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Hazardous Chemicals Associated with Plastics in the Marine Environment

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Hazardous Chemicals Associated with Plastics in the Marine Environment

Volume Editors: Hideshige Takada ·
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Aims and Scope

Since 1980, *The Handbook of Environmental Chemistry* has provided sound and solid knowledge about environmental topics from a chemical perspective. Presenting a wide spectrum of viewpoints and approaches, the series now covers topics such as local and global changes of natural environment and climate; anthropogenic impact on the environment; water, air and soil pollution; remediation and waste characterization; environmental contaminants; biogeochemistry; geoecology; chemical reactions and processes; chemical and biological transformations as well as physical transport of chemicals in the environment; or environmental modeling. A particular focus of the series lies on methodological advances in environmental analytical chemistry.

Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last three decades, as reflected in the more than 70 volumes of *The Handbook of Environmental Chemistry*, there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry*, the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of "pure" chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of Environmental Chemistry* provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via www.springerlink.com/content/110354/. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Editors-in-Chief

Preface

For more than 15 years now, we, both editors, started working on the topic of using microplastics and more specifically plastic pellets as passive samplers of persistent organic pollutants in the marine environment [1–6]. While working on this topic that is both interesting and challenging, we realized that the topic of plastic pollution in the environment is very serious and urgent [7]. Thus, although we both prefer to conduct field or laboratory work with our research groups, we got involved with this topic through several different ways such as scientific conferences, invited talks, policy formulation forums, consulting, educational activities, and public awareness activities.

Nevertheless, the topic of hazardous chemicals found in plastics in the environment remains one of the biggest concerns related to plastic pollution. Considering that lower-trophic-level organisms interact with plastics containing chemicals and that chemicals sorption and desorption from plastics is assisted by body fluids [8], a potential pathway to the human body and potential risk to human health can be identified. Luckily, so far, direct risk due to actual exposure of humans to microplastics has not been observed.

Since we have both worked on this topic for many years, we found that our greatest impact on this topic is to share our knowledge and our viewpoints with other scientists. We decided to publish this book in order to concentrate the fundamentals of "hazardous chemicals associated with plastics in the environment" in one volume and provide solid research tools to new scientists willing to work on this topic. We have invited experts working on different aspects of this topic to provide their insights.

There are four main sections that can be identified in this book. The first section is related to the polymer chemistry, the additives found in the plastic, the degradation that plastic can undergo resulting in the production of microplastics, oligomers, and additive release into the environment. The second section is related to the distribution of marine debris and microplastics and their accumulation into different areas of the earth. The third section is related to the interaction of hazardous chemicals with plastic, which chemicals and at what concentrations they are found in plastics in the marine environment, as well as fundamental information on chemical sorption/desorption, equilibrium, mechanisms, and kinetics. The fourth section is related to the interaction of plastics and associated chemicals with organisms of all levels. At the end of the book, there is a concluding chapter identifying the advancements of science presented in the book by the different authors and the research points that need to be addressed in the future.

We sincerely hope that this book will assist new scientists both in terms of scientific knowledge and in terms of philosophy related to the topic of plastic pollution and its importance and urgency. New scientists entering the field being eager to publish data or identifying new sources or severe effects tend to publish studies that lack clear and accurate objectives. Caution is needed when describing such new phenomena so as not to lose credibility with the general public and government regulators.

Finally, we would like to thank all the authors who contributed their work to this book and Springer editors and staff for their patience and help during all the years that were required for this book to be published.

Tokyo, Japan Hideshige Takada
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Contents

Additives and Chemicals in Plastics

Anthony L. Andrady and Nepali Rajapakse

Abstract Global production of plastics is clearly on the increase and plastic products have become an inextricable part of our everyday life. Over a short span of about 75 years plastics have penetrated diverse application areas replacing conventional materials quite successfully. Continued growth in production is expected in the medium term but questions on the sustainability of plastics are being raised. A key aspect of sustainability of plastics and rubber materials is their potential environmental toxicity and in particular human toxicity. Plastic resins, however, are nontoxic materials, composed of macromolecules that are neither digestible nor absorbable in the gut. Toxicity of plastics often observed is attributed to the numerous additives mixed in with the resin during processing and fabrication of products, the residual monomers, or catalysts trapped in the resin and the chemicals picked up by the plastics from the environment. Of these, the additives are present at the highest concentrations in plastic products. Knowing and evaluating the additives commonly used, their potential toxicity, and their intake routes to human users are essential for the sustainability of plastics.

