that did not capture the effects of interventions to change behavior. However, it is also clear that research on behavior change can be improved. First, details on both intervention and evaluation methods were missing in many published articles. Much like discussions in the natural science around harmonization of assessment methods (e.g., Provencher et al. 2020), reporting needs to be improved in order to improve the science of behavior change. Second, and linked to the first point, we need to systematically assess the quality of the studies undertaken to gain a better understanding of what works, perhaps copying methods from the health and medical sciences on evaluating interventions. It is noticeable that the "gold standard" for testing interventions in those disciplines, randomized controlled trials, is not (yet) applied in the context of plastic pollution. Whether this is due to lack of training or funding or other reasons remains to be seen.

We included a broad range of studies within our criteria, which gave us varied geographical and cultural contexts (for further discussion see Section 15.4), as well as different processes of change and methods. Due to the different sectors we targeted, we used broad search terms, which made the screening process rather difficult and iterative. We would welcome suggestions on how to narrow down searches while not losing the complexity and variety in approaches. Even though we focused the search on behavior change, studies used very different definitions of behavior. Many focused on self-reports or antecedents of behavior (see Section 15.2), with only a minority using objective behavioral indicators or observations. Again, this could be a consequence of lack of training or funding. For future research we encourage using more direct measures of behavior and better research designs, for example including experimental designs with control groups wherever possible (see Pahl and Wyles 2016).

Finally, and although this is difficult to say with certainty given the overall small numbers, there appeared to be fewer examples of effective interventions for the tourism and leisure sector, compared with other sectors. This is concerning considering that tourism has a considerable environmental footprint, for example, polluting air and water and generating waste in some of the most precious areas (Dolnicar et al. 2019). This could be because increasing pro-environmental behavior can be difficult in a tourism context due the generally hedonic nature of tourism, which typically centers on enjoyment and relaxation (Dolnicar et al. 2019). Many people, including members of environmental organizations, do not act in a particularly environmentally friendly way while on holiday (Juvan & Dolnicar, 2014; Dolnicar et al. 2019), countering, for instance, that holidays are a special treat or that destination economies and communities benefit from visits. More research on interventions in the tourism sector would be worthwhile, for example concentrating on the growing sector of environmental tourism, especially if we could learn how to transfer good behavior from one context to another, for example, home to holidays or vice versa.

15.5.2 Public Acceptability

While several approaches have been trialled in efforts to reduce plastic pollution (as reviewed in Section 15.3), what is currently lacking is research on the public acceptability of the various approaches. For example, the food packaging industry has seen promising advancements recently

(Guillard et al. 2018; Huang et al. 2018), but retailers may be hesitant to commit to novel packaging solutions when consumer uptake is unknown or uncertain (but see Neves et al. 2020). Therefore, research on public perceptions is needed to help inform the design and development of innovative solutions and alternatives, even before research focuses on actual behavior. Similarly, all steps of the consumer journey, including disposal, should be considered when examining public acceptance. That is, it is important that consumer uptake meets appropriate disposal options (as highlighted in Taufik et al. 2020).

15.5.3 Economic Value of Behavior Change Interventions

Furthermore, research that quantifies the economic value of behavior change interventions may be needed to persuade various stakeholders to commit to these approaches. That is, while we have evidence on the impacts of behavioral interventions on attitudes, knowledge and (self-reported) behaviors, quantification of this impact in terms of ecological or economic effects and benefits is lacking and could help win over decision-makers not yet convinced. These impacts could be estimated, for example, with respect to gains in ecosystem services (Beaumont et al. 2019). Quantifying behavior change in this way, perhaps in combination with lifecycle approaches, may also help with identifying the most critical points of behavioral intervention within the plastics system.

15.6 Remaining Challenges

Although increased public awareness of plastic pollution creates prospects for behavior change, there are obstacles that are currently limiting the potential for this change. For example, consumers tend to assign responsibility for plastic pollution to companies and manufacturers (Hartley et al. 2018). This "diffusion of responsibility" (also discussed in Heidbreder et al. 2019) may reduce the momentum for change through behavioral interventions. Therefore, coordinated efforts where industries work toward providing product alternatives and refill options, and where consumers are nudged toward these options, may work best to motivate sustained behavior change (Jia et al. 2019), combining top-down and bottom-up approaches (Pahl, Richter and Wyles 2020).

Everyday consumer decisions are still largely driven by convenience and price as well as functional and aesthetic properties of products (Gidlöf et al. 2017). Consideration for plastic waste and pollution is therefore likely not a first priority on the consumer agenda, except for those items that have been explicitly and consistently linked with marine plastic pollution (such as straws or plastic bottles; Marazzi et al. 2020). For items that contribute to plastic pollution more indirectly, making this link is more complicated. Furthermore, often the consumers' desire for convenience is tied to habitual behavior that can be difficult to interrupt. While the UK plastic bag ban was successful in getting consumers to question their need for a plastic bag when faced with a cost (Poortinga et al. 2016), inducing a similar disruption in habitual behavior across other consumer contexts remains a challenge.

It is also important to note, that habit disruption can have unfavorable consequences. For example, when introducing a ban on plastic bags, failure to ensure availability of viable and affordable alternatives can lead to emergence of "black markets for plastic" (e.g., Paul and Mironga 2020). When plastic bags can be obtained from an informal source, consumers fail to see the value in introducing a ban in the first place. The resulting resistance and dissatisfaction with overt governmental efforts to reduce plastic pollution does not help the aim of more responsible management of plastics.

Another challenge that should be recognized in light of recent events is the increase in single-use plastic pollution following the COVID-19 pandemic (Thames21 2020). Personal protective equipment such as disposable face masks, as well as single-use cups used to minimize spreading of the virus are now littering the environment. The pandemic has helped enforce certain consumption habits that to some degree rely on plastic packaging, such as increased the popularity of online deliveries of food and other goods (Vanapalli et al. 2021). In some countries bans on single-use plastics have been relaxed temporarily during the pandemic (Silva et al. 2020), which may have led to consumer confusion and disproval, especially in those consumers who had already adjusted to the plastic-reducing lifestyle. Therefore, the pandemic is likely to have repercussions to consumer behavior and waste management practice. Nevertheless, while public health and safety rightfully remains the priority on the global agenda, responsible management of single-use plastic waste may now be more important than ever.

15.7 Conclusion

The contribution of this chapter is to provide an overview of the role of human behavior in the context of plastic pollution. We have reviewed social and behavioral science approaches to explaining behavior and provided insights from a scoping review assessing behavior change interventions between 2015 and 2020. We find that a variety of methods and approaches are used and human behavior is increasingly the focus of research. However, research and assessment methods should be improved, and quantification of behaviors as well as wider impacts following behavior change interventions is lacking. With better evidence we can direct future efforts to one of the most valuable resources in the fight against plastic pollution: People everywhere in the plastic system.

Acknowledgements

The writing of this chapter was facilitated by EU funding to the first two authors SN and DC from the INTERREG France (Channel) England project “Preventing Plastic Pollution” co-financed by the European Regional Development Fund (https://preventingplasticpollution.com/).

References

Abrahamse, W. and Steg, L. (2013). Social influence approaches to encourage resource conservation: a meta-analysis. *Global Environmental Change* 23(6): 1773–1785.

Abrahamse, W., Steg, L., Vlek, C., and Rothengatter, T. (2007). The effect of tailored information, goal setting, and tailored feedback on household energy use, energy-related behaviors, and behavioral antecedents. *Journal of Environmental Psychology* 27 (4): 265–276.

Anbumani, S., and Kakkar, P. (2018). Ecotoxicological effects of microplastics on biota: a review. *Environmental Science and Pollution Research* 25 (15): 14373–14396.

Anderson, A. G., Grose, J., Pahl, S. et al. (2016). Microplastics in personal care products: exploring perceptions of environmentalists, beauticians and students. *Marine Pollution Bulletin* 113 (1–2): 454–460.

Aoyagi-Usui, M.; Vinken, H., and Kuribayashi, A. Pro-environmental attitudes and behaviors: an international comparison. *Human Ecology Review* 2003 (10): 23–31.

Arksey, H. and O’Malley, L. (2005). Scoping studies: towards a methodological framework. *International Journal of Social Research Methodology* 8 (1): 19–32.

Ashley, R., Blackwood, D., Souter, N. et al. (2005). Sustainable disposal of domestic sanitary waste. *Journal of Environmental Engineering* 131 (2): 206–215.

Barberá-Tomás, D., Castelló, I., De Bakker, F.G. et al. (2019). Energizing through visuals: how social entrepreneurs use emotion-symbolic work for social change. *Academy of Management Journal* 62 (6): 1789–1817.

Barnes, S. J. (2019). Out of sight, out of mind: plastic waste exports, psychological distance and consumer plastic purchasing. *Global Environmental Change* 58: 101943.

Beaumont, N. J., Aanesen, M., Austen, M. C. et al. (2019). Global ecological, social and economic impacts of marine plastic. *Marine Pollution Bulletin* 142: 189–195.

Bolderdijk, J., Steg, L., Geller, E. et al. (2013). Comparing the effectiveness of monetary versus moral motives in environmental campaigning. *Nature Climate Change* 3: 413–416. https://doi.org/10.1038/nclimate1767.

Borg, K., Curtis, J., and Lindsay, J. (2020). Social norms and plastic avoidance: testing the theory of normative social behaviour on an environmental behaviour. *Journal of Consumer Behaviour* 19 (6): 594–607.

Carmi, N., Arnon, S., and Orion, N. (2015). Transforming environmental knowledge into behavior: the mediating role of environmental emotions. *The Journal of Environmental Education* 46 (3): 183–201.

De Groot, J. I., Abrahamse, W., and Jones, K. (2013). Persuasive normative messages: the influence of injunctive and personal norms on using free plastic bags. *Sustainability* 5 (5): 1829–1844.

DiGiacomo, A., Wu, D. W.-L., Lenkic, P. et al. (2018). Convenience improves composting and recycling rates in high-density residential areas. *Journal of Environmental Planning and Management* 61 (2): 309–331.

Dolnicar, S., Knezevic Cvelbar, L. and Grün, B. (2019). A sharing-based approach to enticing tourists to behave more environmentally friendly. *Journal of Travel Research* 58 (2): 241–252.

Dunn, M. E., Mills, M., and Veríssimo, D. (2020). Evaluating the impact of the documentary series Blue Planet II on viewers' plastic consumption behaviors. *Conservation Science and Practice* 2 (10): e280.

Fang, W. T., Ng, E., Wang, C. M. et al. (2017). Normative beliefs, attitudes, and social norms: people reduce waste as an index of social relationships when spending leisure time. *Sustainability* 9 (10): 1696.

Ferronato, N., Lizarazu, E. G. G., Tudela, J. M. V. et al. (2020). Selective collection of recyclable waste in Universities of low-middle income countries: lessons learned in Bolivia. *Waste Management* 105: 198–210.

Fritz, J. N., DuPuis, D. L, Wu, W.-L. et al. (2017). Evaluating increased effort for item disposal to improve recycling at a university. *Journal of Applied Behavior Analysis* 50: 825–829.

Gall, M., Wiener, M., de Oliveira, C. C. et al. (2020). Building a circular plastics economy with informal waste pickers: recyclate quality, business model, and societal impacts. *Resources, Conservation and Recycling* 156: 104685.

Garcia, B., Fang, M. M., and Lin, J. (2019). Marine plastic pollution in Asia: all hands on deck! *Chinese Journal of Environmental Law* 3 (1): 11–46.

Gidlöf, K., Anikin, A., Lingonblad, M. et al. (2017). Looking is buying. How visual attention and choice are affected by consumer preferences and properties of the supermarket shelf. *Appetite* 116: 29–38.

Graham-Rowe, E., Jessop, D. C., and Sparks, P. (2015). Predicting household food waste reduction using an extended theory of planned behaviour. *Resources, Conservation and Recycling* 101: 194–202.

Grazzini, L., Rodrigo, P., Aiello, G. et al. (2018). Loss or gain? The role of message framing in hotel guests' recycling behaviour. *Journal of Sustainable Tourism* 26 (11): 1944–1966.

Grebitus, C., Roscoe, R. D., Van Loo, E. J., et al. (2020). Sustainable bottled water: how nudging and Internet Search affect consumers' choices. *Journal of Cleaner Production*, 267: 121930. https://www.

sciencedirect.com/science/article/pii/S0959652620319776?casa_token=pNTEDQm6Ax4AAAAA:ZeC7RGrA2pe3mW1DoGHEz1wlcLYu3brlugkSdsq_3qkQQBrqP1YRzg6w3_NpsXw8sh3VHQIkKA (accessed August 20, 2021).

Guillard, V., Gaucel, S., Fornaciari, C. et al. (2018). The next generation of sustainable food packaging to preserve our environment in a circular economy context. *Frontiers in Nutrition* 5: 121.

Gutberlet, J., Carenzo, S., Kain, J. H. et al. (2017). Waste picker organizations and their contribution to the circular economy: two case studies from a global south perspective. *Resources* 6 (4): 52.

Harris, P.G. (2006). Environmental perspectives and behavior in China: synopsis and bibliography. *Environment and Behavior* 38: 5–21.

Hartley, B. L., Pahl, S., Veiga, J. et al. (2018). Exploring public views on marine litter in Europe: perceived causes, consequences and pathways to change. *Marine Pollution Bulletin* 133: 945–955.

Hartley, B. L., Thompson, R. C., and Pahl, S. (2015). Marine litter education boosts children's understanding and self-reported actions. *Marine Pollution Bulletin* 90 (1–2): 209–217. https://doi.org/10.1016/j.marpolbul.2014.10.049.

Hawkins, A., Sharpe, R., Spence, K. et al. (2019). Inappropriate flushing of menstrual sanitary products. *Proceedings of the Institution of Civil Engineers – Water Management* 172 (4): 163–169.

Heidbreder, L. M., Bablok, I., Drews, S. et al. (2019). Tackling the plastic problem: a review on perceptions, behaviors, and interventions. *Science of the Total Environment* 668: 1077–1093.

Heidbreder, L. M. and Schmitt, M. (2020). Fasting plastic: an intervention study to break habits of plastic consumption. *PsyEcology* 11 (2): 170–192.

Heidbreder, L. M., Steinhorst, J., and Schmitt, M. (2020). Plastic-free july: an experimental study of limiting and promoting factors in encouraging a reduction of single-use plastic consumption. *Sustainability* 12 (11): 4698.

Henrich, J., Heine, S. J., and Norenzayan, A. (2010). Beyond WEIRD: towards a broad-based behavioral science. *Behavioral and Brain Sciences* 33 (2–3): 111.

Henderson, L., and Green, C. (2020). Making sense of microplastics? Public understandings of plastic pollution. *Marine Pollution Bulletin* 152: 110908.

Hottle, T. A., Bilec, M. M., Brown, N. R. et al. (2015). Toward zero waste: composting and recycling for sustainable venue based events. *Waste Management* 38: 86–94.

Huang, Y., Mei, L., Chen, X. et al. (2018). Recent developments in food packaging based on nanomaterials. *Nanomaterials* 8 (10): 830.

Huddart Kennedy, E., Krahn, H., and Krogman, N. T. (2015). Are we counting what counts? A closer look at environmental concern, pro-environmental behaviour, and carbon footprint. *Local Environment* 20 (2): 220–236.

Hunt, E. (2017). Blue Planet II: From octopus v shark to fish that crawl, the series's biggest discoveries. *The Guardian* (10 December). https://www.theguardian.com/tv-and-radio/2017/nov/20/blue-planet-ii-what-have-we-learned-so-far ().

Jambeck, J., Hardesty, B. D., Brooks, A. L. et al. (2018). Challenges and emerging solutions to the land-based plastic waste issue in Africa. *Marine Policy* 96: 256–263.

Janmaimool, P. (2017). Application of protection motivation theory to investigate sustainable waste management behaviors. *Sustainability* 9 (7): 1079.

Jia, L., Evans, S., and van der Linden, S. (2019). Motivating actions to mitigate plastic pollution. *Nature Communications* 10 (1): 1–3.

Joanna Briggs Institute (2015). *Joanna Briggs Institute Reviewers' Manual: Methodology for JBI Scoping Reviews*. The Joanna Briggs Institute, Adelaide.

Juvan, E. and Dolnicar, S. (2014). The attitude–behaviour gap in sustainable tourism. *Annals of Tourism Research* 48: 76–95.

Kaiser, F. G., Wölfing, S., and Fuhrer, U. (1999). Environmental attitude and ecological behaviour. *Journal of Environmental Psychology* 19 (1): 1–19.

Keshavarz, M., and Karami, E. (2016). Farmers' pro-environmental behavior under drought: application of protection motivation theory. *Journal of Arid Environments* 127: 128–136.

Klaiman, K., Ortega, D. L., and Garnache, C. (2016). Consumer preferences and demand for packaging material and recyclability. *Resources, Conservation and Recycling* 115: 1–8.

Klaiman, K., Ortega, D. L., and Garnache, C. (2017). Perceived barriers to food packaging recycling: Evidence from a choice experiment of US consumers. *Food Control* 73: 291–299.

Klöckner, C. A. (2013). A comprehensive model of the psychology of environmental behaviour – a meta-analysis. *Global Environmental Change* 23 (5): 1028–1038.

Knoblauch, D., Mederake, L., and Stein, U. (2018). Developing countries in the lead – what drives the diffusion of plastic bag policies? *Sustainability* 10 (6): 1994.

Kollmuss, A., and Agyeman, J. (2002). Mind the gap: why do people act environmentally and what are the barriers to pro-environmental behavior? *Environmental Education Research* 8 (3): 239–260.

Koomen, R., and Herrmann, E. (2018). An investigation of children's strategies for overcoming the tragedy of the commons. *Nature Human Behaviour* 2 (5): 348–355.

Leeabai, N., Suzuki, S., Jiang, Q., et al. (2019). The effects of setting conditions of trash bins on waste collection performance and waste separation behaviors; distance from walking path, separated setting, and arrangements. *Waste Management* 94: 58–67.

Liberman, N., and Trope, Y. (2008). The psychology of transcending the here and now. *Science* 322 (5905): 1201–1205.

Loschelder, D. D., Siepelmeyer, H., Fischer, D. et al. (2019). Dynamic norms drive sustainable consumption: norm-based nudging helps café customers to avoid disposable to-go-cups. *Journal of Economic Psychology* 75: 102146.

Macintosh, A., Simpson, A., Neeman, T. et al. (2020). Plastic bag bans: lessons from the Australian Capital Territory. *Resources, Conservation and Recycling* 154: 104638.

Marazzi, L., Loiselle, S., Anderson, L. G. et al. (2020). Consumer-based actions to reduce plastic pollution in rivers: a multi-criteria decision analysis approach. *PloS One* 15 (8): e0236410.

Martin, L., White, M. P., Hunt, A. et al. (2020). Nature contact, nature connectedness and associations with health, wellbeing and pro-environmental behaviours. *Journal of Environmental Psychology* 68: 101389.

McNeill, L., and Moore, R. (2015). Sustainable fashion consumption and the fast fashion conundrum: fashionable consumers and attitudes to sustainability in clothing choice. *International Journal of Consumer Studies* 39 (3): 212–222.

McNicholas, G., and Cotton, M. (2019). Stakeholder perceptions of marine plastic waste management in the United Kingdom. *Ecological Economics* 163: 77–87.

Mellish, S., Pearson, E. L., McLead, E. M. et al. (2019). What goes up must come down: an evaluation of a zoo conservation-education program for balloon litter on visitor understanding, attitudes, and behaviour. *Journal of Sustainable Tourism* 27 (9): 1393–1415.

Meng, M. D. and Trudel, R. (2017). Using emoticons to encourage students to recycle. *The Journal of Environmental Education* 48 (3): 196–204.

Milfont, T. L. (2009). The effects of social desirability on self-reported environmental attitudes and ecological behaviour. *The Environmentalist* 29 (3): 263–269.

Miller, N. D., Meindl, J. N., and Caradine, M. (2016). The effects of bin proximity and visual prompts on recycling in a university building. *Behavior and Social Issues* 25: 4–10.

Misund, A., Tiller, R., Canning-Clode, J. et al. (2020). Can we shop ourselves to a clean sea? An experimental panel approach to assess the persuasiveness of private labels as a private governance approach to microplastic pollution. *Marine Pollution Bulletin* 153: 110927.

Munn, Z., Peters, M. D., Stern, C. et al. (2018). Systematic review or scoping review? Guidance for authors when choosing between a systematic or scoping review approach. *BMC Medical Research Methodology* 18 (1): 1–7.

Muralidharan, S. and Sheehan, K. (2018). The role of guilt in influencing sustainable pro-environmental behaviors among shoppers differences in response by gender to messaging about England's plastic-bag levy. *Journal of Advertising Research* 58 (3): 349–362.

Muralidharan, S and Sheehan, K. (2016). Tax and fee message frames as inhibitors of plastic bag usage among shoppers: a social marketing application of the theory of planned behavior. *Social Marketing Quarterly* 22 (3): 349–362.

Nam, H. V., Lo, A., Yeung, P. et al. (2020). Hotel ICON: towards a role-model hotel pioneering sustainable solutions. *Asia Pacific Journal of Tourism Research* 25 (5): 572–582.

Neves, A. C., Moyne, M. M., Eyre, C. et al. (2020). Acceptability and societal impact of the introduction of bioplastics as novel environmentally friendly packaging materials in Ireland. *Clean Technologies* 2 (1): 127–143.

Nguyen, T. N., Lobo, A., and Greenland, S. (2016). Pro-environmental purchase behaviour: the role of consumers' biospheric values. *Journal of Retailing and Consumer Services* 33: 98–108.

Nigbur, D., Lyons, E., and Uzzell, D. (2010). Attitudes, norms, identity and environmental behaviour: using an expanded theory of planned behaviour to predict participation in a kerbside recycling programme. *British Journal of Social Psychology* 49 (2): 259–284.

Nuojua, S., Pahl, S., & Thompson, R. C. (2022). *Ocean Connectedness and Consumer Responses to Single-use Packaging*. Manuscript under review.

Ofstad, S. P., Tobolova, M., Nayum, A., et al. (2017). Understanding the mechanisms behind changing people's recycling behavior at work by applying a comprehensive action determination model. *Sustainability* 9 (2): 204.

Oreg, S., Katz-Gerro, T. (2006). Predicting proenvironmental behavior cross-nationally values, the theory of planned behavior, and value-belief-norm theory. *Environment and Behavior* 38: 462–483.

Pahl, S., Richter, I., Wyles, K. (2020) Human perceptions and behaviour determine aquatic plastic pollution. In: *The Handbook of Environmental Chemistry*. Springer, Berlin, Heidelberg. https://doi.org/10.1007/698_2020_672.