Keywords Colorants, Fillers, Flame retardants, Lubricants, Plasticizers, Stabilizers

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Contents

1 Introduction

In 2015, the global plastics resin production touched 322 million metric tons (MMT) continuing a general consistent trend of growth in production worldwide since the first introduction of the material into the marketplace in 1950s. Relative to competing materials used in key sectors such as construction and packaging, the success of plastics has been particularly impressive. The strong growth in demand for plastics has been higher than can be attributed to population growth assuming current per capita use rates. This suggests a trend in increasing per capita consumption of resins worldwide, especially in the more affluent regions. It is the Asia/Pacific countries that account for half the resin production dominating the global resin supply. The USA and Western Europe each account for only 15–17 % of the global resin production. This success of plastics is not difficult to understand: plastics provide a low-cost, lightweight (low density) material that is biologically inert, outstandingly durable, and machinable or thermally formed into complex shapes [1]. The feedstock for plastics are derived from only about 4 % of the fossil fuel extracted for use. Compared to metal or glass, plastics require significantly less energy to fabricate as well as recycle (and result in lower carbon emissions). Over the decades, the manufacturing technology for plastic resins has advanced into efficient, low-waste, low-emission processes. Given the global industrial network that underpins this growth, there is little doubt that the demand for plastics will continue to increase into the foreseeable future.

Despite this remarkable success and the present robust state of the industry its environmental sustainability, even in the medium term, has been questioned [2]. Sustainable growth of any industry requires that resources are used responsibly without waste and the natural capital critical to life on earth is not compromised, to ensure the well-being and survival of the present as well as future generations. To ascertain environmental sustainability, the societal cost of a technology in terms of energy expenditure, material demand, and its environmental footprint has to be compared to the societal benefits derived from it [2]. The marked growth in plastics consumption underlines the many societal benefits of the material. Daily, one comes into contact with a bewildering variety of plastics in fabrics, coatings, furniture, transportation, buildings, and packaging [1]. Their widespread use in transportation or building insulation applications conserves very significant amounts of energy and in packaging reduces food waste while preserving food and medicine from spoilage. In uses such as in wind energy installations or in solar panels, plastics directly contribute to cost-effective energy generation. But, how about the societal cost of using plastics? A strong case can be made to justify the use of a mere 4 % of petrochemical feedstock to deliver services and conveniences across many application sectors. Fossil fuel feedstocks are a rapidly depleting limited resource. Increasing levels of materials or chemical recycling of plastics can help ease this demand on feedstock to some extent. In any event, the growing interest in alternative plant-based feedstock for manufacturing plastic resins will reduce reliance of the industry on non-renewable feedstock. However, it is more difficult to justify the cost of externalities, especially those with potential ecological or health impacts, associated with plastics. Sustainable growth of plastics at the very least requires that these externalities, especially those chemicals in plastic resins and products that pose a potential toxic threat, to be phased out.

2 Commodity Thermoplastics

Of the about 50 or so chemically distinct classes of plastics, only a handful (as shown in Table 1) are used in high-volume applications. These are the polyethylenes [PE], polypropylene [PP], polystyrene [PS], poly (ethylene terephthalate) [PET], and poly (vinyl chloride) [PVC]. Polyethylenes, the plastic used in highest volume globally, are available in several grades of slightly different bulk density ranges as high-density resin [HDPE], low-density resin [LDPE], and a linear low-density resin [LLDPE]. Commodity resins are popularly used in plastic packaging; for instance PET is widely used in soda bottle applications. A majority of thermoplastic production (~40 % in the USA) is in fact used in packaging with only about 20 % used in building construction and another 25 % in fabrication of consumer and institutional goods. The most commonly used plastics in building construction are PVC and PE while those in packaging are the polyolefins (PE and PP).

Table 1 Characteristics and global production of commodity thermoplastics

	LDPE	HDPE	LLDPE	PP	PS	PVC	PET
Density (g/cc)	0.92–0.94	0.94–0.97	0.90–0.94	0.90	1.04	1.4	1.34–1.37
Crystallinity (%)	30–54	55–77	22–55	30–50	–	10–30	–
Global production (2008) (%)		29.1		18	7.8	15.3	20

Plastic resins used in fabrication of products are typically mixed with chemicals intentionally added to the plastics either to modify its properties or to control degradation during thermal processing. These chemicals or additives are intimately mixed in with the resin prior to thermally forming the melted plastic into fabricated products. Worldwide, additive production is at 12.6 MMT (in 2013) and grew at the rate of ~4.8 % annually over the last 5 years [3]. Specific additives such as the flame retardants are expected to show a much higher growth rate in the medium term. Plasticized compounds of PVC are by far the plastics that require the highest volume of additives.

While pure plastic resins are nontoxic (and cannot be digested or absorbed by humans) the additives that leach out from the plastic products can present a toxicity concern. With PS, PET, and polycarbonate, some of the residual monomers as well as dimers, trimers, or oligomers trapped within the solid resin and can leach out as well. The presence of these additives (and residual chemicals or catalysts) in plastic products is responsible for their potential environmental and/or human health hazards. Three areas of such concern have been identified.