Pahl, S., Wyles, K. J. (2016). The human dimension: how social and behavioural research methods can help address microplastics in the environment. *Analytical Methods* 9, (9): 1404–1411.

Pahl, S., Wyles, K. J., Thompson, R. C. (2017). Channelling passion for the ocean towards plastic pollution. *Nature Human Behaviour* 1, (10): 697–699.

Pakpour, A. H., Zeidi, I. M., Emamjomeh, M. M. et al. (2014). Household waste behaviours among a community sample in Iran: an application of the theory of planned behaviour. *Waste Management* 34 (6): 980–986.

Phelan, A., Ross, H., Setianto, N. A. et al. (2020). Ocean plastic crisis – mental models of plastic pollution from remote Indonesian coastal communities. *PloS One* 15 (7): e0236149.

Poortinga, W., Sautkina, E., Thomas, G. O. et al. (2016). *The English Plastic Bag Charge: Changes in Attitudes and Behaviour*. Cardiff, Wales, Welsh School of Architecture/School of Psychology, Cardiff University.

Poortinga, W. and Whitaker, L. (2018). Promoting the use of reusable coffee cups through environmental messaging, the provision of alternatives and financial incentives. *Sustainability* 10: 873.

Prakash, G., Choudhary, S., Kumar, A. et al. (2019). Do altruistic and egoistic values influence consumers' attitudes and purchase intentions towards eco-friendly packaged products? An empirical investigation. *Journal of Retailing and Consumer Services* 50: 163–169.

Preventing Plastic Pollution. (n.d.). Preventing plastic pollution, one piece at a time. https://preventingplasticpollution.com/about-the-project/ ().

Provencher, J., Covernton, G., Moore, R, et al. (2020). Proceed with caution: the need to raise the publication bar for microplastics research. *Science of The Total Environment.* 748. 141426. doi:10.1016/j.scitotenv.2020.141426.

Rhein, S., and Schmid, M. (2020). Consumers' awareness of plastic packaging: more than just environmental concerns. *Resources, Conservation and Recycling* 162: 105063.

Rubens, L., Gosling, P., Bonaiuto, M., et al. (2015). Being a hypocrite or committed while I am shopping? A comparison of the impact of two interventions on environmentally friendly behavior. *Environment and Behavior* 47 (1): 3–16.

SAPEA (Science Advice for Policy by European Academies). (2019). *A Scientific Perspective on Microplastics in Nature and Society*. Berlin: SAPEA. https://doi.org/10.26356/microplastics.

Schmaltz, E., Melvin, E. C., Diana, Z. et al. (2020). Plastic pollution solutions: emerging technologies to prevent and collect marine plastic pollution. *Environment International* 144: 106067.

Schmidt, C. W. (2008). The yuck factor: when disgust meets discovery. *Environews* 116 (12).

Schnurr, R. E., Alboiu, V., Chaudhary, M. et al. (2018). Reducing marine pollution from single-use plastics (SUPs): a review. *Marine Pollution Bulletin* 137: 157–171.

Schultz, P. W. (1999). Changing behavior with normative feedback interventions: a field experiment on curbside recycling. *Basic and Applied Social Psychology* 21 (1): 25–36.

Schultz, P. W., Bator, R. J., Large, L. B. et al. (2013). Littering in context: personal and environmental predictors of littering behavior. *Environment and Behavior* 45 (1): 35–59.

Silva, A. L. P., Prata, J. C., Walker, T. R. et al. (2020). Rethinking and optimising plastic waste management under COVID-19 pandemic: policy solutions based on redesign and reduction of single-use plastics and personal protective equipment. *Science of the Total Environment* 742: 140565.

Silva, A. L. P., Prata, J. C., Walker, T. R. et al. (2020). Increased plastic pollution due to COVID-19 pandemic: challenges and recommendations. *Chemical Engineering Journal* 405: 126683.

Simmons, E. C., and Fielding, K. S. (2019). Psychological predictors of fishing and waste management intentions in Indonesian coastal communities. *Journal of Environmental Psychology* 65: 101324.

Sisson, A., Grisamore, A., and Jang, J. (2020). Green practices with reusable drinkware at music and sporting events: a hospitality undergraduate student perspective. *Journal of Hospitality & Tourism Education* 33: 1–13.

Siyavooshi, M., Foroozanfar, A., and Sharifi, Y. (2019). Effect of Islamic values on green purchasing behavior. *Journal of Islamic Marketing* 10 (1): 125–137.

Steer, M., and Thompson, R. C. (2020). Plastics and microplastics: impacts in the marine environment. In: Streit-Bianchi, M., Cimadevila, M., Trettnak, W. (Eds.) *Mare Plasticum – The Plastic Sea*. Cham: Springer, pp. 49–72.

Steg, L., Bolderdijk, J. W., Keizer, K. et al. (2014). An integrated framework for encouraging pro-environmental behaviour: the role of values, situational factors and goals. *Journal of Environmental Psychology* 38: 104–115.

Stern, P. C., and Dietz, T. (1994). The value basis of environmental concern. *Journal of Social Issues* 50 (3): 65–84.

Strydom, W. F. (2018). Applying the theory of planned behavior to recycling behavior in South Africa. *Recycling* 3 (3): 43.

Syberg, K., Hansen, S. F., Christensen, T. B. et al. (2018). Risk perception of plastic pollution: importance of stakeholder involvement and citizen science. In: Wagner, M., Lambert, S. (Eds.) *Freshwater Microplastics*. Cham: Springer, pp. 203–221.

Tabuenca, B., Kalz, M., and Löhr, A. (2019). Massive open online education for environmental activism: the worldwide problem of marine litter. *Sustainability* 11 (10): 2860.

Tangwanichagapong, S., Nitivattananon, V., Mohanty, B. et al. (2017). Greening of a campus through waste management initiatives. *International Journal of Sustainability in Higher Education* 18 (2) 203–217.

Taufik, D., Reinders, M. J., Molenveld, K. et al. (2020). The paradox between the environmental appeal of bio-based plastic packaging for consumers and their disposal behaviour. *Science of the Total Environment* 705: 135820.

Thames21 (2020). Latest river Thames survey confirms COVID-19 plastic impact. https://www.thames21.org.uk/2020/12/latest-river-thames-survey-confirms-covid-19-plastic-impact (accessed December 21, 2020).

Thomas, G. O., Poortinga, W. and Sautkina, E. (2016). The Welsh single-use carrier bag charge and behavioural spillover. *Journal of Environmental Psychology* 47: 126–135.

Thomas, C. and Sharp, V. (2013). Understanding the normalisation of recycling behaviour and its implications for other pro-environmental behaviours: a review of social norms and recycling. *Resources, Conservation and Recycling* 79: 11–20.

Thompson, R.C. (2019). Has Blue Planet II had an impact on plastic pollution? Science Focus (12 April). https://www.sciencefocus.com/nature/has-blue-planet-ii-had-an-impact-on-plastic-pollution/ ().

Thongplew, N. and Kotlakome, R. (2019). Getting a drink: an experiment for enabling a sustainable practice in Thai university settings. *Journal of Cleaner Production* 218: 294–303.

Torres-Pereda, P., Parra-Tapia, E., Rodríguez, M. A. et al. (2020). Impact of an intervention for reducing waste through educational strategy: a Mexican case study, what works, and why? *Waste Management* 114: 183–195.

United Nations Environment Programme (2019). *Legal Limits on Single-Use Plastics and Microplastics: A Global Review of National Laws and Regulations*. UNEP Report, pp. 118. https://www.unep.org/resources/report/legal-limits-single-use-plastics-and-microplastics

Vanapalli, K. R., Sharma, H. B., Ranjan, V. P. et al. (2021). Challenges and strategies for effective plastic waste management during and post COVID-19 pandemic. *Science of the Total Environment* 750: 141514.

Van de Mortel, T. F. (2008). Faking it: social desirability response bias in self-report research. *The Australian Journal of Advanced Nursing* 25 (4): 40.

Van der Werff, E., Steg, L., and Keizer, K. (2013). The value of environmental self-identity: the relationship between biospheric values, environmental self-identity and environmental preferences, intentions and behaviour. *Journal of Environmental Psychology* 34: 55–63.

Vesely, S., and Klöckner, C. A. (2020). Social desirability in environmental psychology research: three meta-analyses. *Frontiers in Psychology* 11: 1395.

Wagner, M., and Lambert, S. (2018). *Freshwater microplastics: emerging environmental contaminants?* Berlin: Springer Nature.

Wang, T., Mukhopadhyay, A. and Patrick, V. M. (2017). Getting consumers to recycle NOW! When and why cuteness appeals influence prosocial and sustainable behavior. *Journal of Public Policy and Marketing* 36 (2): 269–283.

Wiederhold, M., and Martinez, L. F. (2018). Ethical consumer behaviour in Germany: the attitude-behaviour gap in the green apparel industry. *International Journal of Consumer Studies* 42 (4): 419–429.

Willis, K., Hardesty, B. D., Vince, J. et al. (2019). The success of water refill stations reducing single-use plastic water litter. *Sustainability* 11 (19): 5232.

WIN-Gallup International (2012). Global Index of Religiosity and Atheism. RED C Press Release – Religion and Atheism (25 July 2012). https://www.redcresearch.ie/wp-content/uploads/2015/10/RED-C-press-release-Religion-and-Atheism-25-7-12.pdf

Winterich, K. P., Nenkov, G. Y., and Gonzales, G. E. (2019). Knowing what it makes: how product transformation salience increases recycling. *Journal of Marketing* 83 (4): 21–37.

Wu, D. W.-L., Lenkic, P. J., DiGiacomo, A. et al. (2018). How does the design of waste disposal signage influence waste disposal behavior? *Journal of Environmental Psychology* 58: 77–85.

Wyles, K. J., Pahl, S., Holland, M. et al. (2017). Can beach cleans do more than clean-up litter? Comparing beach cleans to other coastal activities. *Environment and Behavior* 49 (5): 509–535.

Xanthos, D., and Walker, T. R. (2017). International policies to reduce plastic marine pollution from single-use plastics (plastic bags and microbeads): a review. *Marine Pollution Bulletin* 118 (1–2): 17–26.

Zambrano-Monserrate, M. A., and Ruano, M. A. (2020). Do you need a bag? Analyzing the consumption behavior of plastic bags of households in Ecuador. *Resources, Conservation and Recycling* 152: 104489.

Zelenika, I., Moreau, T., and Zhao, J. (2018). Toward zero waste events: reducing contamination in waste streams with volunteer assistance. *Waste Management* 76: 39–45.

16

Legal and Policy Frameworks for Preventing and Reducing Marine Plastic Pollution

Karen Raubenheimer

Australian National Centre for Ocean Resources and Security (ANCORS), University of Wollongong, Wollongong, Australia

16.1 Introduction to the Governance of Plastic Pollution

Policy plays an important role in stimulating action across multiple sectors and can target actors and stakeholders across the plastics value chain. Supportive actions include awareness and education, which can be included in the design of policies. More recently, policy and regulatory frameworks have developed beyond post-pollution punitive actions to "upstream" preventive actions, including economic instruments to incentivize desired behavior change within industry and consumers.

Underpinning the development of policy has been the ongoing development of our understanding of the issue. Since the early 1970s, scientists have reported on the presence of plastic wastes in the environment, warning about the impacts on biodiversity. More recently, the socio-economic impacts are being investigated, including the possible effects on human health. These issues have been reflected in policy to a lesser degree. Other areas not well reflected are the many sources of microplastics other than microbeads in cosmetics and, also to a disappointingly lesser degree, pre-production plastic pellets. The latter shortcoming is despite an industry voluntary program being in place for a number of years and proven successful, albeit with some shortcomings.

Science is therefore critical in supporting the development of policy. Monitoring the effects of plastics and associated chemicals on the environment and socio-economic outcomes provides the quantitative and qualitative data necessary to review the effectiveness of policy and regulatory frameworks in place. Research into the design of products, including new materials, provides another important component of the science–policy interface.

Ultimately, science and policy should be complementary, aiming to reach a point where waste management is not playing catch-up or requiring a never-ending cycle of reverse engineering of the constant stream of new products and materials placed on the global market. The complexity of these products and materials, along with the volume, has presented a difficult environment to navigate and manage.

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

16.1.1 Evolving Concepts of Marine Litter Governance

Marine litter has played a crucial role in raising global awareness of the issue of plastic pollution. The focus for many years was therefore on regulating maritime activities, particularly abandoned, lost or otherwise discarded fishing gear (ALDFG), and dumping of wastes generated on land and discharge of operational garbage from vessels and ocean platforms. Marine litter, however, is a symptom of a more complex problem and results from a failure of governance on both land and sea.

As land-based sources of marine litter became recognized as a major contributor, the link to improved solid waste management practices was increasingly promoted. Strengthening national action in this regard has therefore been a consistent component of international and regional legal and policy frameworks.

In more recent years, policy focus has turned to the actions taken further "upstream" in the value chain. These actions include product design, waste reduction, and financial and/or physical responsibility for products at the end of life.

Environmental principles have also progressed from the precautionary principle and polluter pays to extended producer responsibility, sustainable consumption and production, circular economy, and environmental justice, to name a few (Raubenheimer and Urho 2020).

As our understanding of the issue of marine plastic litter and the drivers thereof has matured, action has progressed from a remedial nature (removal from the coastal zone through, for example, beach cleans), to mitigation (reducing the effect of leakage through, for example, capture devices), and finally to prevention (reducing the generation of problematic products and materials through, for example, waste reduction practices). The latter has been promoted as more cost effective than mitigation and remediation (Lebreton and Andrady 2019).

Thus, the focus has moved from marine plastic litter being a marine issue originating from sea-based sources, to a waste management issue originating from land-based sources, to the more systemic approach of sustainable consumption and production and resource efficiency (Raubenheimer and Urho 2020).

Awareness raising has been a common theme and has also progressed from consumer awareness of the impacts of marine litter to education on the solutions and industry responsibility. Increasingly, awareness through action is employed through citizen science, particularly in gathering data during beach cleans.

eWaste has been a focal point of international discussions for a number of years. More recently, much of the focus has been on plastic packaging, including beverage containers, shopping bags, and other single-use items, particularly related to the hospitality sector. Research is now highlighting the contribution by the fisheries, construction and demolition, and agricultural sectors, amongst others. Quantification of these sources is still in its infancy. Microbeads and textiles were considered the major components of marine pollution by microplastics, but research is again indicating that other sources, such as car tires, are of far greater concern (Eunomia 2018).

Another focal area rapidly gaining recognition is the contribution of the plastics life cycle to climate change (CIEL 2019a). Although the risks to humans and the environment from chemicals associated with the plastics life cycle have been documented to a some degree for particular life cycle phases, the true extent of the cumulative impact of chemicals across the full life cycle is poorly understood (CIEL 2019b).

16.1.2 Industry Involvement

The cost of marine litter, and plastic pollution more generally, is increasingly recognized as an externality to those businesses that produce and use plastic products. Estimations of costs of a 1% decline in global marine ecosystem services are in the region of $500 billion annually

(Beaumont et al. 2019). It is therefore appropriate that industry contributes to the management of plastic pollution throughout the life cycle of the products they produce, giving effect to the polluter pays principle. Implementation of this approach ranges from voluntary commitments by industry to regulatory and co-regulatory mechanisms administered in conjunction with government.

16.2 Overview of Legal and Policy Instruments

16.2.1 International Instruments

There is no single binding agreement at the international level that governs marine litter or the full life cycle of plastics. Instead, there is a mix of binding and voluntary instruments at the international and regional level that have, to varying degrees, application to the issue of marine litter. This may be explicit or inferred through broader measures, such as those targeting solid waste management. A 2017 UNEP report grouped the existing international and regional instruments by their primary focus into those that are pollution oriented, chemicals and waste oriented, and biodiversity and species oriented (UNEP 2017).

16.2.1.1 Pollution Prevention

The *United Nations Law of the Sea Convention* (UNCLOS) is considered the framework agreement that sets the overarching obligation to protect and preserve the marine environment (Article 197), including from pollution and extractive activities. Prevention is promoted, together with reduction and control of marine pollution (UNCLOS 1982).

Although UNCLOS does not explicitly refer to plastic pollution, the definition of pollution provided would include plastics and microplastics, namely,

> the introduction by man, directly or indirectly, of substances or energy into the marine environment, including estuaries, which results or is likely to result in such deleterious effects as harm to living resources and marine life, hazards to human health, hindrance to marine activities, including fishing and other legitimate uses of the sea, impairment of quality for use of sea water and reduction of amenities. (Article 1)

UNCLOS sets the common themes of cooperation at the global and regional levels (Article 197), including for research (Article 200). In addition, rules, standards, and recommended practices and procedures for the prevention, reduction, and control of pollution of the marine environment should be based on appropriate scientific criteria (Article 201). Capacity building and assistance for developing states in scientific research is mandated (Article 202). States must also monitor the state of the marine environment, particularly for those activities they are responsible for (Articles 204 and 206) and share their findings in this regard (Article 205).

Many international and regional instruments include the precautionary principle, now regarded as customary law (Warner and Marsden 2012). Although the principle is not explicitly mentioned in UNCLOS, it can be argued that it is embodied in part XII, section 1 of UNCLOS on the general provisions for protection and preservation of the marine environment (Articles 192–196). More specifically applicable to the prevention of marine plastic litter, UNCLOS establishes a global duty to prevent marine pollution from land-based sources (Article 207), from vessels (Article 211), and by dumping (Article 210).

The definition of dumping provided by UNCLOS includes “any deliberate disposal of wastes or other matter from vessels, aircraft, platforms or other man-made structures at sea” and is further elaborated in the *Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter 1972* (London Convention 1972) and its 1996 Protocol (London Protocol 1996). Both the London Convention and London Protocol regulate the dumping of wastes at sea that were generated on land. Contracting parties must "take all practicable steps to prevent the pollution of the sea by the dumping of waste and other matter that is liable to create hazards to human health, to harm living resources and marine life, to damage amenities or to interfere with other legitimate uses of the sea." Annex I lists the wastes and matter that are banned from dumping (Article IV) and includes "persistent plastics and other persistent synthetic materials, for example, netting and ropes, which may float or may remain in suspension in the sea in such a manner as to interfere materially with fishing, navigation or other legitimate uses of the sea." Industrial wastes are also included in Annex I, but dredged material and sewage sludge are explicitly excluded from this category. In recognition of the potential presence of plastics in dredged material, the IMO is reviewing the process for approving permits for the dumping of such matter. In contrast to the London Convention, the London Protocol provides a blanket ban on the dumping of all material unless listed in Annex I of the protocol (Article 4). This ban includes the incineration at sea of wastes generated on land (Article 5). The duty to prevent, reduce, and, where practicable, eliminate such pollution is also extended into marine internal waters (Article 7). In addition, the export of wastes for the purpose of dumping or incineration at sea is prohibited (Article 6).

Article 211 of UNCLOS is given effect through Annex V of the *International Convention for the Prevention of Pollution from Ships* (MARPOL 1973). The discharge of garbage from vessels, as well as fixed or floating platforms, is prohibited in all maritime zones (Regulation 3.2), even if wastes are mixed or contaminated with a small amount of plastics (Regulation 6.4). Specific reference is made to fishing gear in the definition of garbage (Regulation 1.9). A definition of plastics is also provided, meaning "all garbage that consists of or includes plastic in any form, including synthetic ropes, synthetic fishing nets, plastic garbage bags and incinerator ashes from plastic products" (Regulation 1.13). Exceptions are allowed in specific emergency situations listed (Regulation 7). Any accidental loss or discharge of fishing gear specifically that may present a "significant risk" to the marine environment or a navigation hazard must be reported (Regulation 10.6). Fishing gear is further addressed in the *United Nations Agreement for the Implementation of the Provisions of the United Nations Convention on the Law of the Sea of 10 December 1982 relating to the Conservation and Management of Straddling Fish Stocks and Highly Migratory Fish Stocks* (Fish Stocks Agreement 1995) and the *FAO Code of Conduct for Responsible Fisheries* (Code of Conduct 1995, discussed below). Garbage management plans and garbage record books must be maintained for larger vessels only (Regulation 10), and adequate port reception facilities must be provided that are appropriate for the types of vessels frequenting the port (Regulation 8).

Microplastics are not directly addressed at the international level, except for the voluntary Honolulu Strategy (discussed below). Emerging science has shown the presence of microplastics in the air (Zhang et al. 2020), thus adding wind and rain as pathways for these pollutants to enter the marine environment. UNCLOS mandates that states adopt regulations to prevent, reduce, and control marine pollution from or through the atmosphere (Article 212). This applies to sovereign air space as well as vessels or aircraft of their registry.

Covering a smaller geographic scope, but an important pathway for wastes to enter the oceans, the *Convention on the Law of Non-Navigational Uses of International Watercourses* (UN Watercourses Convention, 1997) aims to protect and preserve the ecosystems of watercourses situated in more than one state (Article 20). This includes preventing pollution of the watercourse, defined as "any detrimental alteration in the composition or quality of the waters of an international watercourse which results directly or indirectly from human conduct" (Article 21). Harm to human health and safety are also to be prevented. Watercourse states must “take all appropriate measures to prevent the causing of significant harm to other watercourse States” (Article 7) and must cooperate and regularly exchange data and information in this regard (Articles 8 and 9). In addition, water quality objectives and criteria must be jointly set, practices to address pollution from point and non-point sources must be established, and lists established of substances that may pollute that should be prohibited, limited, investigated, or monitored (Article 21.3). The marine environment is explicitly mandated for protection and preservation, as well as estuaries (Article 23).

The *Global Programme of Action for the Protection of the Marine Environment from Land-based Activities* (GPA) is the primary non-binding instrument that aims to protect the marine environment from land-based pollution through a source-to-sea approach. With application to marine plastic litter, the GPA has listed marine litter and wastewater as priority source categories since 2012. This intergovernmental mechanism promotes technical and policy support, including demonstration sites, toward a strengthened global coordinated response to the issue of marine litter (UNEP 2020). The Global Partnership on Marine Litter (GPML) is the primary mechanism for driving this.