2.1 Migration of Additives from Packaging or from Food Service Items into Food and Beverage

Hydrophobic additives incorporated into packaging plastics that come into contact with food can migrate into the food, especially into those with a high lipid content [6, 7]. This affords a credible route for human intake of these additives. Where the additive chemicals can bio-accumulate in the individual this is even a more serious concern. Relevant products include plastic films coating the interior of paperboard packages, epoxy lining inside tin cans, some varieties of plastic bottles, and other plastic food packages. With most packaged food the duration of contact is long and significant migration can occur even when kinetics of leaching is slow. In general, the temperature, pH, and hydrophobicity of the food invariably determine the extent of migration and therefore the toxicity posed by additives [8, 9]. Plastic toys that are mouthed by infants also present a similar pathway for ingestion of leached additives. Recent regulatory controls on the use of some phthalate plasticizers in toys have partially addressed this issue. Ingestion is the principal, but certainly not the only, route of exposure. Medical plastics that come into contact with body fluids and inhalation of volatile additives from interior of automobiles are also significant routes of exposure [2].

2.2 Additives Leaching from Waste Plastics During Disposal

The largest fraction of plastics produced is used in packaging or in food service applications and these products typically have a short service life. Most of the plastics in the municipal solid waste [MSW] stream are in fact derived from packaging. In countries such as the USA where landfilling is the main disposal strategy for MSW this can be a serious concern. Similarly, in locations where waste is uncollected or unmanaged, packaging plastics are likely to end up as litter where additives are released into the open environment [58]. For instance, BPA as well as PBDEs have been reported in landfill leachate. Furthermore, plastic litter which is a major aesthetic problem in urban areas, presents an even more serious concern in the marine environment.

2.3 Additives Leaching from Ingested Plastic Debris

An emerging problem in the marine environment is the potential of microplastic litter to concentrates persistent chemicals in seawater. These plastics can be ingested by marine organisms and thereby enter the marine food web [4, 5]. A wide range of marine animals including invertebrate species, fish, birds, turtles, and marine mammals are known to ingest plastics [10]. Plastic debris at sea is known to affect at least 600 species, and a great majority of these via ingestion [11, 12]. If the additives in them are bioavailable to the organism, resulting toxicity may potentially be significant [10, 11]. Additives that are bioavailable [13] can be biomagnified when they are transferred across trophic levels in the marine food chain. The net influx of additives via this mechanism depends on the pH, surfactants, and hydrophobicity in the gut environment and the residence time of the plastic in the organism [14, 15]. Gut contents that include a high fraction of lipids naturally enhance the bioavailability of hydrophobic additives such as the phthalates in PVC.

The threat to the ingesting organism is even more pronounced if the additives are endocrine disruptor chemicals [EDCs]; very low dosages of these chemicals, well below their accepted conventional toxicity levels, can markedly interfere with their physiology resulting in long-term or even intergenerational adverse effects.

The endocrine system plays a key role in the development of the fetus, in reproduction, behavior, and metabolism. It is a complex system that requires coordinated hormonal cues acting in concert to manage physiology. EDC compounds [47] either mimic or interfere with hormones in the body resulting in abnormal outcomes or disease. Hormones secreted by the endocrine system generally act at very low concentrations; therefore, EDCs also work at very low concentrations. Therein lies the main problem in assessing the toxicity of this class of additives. Their dose-response curves in modifying human physiology are nonlinear, often U-shaped or inverted U-shaped [48]. Therefore, EDCs can elicit physiological responses well below the reference or “safe” dosages established by conventional toxicological studies but may show little or no effect at higher concentrations [49]. Thus, EDCs when evaluated for toxicity with conventional screening tests generally carried out at higher concentrations may not show a negative effect. A second complication is that the effects are often long-term; in animal models, exposure of one generation to EDCs may result in adverse impacts in animals in the following generations.

3 Types of Additives Used in Common Plastics

Additives used in commodity thermoplastics might be classified according to the function they perform in the formulation or in the fabricated product (see Table 2). In some formulations, additives such as chalk {$Ca(CO_3)$} or extending oil compounds may be used merely as an inert component to lower the cost of the mix. Typically, the resin is higher in cost compared to chalk, some clays, or organic fillers. Using a small volume fraction of an inert non-reinforcing filler often does not compromise the functional properties of the mix but can significantly lower the cost of the material. However, most additives serve a functional purpose such as improving outdoor durability of the product or making the plastic antistatic. Reinforcing fillers improve

Table 2 Common classes of additives used in plastics compounding with their typical loading levels (%)