The *Honolulu Strategy: A Global Framework for Prevention and Management of Marine Debris* (Honolulu Strategy 2011) was developed by UNEP and the National Oceanic and Atmospheric Administration (NOAA) Marine Debris Program as a voluntary framework to guide national action. Three primary goals aim to reduce the amount and impact of (i) land-based sources of marine debris introduced into the sea; (ii) sea-based sources of marine debris, including solid waste, lost cargo, abandoned, lost, or otherwise discarded fishing gear (ALDFG) and abandoned vessels; and (iii) accumulated marine debris on shorelines, in benthic habitats, and in pelagic waters. Monitoring and evaluation are a strong focus of each goal, and a list of suggested actions is provided for each strategy listed under each goal. These actions include measures for pre-production pellets and other microplastics, as well as product design. Although the Honolulu Strategy does not set targets or timelines for achieving the goals and does not aim to replicate current efforts toward integrated solid waste management, it provides a solid foundation for preventive and restorative action at the national level. Extended producer responsibility is not addressed in the strategy. However, market-based instruments are promoted to support solid waste management, particularly waste minimization (Honolulu Strategy 2011).

The *IMO Action Plan to address marine plastic litter from ships* was adopted in 2018 by the IMO’s Marine Environment Protection Committee (MEPC). Importantly, this voluntary instrument relates to all ships, including fishing vessels that are mostly exempt from the MARPOL Annex V regulations for maintaining garbage management plans and garbage record books. Measures are to be completed by 2025 (paragraph 3.1) and implemented in cooperation with the Food and Agriculture Organization of the United Nations (FAO), UNEP, the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP), Regional Fisheries Management Organisations (RFMOs), and the Regional Seas Conventions and Action Plans, amongst others. Activities focus on assessing the contribution to marine plastic litter from ships, the availability and adequacy of port reception facilities, whether marking of fishing gear should be mandatory, promoting reporting the loss of fishing gear, and consideration of a mandatory reporting of container losses at sea to better understand the number of losses. These are to be supported by training of vessel personnel on the impacts of marine plastic litter and strengthened international cooperation (IMO 2018).

16.2.1.2 Chemicals and Waste

The *Stockholm Convention on Persistent Organic Pollutants* (Stockholm Convention 2001) has the objective of protecting human health and the environment from persistent organic pollutants (POPs). The POPs listed in the Convention must be prohibited from production and use, and the import and export of these are to be regulated in accordance with the convention (Article 3). Export is permitted for the purpose of environmentally sound disposal, as allowed for in the Convention. The inclusion of POPs in the production of plastics is therefore regulated by the Stockholm Convention. In addition, stockpiles of wastes that may contain chemicals regulated by the Convention may not be disposed of in such a way that leads to the recycling, recovery, reclamation, direct reuse, or alternative uses of the POPs they may contain, and such wastes may also not be exported unless this is done in accordance with agreed international procedures (Article 6). Parties to the Convention must develop national plans of implementation for the management of POPs and update these on a regular basis (Article 7).

Within the existing international legal framework, the *Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal* (Basel Convention 1989) may hold the greatest potential for preventing marine plastic litter. The Convention provides for waste minimization and environmentally sound management of wastes and promotes the principle of proximity, requiring wastes to be treated in the state they are generated where possible (Article 4). The Convention was amended in 2019 to strengthen the regulation of trade in plastic waste. Annex VIII to the Convention lists wastes requiring the exporting party to obtain prior informed consent from the importing country before the transaction can take place. This annex was amended to include a new entry (A3210) to clarify which plastic wastes would fall into this category and be considered hazardous wastes. Annex IX saw an entry removed (B3010) and replaced with a new entry (B3011) that describes plastic wastes that may be considered non-hazardous, and the trade thereof would not require procedures for prior informed consent to be initiated. Such wastes are described as being "almost free from contamination and other types of wastes," with some groupings of commonly recycled resins being provided, in order to facilitate recycling at the destination with minimal preparatory treatment processes. A third amendment was made to Annex II, inserting a new entry (Y48) that covers all other plastic wastes of a mixed nature that do not fall within the previous two categories of hazardous or non-hazardous. Such wastes are subject to prior informed consent procedures. Importantly, parties to the Basel Convention may not trade wastes covered by the Convention with non-parties, unless an agreement exists between the countries that meets the standards set by the Convention.

The *Strategic Approach to International Chemicals Management* (SAICM) is a voluntary framework that promotes the sound management of chemicals. This expands on the POPs regulated under the Stockholm Convention and would include all chemicals used in the manufacture of plastics and their final treatment at the end of life, although these do not expressly address the plastic life cycle. The aim of this multi-stakeholder platform was that by 2020, the production and use of chemicals would minimize significant adverse impacts on human health and the environment. Chemicals in products has been a key focal area of SAICM (2019), and attention has turned to plastic products in particular, including microplastics. The mandate of SAICM came to an end in 2020. The Beyond 2020 process was launched in 2017, and the role of SAICM was highlighted in "promoting safer chemicals policy through toxics reduction, elimination and substitution to avoid and ultimately eliminate the adverse toxic impacts," including suggestions of eliminating toxics in plastic production and prohibiting technologies for burning plastic waste (IPEN 2017). It is possible that the new framework will include goals specific to plastics and associated chemicals.

16.2.1.3 Biodiversity and Species Protection

The *Convention on Biological Diversity* (CBD 1992) addresses the conservation of biodiversity. In this context, the impact of marine litter broadly on marine species was recognized in a number of decisions adopted by the parties. These include voluntary guidance on preventing and mitigating the impacts of marine debris on marine and coastal biodiversity and habitats, suggesting economic incentives, market-based instruments, reducing the production and consumption of plastics, best practices in resource-efficient and closed product-to-waste cycles, and assessing legislation to prevent primary and secondary microplastics, as well as deposit schemes and extended producer responsibility within the fishing sector (CBD 2016). Such guidance is designed to assist contracting parties in developing national action plans for the conservation and sustainable use of biological diversity, as mandated by the Convention (Article 6).

The *Agreement for the Implementation of the Provisions of the United Nations Convention on the Law of the Sea of 10 December 1982 relating to the Conservation and Management of Straddling Fish Stocks and Highly Migratory Fish Stocks* (UN Fish Stocks Agreement) is an implementing agreement of UNCLOS, elaborating on Article 63 (paragraph 2) and Article 64 of the Convention. Its objective is restricted to the conservation and management of straddling fish stocks and highly migratory fish stocks in the high seas (beyond national jurisdiction) and areas under national jurisdiction where these stocks occur (Tsamenyi and Hanich 2012). The precautionary approach (Article 6) and ecosystem-based approach are promoted (Articles 5[d] and [e]). According to Article 5(f) of the UN Fish Stocks Agreement, states must minimize pollution, waste, discards, and catch by lost or abandoned gear, including through the development and use of selective, environmentally safe and cost-effective fishing gear and techniques. Vessels flying the flag of contracting parties should also be required to mark fishing gear to allow for identification as per international systems (Article 18.3). The agreement applies to other fishing entities whose vessels fish on the high seas for regulated stocks (Article 1.3). Regional fisheries bodies should promote compliance with the agreement.

The *Code of Conduct for Responsible Fisheries* is a voluntary instrument that is global in scope and provides principles and standards applicable to the conservation, management, and development of all fisheries (Article 1). It echoes the UN Fish Stocks Agreement by promoting the minimization of pollution, waste, discards, catch by lost or abandoned gear, catch of non- target species, both fish and non-fish species, and impacts on associated or dependent species, including through the development and use of selective, environmentally safe, and cost-effective fishing gear and techniques (Article 7.2.2).

Parties to the *Convention on the Conservation of Migratory Species of Wild Animals* (CMS 1979) adopted a resolution in 2017 on the management of marine debris (UNEP/CMS/Resolution 12.20). Measures promote addressing of knowledge gaps in the management of marine debris; commercial marine vessel best practice (including prevention of ALDFG and deliberate abandonment of fish aggregating devices); industry action, public awareness, and education campaigns; and collaboration and policy interventions (CMS 2017).

Table 16.1 provides a list of the existing international binding and voluntary instruments adapted from the 2017 UNEP report that could be applied to the prevention and management of marine plastic litter, including the geographic scope covered based on land, maritime areas within national jurisdiction and maritime areas beyond national jurisdiction. Orange indicates those instruments that explicitly mention marine debris, marine litter, or plastics.

16.2.2 Global Targets

The issue of marine litter is not new to the global arena. Resolutions adopted by the United Nations General Assembly (UNGA) and the newly formed United Nations Environment Assembly (UNEA) are voluntary but reflect international consensus on issues to be prioritized, often accompanied by actions that all countries agree are desired on a global level. Since 1989, UNGA resolutions have recognized issues directly or indirectly related to marine plastic pollution. The importance of

Table 16.1 International legal and policy framework applicable to marine plastic litter.

Primary focus	Agreement	Binding/ voluntary	Geographic scope
Pollution	United Nations Convention on the Law of the Sea (UNCLOS)	Binding	Land Sea – within national jurisdiction Sea – beyond national jurisdiction
	The Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter 1972 (London Convention) and its 1996 Protocol (London Protocol)	Binding	Sea – within national jurisdiction
	Annex V of the International Convention for the Prevention of Pollution from Ships (MARPOL)	Binding	Sea – within national jurisdiction Sea – beyond national jurisdiction
	The Convention on the Law of Non-Navigational Uses of International Watercourses (1997) (International Watercourses Convention)	Binding	Land (shared watercourses)
	Global Programme of Action for the Protection of the Marine Environment from Land-based Activities (GPA)	Voluntary	Land Sea – within national jurisdiction Sea – beyond national jurisdiction
	Honolulu Strategy	Voluntary	Land Sea – within national jurisdiction Sea – beyond national jurisdiction
	IMO Action Plan to address marine plastic litter from ships	Voluntary	Sea – within national jurisdiction Sea – beyond national jurisdiction
Chemicals and waste	The Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention)	Binding	Land Sea – within national jurisdiction Sea – beyond national jurisdiction
	The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal (Basel Convention)	Binding	Land Sea – within national jurisdiction
	Strategic Approach to International Chemicals Management (SAICM)	Voluntary	Land Sea – within national jurisdiction Sea – beyond national jurisdiction
Biodiversity and species	The Convention on Biological Diversity (CBD)	Binding	Land Sea – within national jurisdiction Sea – beyond national jurisdiction
	The Agreement for the Implementation of the Provisions of the United Nations Convention on the Law of the Sea of 10 December 1982 relating to the Conservation and Management of Straddling Fish Stocks and Highly Migratory Fish Stocks (United Nations Fish Stocks Agreement)	Binding	Sea – within national jurisdiction Sea – beyond national jurisdiction

Table 16.1 (Continued)

Primary focus	Agreement	Binding/ voluntary	Geographic scope
	FAO Code of Conduct for Responsible Fisheries (Code of Conduct)	Voluntary	Sea – within national jurisdiction Sea – beyond national jurisdiction
	The Convention on the Conservation of Migratory Species of Wild Animals (CMS)	Binding	Land Sea – within national jurisdiction Sea – beyond national jurisdiction

effective waste management in protecting the marine environment from pollution was highlighted in 1989 (UNGA 1989b), as well as the risks that lost or abandoned fishing nets pose to living marine resources and ecosystems (UNGA 1989a, 2002, 2005, 2008b). Waste management was highlighted as a way to prevent marine debris (UNGA 2005) and recycling, reuse, and reduction promoted, as well as the role of economic incentives (UNGA 2008a). Microplastics only featured in 2015 when the negative impacts of this pollutant on ocean health and marine biodiversity were emphasized (UNGA 2015).

Illustrating the importance of the issue at the global level, resolutions on marine litter and microplastics have been adopted at each of the four UNEA meetings, the first of which was held in 2014. The fourth meeting saw two resolutions adopted, one addressing marine litter and microplastics (UNEA 2019b) and the other on single-use plastics (UNEA 2019a). Consensus has been found in promotion of the precautionary approach (UNEA 2014), sustainable consumption and production, the polluter pays (UNEA 2016), resource efficiency (UNEA 2017), and the circular economy (UNEA 2019b). Design, production, and use that employ the resource-efficient approach have been suggested to address the growing issue of single-use plastics (UNEA 2019a).

In the absence of an international binding agreement to address marine litter, the only instruments at the global level that address marine plastic pollution explicitly are the Honolulu Strategy, adopted in 2011, and the IMO Action Plan to address marine plastic litter from ships, adopted in 2018. Both instruments are voluntary, do not address the full life cycle of plastics and neither set reduction targets. However, targets have been agreed at the global level under other fora. The outcome document of the United Nations Conference on Sustainable Development, titled “The Future We Want,” set the first real global target in 2012. A commitment was made to take action based on collected scientific data to achieve “significant reductions” in marine debris by 2025 in order to prevent harm to the coastal and marine environment (UNGA 2012). In 2017, the resolution on marine plastic litter and microplastics adopted at the third UNEA meeting set a target of “long-term elimination of discharge of litter and microplastics to the oceans” (UNEA 2017). The most meaningful target at the global level can be found within the 17 Sustainable Development Goals (SDGs) adopted by all UN member states in 2015 as part of the 2030 Agenda for Sustainable Development. SDG14 aims to conserve and sustainably use the oceans, seas, and marine resources, setting a global target to prevent and “significantly reduce” marine debris by 2025 (UN 2015). A number of indicators have been developed to enable the measurement of the reduction in plastic debris density as per target 14.1.1.b. Seventeen monitoring parameters are listed, such as litter found in different environmental compartments, biota ingestion rates and entanglement. Eleven of the 17 monitoring parameters are suggested for consideration by countries. These include “Plastic pollution potential (based on the use and landfilling of plastics)” and “Other parameters related to plastic consumption and recycling” (UN 2020).

16.3 Regional Instruments

UNCLOS requires states to cooperate in the adoption of laws and regulations to address land-based sources of marine pollution, including from rivers, estuaries, pipelines, and outfall structures (Article 207). States must also harmonize their policies at the regional level toward achieving this goal. A number of regional fora have adopted instruments applicable to the issue of marine plastic litter and also specific to the broader issue of marine litter. These include UNEP's Regional Seas Programme and various economic fora, such as the European Union (EU), the Group of Seven (G7), the Group of Twenty (G20), the Asia-Pacific Economic Cooperation (APEC), and the Association of Southeast Asian Nations (ASEAN). While the focus of the Regional Seas Programme tends toward research and monitoring of the issue within the coastal and marine environment, the opportunity exists within the economic fora to foster a value chain approach, promoting upstream and downstream activities, as well as policy interventions and market-based instruments to deliver on the global goals agreed upon.

16.3.1 The Regional Seas Programme

The Regional Seas Programme was launched in 1974 under the UNEP umbrella. In total, 146 coastal states are members of one or more of the 18 Regional Seas Conventions and Action Plans (RSCAPs). These operate under varying legal frameworks. Of the 18 RSCAPs, 14 have adopted legally binding overarching conventions. Four therefore operate within a voluntary framework. Of the 14 RSCAPs that have adopted conventions, nine have adopted protocols to the convention that addresses land-based sources of marine pollution. However, four of these protocols are not yet in force. The first marine litter action plans were adopted in 2007/2008, and since 2013, a number of action plans have been adopted or are under development/review, covering nearly all of the RSCAPs. The Regional Plan on Marine Litter Management in the Mediterranean was adopted in 2013 and is the only legally binding action plan within this framework. This is because Article 15 of the protocol on land-based sources for the region makes it mandatory for parties to adopt relevant action plans that outline measures and timetables for their implementation (paragraph 1). These measures and timetables will become binding after a specified time period for those parties that have not notified the secretariat of their objection (paragraph 3; LBS/A Protocol for the Mediterranean 1980).

The mandate set by the legal instruments of the RSCAPs is broadly similar within the context of marine plastic pollution. For example, the Convention on the Protection of the Marine Environment of the Baltic Sea Area (Helsinki Convention 1992) mandates the prevention of pollution by deliberate dumping (Article 11) and from ships (Article 8), giving effect to Articles 210 and 211 of UNCLOS, respectively. Incineration at sea is also prohibited (Article 10). The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention 1992) requires the prevention of pollution from land-based sources (Article 3), outlining mandatory measures in Annex I. Similarly, Annex II outlines measures to be implemented for the prevention of pollution by dumping and incineration as per Article 4 of the Convention. This region has, therefore, not adopted protocols specific to these two sources of pollution. Other regions have adopted protocols to specifically address dumping, such as the Black Sea, the Mediterranean, and the South Pacific regions.

In the Mediterranean region, Article 1 of the LBS/A Protocol for the Mediterranean establishes an obligation for contracting parties to the Protocol to:

> take all appropriate measures to prevent, abate, combat and eliminate to the fullest possible extent pollution of the Mediterranean Sea Area caused by discharges from rivers, coastal establishments or outfalls, or emanating from any other land-based sources and activities within their territories, giving priority to the phasing out of inputs of substances that are toxic, persistent and liable to bioaccumulate.

Point sources as well as diffuse sources are specified within the scope of the Protocol, including coastal disposals, rivers, outfalls, canals, or other watercourses, including ground water flow, or through run-off and disposal under the seabed with access from land. In addition, polluting substances that may be transported by the atmosphere (Article 4), which would include microplastics, are included. Where applicable, permit systems must be established to regulate discharges from point sources, and standards and criteria set for sea-water quality for the protection of human health, living resources, and ecosystems (Article 6). Monitoring, scientific cooperation, technical assistance (Articles 8–10), and reporting timeframes (Article 13) are also mandated. Although plastics are not specifically mentioned as a pollutant, Annex I lists sectors recognized as common sources of plastic pollution, including the textile industry, tourism, agriculture, aquaculture, municipal solid waste, sewage sludge disposal, and incineration of wastes.

The Regional Seas Programme provides the most comprehensive geographic coverage of instruments specific to the prevention and management of marine plastic litter. The adoption of regional marine litter action plans has increased in recent years, with some regions completing a review of their plans or in the process thereof. As mentioned, these are voluntary instruments with the exception of the Mediterranean region. The only region that has no instrument specific to marine litter, or is in the process of developing one, is the Antarctic.

Measures outlined in Regional Seas marine litter action plans are commonly grouped into actions that address land-based sources (e.g. solid waste management, wastewater treatment plants, dumping, and littering), sea-based sources (e.g. fisheries, aquaculture, and shipping), removal activities (e.g. beach cleans and fishing gear), monitoring and reporting, cooperation and education, and awareness. The emphasis varies, depending on the region, the maturity of solid waste management services and the level of engagement by the public. Actions listed are suggested for consideration in national programs of measures (OSPAR 2014). Increasingly, joint regional actions to be undertaken by the administering body are listed separately to national actions (UNEP-CAR/RCU 2014). Regional actions include the development of guidelines that further elaborate options to address specific measures, issues and sources in the region, as well as identify and contribute to research priorities. A common research topic is the sources of primary and secondary microplastics (HELCOM 2015). The development of regionally harmonized monitoring programs is another common regional goal, supported by training (COBSEA 2019).

National actions have progressed from a list of broader actions listed in earlier regional action plans, such as improving waste management services, to including regulatory and policy measures that go beyond enforcement of littering and dumping prohibitions. Increasingly, regional action plans are promoting bans on certain single-use plastic items, container deposit schemes, and extended producer responsibility schemes, amongst others. Key performance indicators have also been included for the number of participating countries that adopt such regulatory measures

(SPREP 2018). The principles of circular economy, sustainable consumption and production, and resource efficiency are also promoted. However, the development of indicators to measure a reduction in plastic litter in the marine environment has been limited to only a few regions, such as the Mediterranean, Baltic Sea, and North-East Atlantic where data are more robust.

16.3.2 The European Union and Other Regional Economic Fora

The European Union (EU) has established a comprehensive legal framework which includes instruments that explicitly address marine plastic litter, in particular the adoption of upstream preventive measures. The overarching Marine Strategy Framework Directive (MSFD) provides the foundation for protecting the marine environment from plastic pollution. Indicators have also been defined within this framework for the amount of litter washed ashore and/or deposited on coastlines; the amount of litter in the water column (including floating on the surface) and deposited on the seafloor; the amount, distribution and, where possible, composition of microparticles; the amount and composition of litter ingested by marine animals; and the number of individuals of each species which are adversely affected due to litter (e.g. by entanglement).

Since the adoption of the MSFD in 2008, a number of additional binding Directives and Strategies have placed greater emphasis on the issue of plastic pollution. In 2018, the European Strategy for Plastics in a Circular Economy (European Commission 2018) was adopted that lists recommended measures for national authorities and industry, including measures to specifically reduce pollution of the marine environment from plastics and microplastics. The subsequent Directive on single-use plastics and fishing gear (EU 2019b) bans a number of single-use plastics and promotes the adoption of national measures to reduce the consumption of plastic beverage and food containers. Where sustainable alternatives to single-use products are not available, extended producer responsibility schemes are promoted to cover the costs of waste management, cleanup, and awareness raising. Fishing gear is also targeted for extended producer responsibility schemes. The 2019 Directive on port reception facilities for the delivery of waste from ships (EU 2019a) importantly targets fishing and other maritime activities to deliver waste to ports through the use of economic incentives, supported by the provision of adequate port reception facilities, mandatory delivery of wastes, and improved monitoring procedures.

Other regional economic fora that have adopted voluntary instruments to address marine litter specifically are the G7, the G20, APEC, and ASEAN. The G7 marine litter action plan (G7 2015) recognizes the role of policy instruments, including economic incentives, market-based instruments, and public private partnerships in combating marine litter. Individual and corporate behavior change is promoted through public awareness and education. The G20 marine litter action plan emphasizes the polluter pays principle, extended producer responsibility, and the promotion of the socio-economic benefits to be gained from preventing marine litter (G20 2017). Subsequently, the G20 adopted an Implementation Framework for Actions on Marine Plastic Litter in 2019, promoting a life cycle approach to prevent and reduce discharge of plastic litter to the oceans (G20 2019a). In 2019, the APEC endorsed a roadmap on marine debris (APEC 2019a), followed by a Compendium of Policies and Preventive Measures to Reduce Land-based Marine Debris in APEC Economies (APEC 2019b). The roadmap promotes consideration of applying approaches for sustainable materials management as a method to strengthen end-markets for plastic wastes, thereby driving sustainable waste management. The ASEAN Framework of Action on Marine Debris (ASEAN 2019) encourages national authorities to strengthen markets for sustainable products and recyclable materials by working with industry to “develop and promote product sustainability and circularity criteria.” The use and disposal of single-use plastic products is recognized as unsustainable and should be addressed.

16.3.2.1 Regional Targets

The only binding target set at the regional level specific to marine litter is in the European Union (EU). The MSFD sets a binding target for EU Member States to achieve a status where "properties and quantities of marine litter do not cause harm to the coastal and marine environment" by 2020 (EU 2008). The Directive on single-use plastics and fishing gear sets a target of 77% separate collection of plastic bottles, increasing to 90% by 2029. For PET bottles, a 25% recycled content target has been set from 2025, with all plastic bottles requiring recycled content from 2030 (EU 2019b).

The regional marine litter action plan for the Baltic Sea promotes the development of regional and national actions that aim to achieve a significant quantitative reduction of marine litter by 2025 compared to 2015 (HELCOM 2015). In some regions, an expiry date is placed on the marine litter action plan, placing an implied target on implementation of the measures listed. For example, the Pacific action plan has a timeframe of 2018–2025 to coincide with the Cleaner Pacific 2025 – Pacific Regional Waste and Pollution Management Strategy 2016–2025 (SPREP 2016).

Under the presidency of Japan, the Osaka Blue Ocean Vision sets the target agreed by the G20 member states to "reduce additional pollution by marine plastic litter to zero by 2050" (G20 2019b). Similarly, under the presidency of Canada, the G7 Ocean Plastic Charter was endorsed in 2018 by five of the seven member countries and the European Union. Described as "a new partnership with businesses" to reduce plastic waste, the Charter includes commitments by leading industry actors toward measurable targets of 100% reusable, recyclable, or recoverable plastics by 2030; increasing recycled content by at least 50% in plastic products by 2030; and to recycle and reuse at least 55% of plastic packaging by 2030 and recover 100% of all plastics by 2040. Importantly, the establishment of secondary markets for plastics is included to support the targets for actual recycling, reuse, and recovery (G7 2018).

16.4 National Regulations and Policies

The international and regional legal and policy instruments form a framework of priority actions agreed by states. These, however, are given effect at the national level where implementation is key to the effectiveness of this framework. Implementation by government authorities, the private sector, and other actors can be promoted through national regulatory measures, voluntary measures, or a combination thereof in a co-regulatory manner.

Responses by national authorities to the issue of marine litter more generally initially tended toward the enforcement of littering and dumping fines, combined with public awareness campaigns. Recent research has indicated that bans, taxes, and levies to reduce consumption of plastic bags have been introduced in 43 countries, while single-use plastic products or packaging is banned in 25 or more countries. As of 2018, these initiatives covered an estimated two billion people (Pew Trusts 2020).

Focusing on effective solid waste management as a means to manage plastic waste, the Plastics Policy Playbook (Ocean Conservancy 2019) provides targeted measures across five guiding principles, particularly those aimed at improving the economic feasibility of waste management. These guiding principles are as follows: (i) combine measures across the value chain, (ii) engage and include the informal sector, (iii) drive consumer awareness and behavior change, (iv) inspire political will, and (v) improve enforcement at national and local levels.

The Organisation for Economic Co-operation and Development (OECD) hosted a workshop in 2020 to take stock of current policies to reduce marine plastic litter and discuss options toward longer-term goals. In addition to improved enforcement, bans on single-use plastics where appropriate alternatives exist, cleanups, and awareness raising, it was recognized that leakage of plastics into the environment takes place along the entire plastics value chain. Upstream measures were therefore important (improved design, reduced consumption of unnecessary plastics, and reuse models), as well as downstream measures (improved sorting and collection, recycling, and capture technologies) and specific policies to prevent leakage of microplastics (OECD 2020).

Waste management is a core component in preventing marine plastic pollution. The social aspects thereof are increasingly being recognized, particularly the role of women (GA Circular 2019) and waste pickers in developing countries. National authorities are strongly encouraged to protect the livelihoods of these sectors when designing policies, particularly extended producer responsibility schemes which may formalize their functions within the private sector.

A number of countries have developed national action plans, strategies, and roadmaps specific to marine litter. These include South Korea, Indonesia, and Vietnam. Canada has developed a zero plastic waste strategy, and Finland adopted a national plastics roadmap. Kenya has a plastic action plan, Thailand adopted a roadmap on plastic waste management, and Malaysia developed a roadmap toward zero single-use plastics. These all serve as examples of instruments that will directly or indirectly contribute to a reduction in marine plastic litter, designed to meet the needs and context of each country.

16.4.1 National Targets

There are few national targets specific to marine litter. The 3rd National Marine Litter Management Plan of Korea aims to reduce marine plastic litter by 50% by 2030. The Indonesian marine plastic debris action plan operates from 2017 to 2025 and aims to achieve a 70% reduction in marine litter by 2025. Vietnam's marine litter action plan is to be implemented by 2030 and aims to eliminate plastic litter from land-based and ocean-based sources. Targets have been set as follows:

By 2025	By 2030
Reduce marine plastic litter by 50%	Reduce marine plastic litter by 75%
Prevent the use of single-use plastics and non-biodegradable plastic bags in 80% of coastal tourism areas and activities	Prevent the use of single-use plastics and non-biodegradable plastic bags in 100% of coastal tourism areas and activities
80% of marine protected areas are free of plastic litter	100% of marine protected areas are free of plastic litter
Collect 50% of abandoned, lost, or discarded fishing gear	Collect 100% of abandoned, lost, or discarded fishing gear, and eliminate disposal of fishing gear into the sea
Conduct nationwide beach clean-up campaigns at least twice a year	

16.5 Conclusion

The risk that marine plastic pollution presents to the health of marine ecosystems has been recognized for nearly five decades, yet legal and policy frameworks have lagged behind the constantly evolving science. A number of instruments exist at the international and regional level to guide national implementation. However, no single instrument exists at the international level to manage the issue across the global plastics value chain. Monitoring progress specific to the reduction of marine plastic litter across multiple instruments with varying objectives will be challenging (UNEP 2017).

The existing framework has evolved over recent years to include principles and approaches that could address the issue upstream, moving beyond improvements to waste management and environmental monitoring of the presence of plastic pollution. A circular economy approach and ecodesign criteria could assist in improving rates of collection and sorting and enhancing the economic feasibility of sustainable end-of-life treatment of plastics. To progress discussions at the global level on the need for a binding global agreement to prevent plastic pollution, the Government of Norway has commissioned a report outlining possible elements of such an agreement, submitted to the ad hoc open-ended expert group on marine litter and microplastics (Raubenheimer and Urho 2020) established at the third session of UNEA.

While the global begin the potentially lengthy process of negotiating a new binding global agreement of a new binding global agreement, efforts continue within the existing framework. The Regional Seas Programme has continued to strengthen and expand the regional marine litter action plans. The Basel Convention plastic waste amendments came into force on 1 January 2021. The Plastic Waste Partnership recently established under the Basel Convention provides a platform to engage industry in seeking options within the mandate of the Convention. UNEP continues to strengthen the Global Partnership on Marine Litter, providing a multi-stakeholder platform and an international #Clean Seas campaign to raise awareness and encourage pledges.

In addition to the legal and policy framework outlined in this chapter, industry and non-government organizations are tackling the issue. Marine plastic litter and waste management have risen to greater prominence on government agendas. It remains to be seen whether the collective political will is sufficient to address the systemic integration of plastics into everyday life and the rapidly increasing production rates associated with the global reliance on the material.

References

APEC. 2019a. APEC roadmap on marine debris. https://www.apec.org/Meeting-Papers/Annual-Ministerial-Meetings/2019/2019_AMM/Annex-B (accessed August 19, 2021).

APEC. 2019b. Compendium of policies and preventive measures to reduce land-based marine debris in APEC economies https://www.apec.org/-/media/APEC/Publications/2019/12/Compendium-of-Policies-and-Preventive-Measures-to-Reduce-Land-based-Marine-Debris-in-APEC-Economies/219PSUCompendium-of-Policies-and-Preventive-Measures-to-Reduce-Landbased-Marine-Debris-in-APEC-Econo.pdf (accessed August 19, 2021).

ASEAN. 2019. ASEAN framework of action on marine debris. https://asean.org/storage/2019/06/3.-ASEAN-Framework-of-Action-on-Marine-Debris-FINAL.pdf (accessed August 19, 2021).

Basel Convention. 1989. Basel convention on the control of transboundary movements of hazardous wastes and their disposal. http://www.austlii.edu.au/au/other/dfat/treaties/1992/7.html (accessed August 19, 2021).

Beaumont, N.J., Asnesen, M., Austen, M.C., Börger, T., Clark, J.R., Cole, M., Hooper, T., Lindeque, P.K., Pascoe, C., Wyles, K.J. 2019. Global ecological, social and economic impacts of marine plastic. *Marine Pollution Bulletin.* 142, 189–195. doi:10.1016/j.marpolbul.2019.03.022

CBD. 1992. Convention on biological diversity. http://www.austlii.edu.au/au/other/dfat/treaties/1993/32.html (accessed August 19, 2021).

CBD. 2016. Addressing impacts of marine debris and anthropogenic underwater noise on marine and coastal biodiversity (CBD/COP/DEC/XIII/10). https://www.cbd.int/doc/decisions/cop-13/cop-13-dec-10-en.pdf (accessed August 19, 2021).

CIEL. 2019a. Plastic and climate: the hidden costs of a plastic planet. www.ciel.org/plasticandclimate (accessed August 19, 2021).

CIEL. 2019b. Plastic and health: the hidden costs of a plastic planet. https://www.ciel.org/wp-content/uploads/2019/02/Plastic-and-Health-The-Hidden-Costs-of-a-Plastic-Planet-February-2019.pdf (accessed August 19, 2021).

CMS. 1979. The convention on the conservation of migratory species of wild animals. http://www.austlii.edu.au/au/other/dfat/treaties/1991/32.html (accessed August 19, 2021).

CMS. 2017. Management of marine debris (UNEP/CMS/Resolution 12.20). https://www.cms.int/sites/default/files/document/cms:cop12_res.12.20_marine_debris_e.pdf (accessed August 19, 2021).

COBSEA. 2019. COBSEA regional action plan on marine litter 2019. http://wedocs.unep.org/handle/20.500.11822/30162 (accessed August 19, 2021).

Code of Conduct. 1995. FAO code of conduct for responsible fisheries. http://www.fao.org/docrep/005/v9878e/v9878e00.HTM (accessed August 19, 2021).

EU. 2008. Directive 2008/56/EC of the European Parliament and of the Council of 17 June 2008 establishing a framework for community action in the field of marine environmental policy (Marine Strategy Framework Directive). https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0056&from=EN (accessed August 19, 2021).

EU. 2019a. Directive (EU) 2019/883 of the European Parliament and of the Council of 17 April 2019 on port reception facilities for the delivery of waste from ships, amending Directive 2010/65/EU and repealing Directive 2000/59/EC. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32019L0883&from=IT (accessed August 19, 2021).

EU. 2019b. Directive (EU) 2019/904 of the European Parliament and of the Council of 5 June 2019 on the reduction of the impact of certain plastic products on the environment. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32019L0904&from=EN (accessed August 19, 2021).

Eunomia. 2018. Investigating options for reducing releases in the aquatic environment of microplastics emitted by (but not intentionally added in) products. https://www.eunomia.co.uk/reports-tools/investigating-options-for-reducing-releases-in-the-aquatic-environment-of-microplastics-emitted-by-products/

European Commission. 2018. A European strategy for plastics in a circular economy. https://ec.europa.eu/environment/circular-economy/pdf/plastics-strategy.pdf (accessed August 19, 2021).

Fish Stocks Agreement. 1995. The United Nations Agreement for the implementation of the provisions of the United Nations Convention on the Law of the Sea of 10 December 1982 relating to the Conservation and Management of Straddling Fish Stocks and Highly Migratory Fish Stocks. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A21998A0703%2801%29&qid=1645446070127 (accessed February 21, 2022)

G7. 2015. G7 action plan to combat marine litter (Annex to the Leaders' Declaration G7 Summit). https://www.env.go.jp/water/marine_litter/07_mat13_2_%EF%BC%93-2ALD.pdf (accessed August 19, 2021).

G7. 2018. Ocean plastics charter. https://www.canada.ca/en/environment-climate-change/services/managing-reducing-waste/international-commitments/ocean-plastics-charter.html (accessed August 19, 2021).

G20. 2017. G20 action plan on marine litter (Annex to G20 Leaders Declaration). https://www.g20.org/Content/DE/_Anlagen/G7_G20/2017-g20-marine-litter-en.pdf?__blob=publicationFile&v=3 (accessed August 19, 2021).

G20. 2019a. Implementation framework for actions on marine plastic litter. https://www.mofa.go.jp/policy/economy/g20_summit/osaka19/pdf/documents/en/annex_14.pdf (accessed August 19, 2021).

G20. 2019b. Osaka blue ocean vision. https://g20mpl.org (accessed August 19, 2021).

GA Circular. 2019. The role of gender in waste management. Gender perspectives on waste in India, Indonesia, the Philippines and Vietnam. Commissioned by Ocean Conservancy. https://oceanconservancy.org/wp-content/uploads/2019/06/The-Role-of-Gender-in-Waste-Management.pdf ().

HELCOM. 2015. Regional action plan for marine litter in the Baltic Sea. http://helcom.fi/Lists/Publications/Regional%20Action%20Plan%20for%20Marine%20Litter.pdf (accessed August 19, 2021).

Helsinki Convention. 1992. Convention on the protection of the marine environment of the Baltic Sea area. https://helcom.fi/about-us/convention/ (accessed February 21, 2022)

Honolulu Strategy. 2011. The Honolulu strategy: a global framework for prevention and management of marine debris. https://marinedebris.noaa.gov/sites/default/files/publications-files/Honolulu_Strategy.pdf (accessed February 21, 2022)

IMO. 2018. Action plan to address marine plastic litter from ships (MEPC 73/19/Add.1). https://wwwcdn.imo.org/localresources/en/MediaCentre/HotTopics/Documents/IMO%20marine%20litter%20action%20plan%20MEPC%2073-19-Add-1.pdf (accessed August 19, 2021).

IPEN. 2017. Beyond 2020: chemical safety and agenda 2030. https://www.saicm.org/Portals/12/documents/meetings/IP1/Beyond-2020-Chemical-safety-and-Agenda-2030-24-Jan-2017.pdf (accessed August 19, 2021).

LBS/A Protocol for the Mediterranean. 1980. Protocol for the protection of the Mediterranean Sea against pollution from land-based sources and activities, as amended 7 March 1996. https://www.unep.org/unepmap/who-we-are/barcelona-convention-and-protocols (accessed February 21, 2022)

Lebreton, L., & Andrady, A. 2019. Future scenarios of global plastic waste generation and disposal. *Palgrave Communications*, 5: 6. doi:10.1057/s41599-018-0212-7.

London Convention. 1972. International convention on the prevention of marine pollution by dumping of wastes and other matter. http://www.austlii.edu.au/au/other/dfat/treaties/1985/16.html (accessed August 19, 2021).

London Protocol. 1996. *Protocol to the convention on the prevention of marine pollution by dumping of wastes and other matter*, 1972. http://www.austlii.edu.au/au/other/dfat/treaties/2006/11.html ().

MARPOL. 1973. International convention for the prevention of pollution from ships. https://www.ecolex.org/details/treaty/international-convention-for-the-prevention-of-pollution-from-ships-marpol-as-modified-by-the-protocol-of-1978-marpol-7378-tre-000112 (accessed August 19, 2021).

Ocean Conservancy. 2019. Plastics policy playbook. Strategies for a plastic-free ocean. https://act.oceanconservancy.org/wp-content/uploads/2019/10/Plastics-Policy-Playbook-10.17.19.pdf ().

OECD. 2020. OECD workshop on reducing marine plastic litter: taking stock of current policies and paving the way towards longer term goals. Summary record. https://www.oecd.org/environment/waste/agenda-workshop-on-reducing-plastic-litter-2020.pdf ().

OSPAR. 2014. Regional action plan for prevention and management of marine litter in the North-East Atlantic (2014–2021). https://www.ospar.org/documents?v=34422 (accessed August 19, 2021).

OSPAR Convention. 1992. Convention for the protection of the marine environment of the North-East Atlantic. http://www.ospar.org/convention/text (accessed August 19, 2021).

Pew Trusts. 2020. Breaking the plastic wave. A comprehensive assessment of pathways towards stopping ocean plastic pollution. https://www.pewtrusts.org/-/media/assets/2020/07/breakingtheplasticwave_report.pdf ().

Raubenheimer, K., & Urho, N. 2020. Possible elements of a new global agreement to prevent plastic pollution. https://www.nordicreport2020.com ().

SAICM. 2019. Understanding chemicals in products. Policy brief. http://www.saicm.org/Portals/12/Documents/EPI/CiP_policy_brief_Nov2019.pdf ().

SPREP. 2016. *Cleaner Pacific 2025: Pacific Regional Waste and Pollution Management Strategy 2016–2025: Implementation Plan*. SPREP, Apia, Samoa. http://www.sprep.org/attachments/Publications/WMPC/cleaner-pacific-strategy-imp-plan-2025.pdf (accessed August 19, 2021).

SPREP. 2018. Pacific regional action plan. Marine litter 2018–2025. https://www.sprep.org/publications/pacific-regional-action-plan-marine-litter#:~:text=This%20Action%20Plan%20sets%20out,Pacific%20island%20Countries%20and%20Territories ().

Stockholm Convention. 2001. Stockholm convention on persistent organic pollutants. http://www.austlii.edu.au/au/other/dfat/treaties/2004/23.html (accessed August 19, 2021).

Tsamenyi, M., & Hanich, Q. 2012. Fisheries jurisdiction under the Law of the Sea Convention: rights and obligations in maritime zones under the sovereignty of Coastal States. http://ro.uow.edu.au/lawpapers/625 ().

UN (2015). Sustainable Development Goal 14: Conserve and sustainably use the oceans, seas and marine resources. https://www.un.org/sustainabledevelopment/oceans (accessed December 2020)

UN. 2020. Indicator 14.1.1: (a) Index of coastal eutrophication; and (b) plastic debris density. Metadata. https://unstats.un.org/sdgs/metadata/files/Metadata-14-01-01.pdf (accessed August 19, 2021).

UN Watercourses Convention. 1997. Convention on the law of the non-navigational uses of international watercourses. http://legal.un.org/ilc/texts/instruments/english/conventions/8_3_1997.pdf (accessed August 19, 2021).

UNCLOS. 1982. United Nations convention on the Law of the Sea. http://www.un.org/depts/los/convention_agreements/texts/unclos/unclos_e.pdf (accessed August 19, 2021).

UNEA. 2014. Marine plastic debris and microplastics. Resolution 1/6 (UNEP/EA.1/10, Annex I). https://environmentassembly.unenvironment.org/proceedings-and-report-resolutions-and-decisions-unea-1 ().

UNEA. 2016. Marine plastic litter and microplastics. Resolution 2/11 (UNEP/EA.2/Res.11). https://environmentassembly.unenvironment.org/proceedings-report-resolutions-and-decisions-unea-2 ().

UNEA. 2017. Marine litter and microplastics. Resolution 3/7 (UNEP/EA.3/Res.7). https://environmentassembly.unenvironment.org/proceedings-report-ministerial-declaration-resolutions-and-decisions-unea-3 ().

UNEA. 2019a. Addressing single-use plastic products pollution. Resolution 4/9 (UNEP/EA.4/Res.9). https://environmentassembly.unenvironment.org/proceedings-report-ministerial-declaration-resolutions-and-decisions-unea-4 ().

UNEA. 2019b. Marine plastic litter and microplastics. Resolution 4/6 (UNEP/EA.4/Res.6). https://environmentassembly.unenvironment.org/proceedings-report-ministerial-declaration-resolutions-and-decisions-unea-4 ().

UNEP. 2017. Combating marine plastic litter and microplastics: an assessment of the effectiveness of relevant international, regional and subregional governance strategies and approaches. https://papersmart.unon.org/resolution/uploads/unep_aheg_2018_inf3_full_assessment_en (accessed August 19, 2021).

UNEP (2020). Global action to protect the marine environment from land-based pollution. https://www.unenvironment.org/explore-topics/oceans-seas/what-we-do/addressing-land-based-pollution/global-action-protect-marine (accessed December 2020)

UNEP-CAR/RCU. 2014. *Regional Action Plan on Marine Litter Management (RAPMaLI) for the Wider Caribbean Region 2014 (CEP Technical Report: 72)*. United Nations Environment Programme

Caribbean/Regional Coordinating Unit (UNEP-CAR/RCU). http://www.cep.unep.org/cep-documents/rapmali_web.pdf (accessed August 19, 2021).

UNGA. 1989a. Large-scale pelagic driftnet fishing and its impact on the living marine resources of the world's oceans and seas. Resolution A/RES/44/225, 85. http://www.un.org/documents/ga/res/44/a44r225.htm

UNGA. 1989b. United Nations Conference on Environment and Development, Resolution A/RES/44/228. https://undocs.org/en/A/RES/44/228 (accessed August 19, 2021).

UNGA. 2002. Large-scale pelagic drift-net fishing, unauthorized fishing in zones of national jurisdiction and on the high seas/illegal, unreported and unregulated fishing, fisheries by-catch and discards, and other developments (A/RES/57/142). http://www.un.org/depts/los/general_assembly/general_assembly_resolutions.htm (accessed August 19, 2021).

UNGA. 2005. Oceans and the Law of the Sea (A/RES/60/30). http://www.un.org/depts/los/general_assembly/general_assembly_resolutions.htm (accessed August 19, 2021).

UNGA. 2008a. Oceans and the law of the sea (A/RES/63/111). http://www.un.org/depts/los/general_assembly/general_assembly_resolutions.htm (accessed August 19, 2021).

UNGA. 2008b. Sustainable fisheries, including through the 1995 Agreement for the Implementation of the Provisions of the United Nations Convention on the Law of the Sea of 10 December 1982 relating to the Conservation and Management of Straddling Fish Stocks and Highly Migratory Fish Stocks, and related instruments (A/RES/63/112). http://www.un.org/depts/los/general_assembly/general_assembly_resolutions.htm (accessed August 19, 2021).

UNGA. 2012. The future we want (A/RES/66/288). https://www.un.org/en/development/desa/population/migration/generalassembly/docs/globalcompact/A_RES_66_288.pdf (accessed August 19, 2021).

UNGA. 2015. *Oceans and the law of the sea. Resolution* 70/235. https://www.un.org/en/development/desa/population/migration/generalassembly/docs/globalcompact/A_RES_70_235.pdf ().

Warner, R., & Marsden, S. 2012. *Transboundary Environmental Governance*. Farnham, Surrey, UK: Ashgate. https://www.123library.org/ebook/isbn/9781409444947/

Zhang, Y., Kang, S, Allen, S. et al. 2020. Atmospheric microplastics: a review on current status and perspectives. *Earth-Science Reviews*, 203, 103118. https://doi.org/10.1016/j.earscirev.2020.103118

Index

Plastics and the Ocean: Origin, Characterization, Fate, and Impacts, First Edition. Edited by Anthony L. Andrady.

WILEY END USER LICENSE AGREEMENT