Class of additive	Typical loading	Example	Function
Fillers (as powders, fibers, or nanotubes)	Up to about ~50 %	Clays, silica, glass, chalk, talc, asbestos, alumina, rutile, carbon black, carbon nanotubes	Reinforcement or reduction of cost
Plasticizers	10–70 %	Di-n-octyl phthalate Other phthalates[a] Tris(2-chloroethyl) phosphate	Soften the polymer making it more flexible and extensible
Flame retardants	10–20 %	Poly(bromo diphenyl ethers). For example Poly(deca-bromo dibenzyl ether). Inorganic agents such as alumina and phosphites are also used[b]	Prevent ignition and/or flame propagation
Colorants	1–4 %	Cadmium, chromium, lead, and cobalt compounds. Organic dyes may also be used	To impart the desired color to the product
UV stabilizers	0.1–2 %	Hindered amine light stabilizers, benzo-phenone light-absorbing compounds	To control degradation of plastic on routine exposure to solar radiation
Thermal stabilizers	0.1–8 %	Dialkyl maleates or laureates and dialkyl mercaptides of tin in PVC formulations to retard HCl evolution during processing	To control degradation during processing
Processing aids	0.5–2 %	Waxes, oils, long-chain esters of polymeric alcohols	Lubricants used to make processing of polymer easier
Others {antistatics, biocides, antiozonants, odorants}	Variable but usually less than 1–2 % by weight of polymer		To obtain the desired property in the product

[a] Other commonly used phthalates are given in table 3.

[b] Where phosphites are used, the level can be higher than the range indicated

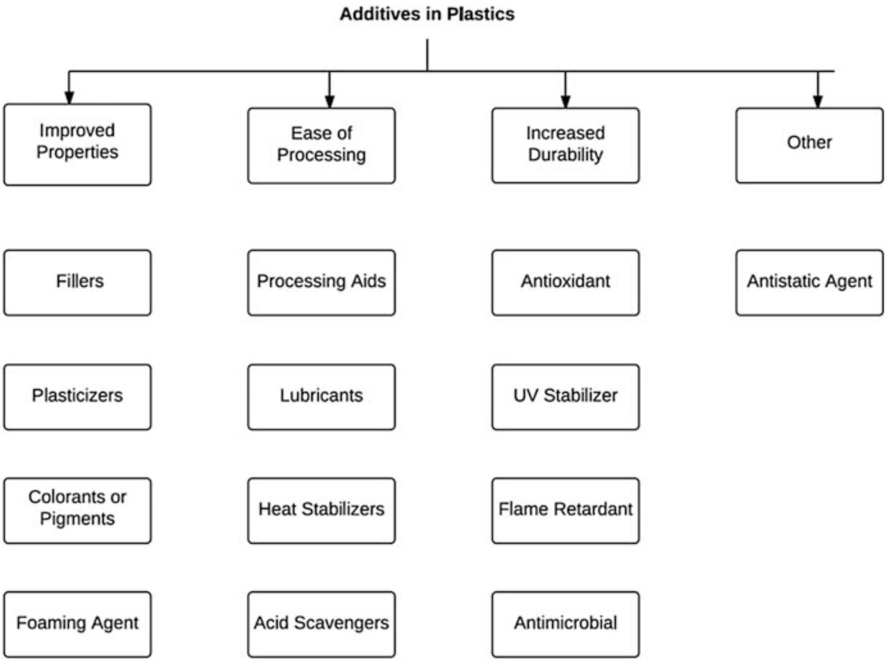


Fig. 1 A simple classification of plastic additives

the mechanical integrity of the plastic. A classification of commonly used additives based on their functional contribution to the product is given in Fig. 1.

Most of the additives are used at very low levels of a few percentages by weight of the polymer. Three classes of additives, however, are typically used at much higher volume fractions in the plastic "compound" or formulation. These are the plasticizers, fillers, and flame retardants. Given their relatively higher concentration in plastic products these pose more of an environmental as well as human health concern.

4 Additives Used at a High Weight Fraction

4.1 Fillers

Reinforcing fillers are primarily used in plastics to improve their mechanical properties. These fillers (such as carbon black in rubber) mixed in with the polymer result in an interface volume generated at the filler-resin contact surface. It is the superior properties of this interface layer that obtain increased modulus and mechanical properties such as impact strength or tensile strength in the composite polymer. As the effect is surface related, the smaller particle sizes of fillers generally yield a better reinforcing effect. The degree of reinforcement attained with spherical filler particles is estimated by various equations, where the Young's modulus of the composite E_c is expressed as a function of the volume fraction of the filler V_f and the ratio ($E_\mathrm{f}/E_\mathrm{m}$) of the modules of the filler E_m and that of the polymer E_f. One of the most used is the Tsai–Halpin equation [16] given below:

$$E_\mathrm{C} = E_\mathrm{m}\left\{\frac{1+2CV_\mathrm{f}}{1-CV_\mathrm{f}}\right\}$$

where $C = \{E_\mathrm{f}/E_\mathrm{m} - 1\}/\{E_\mathrm{f}/E_\mathrm{m}+2\}$

The reinforcing effect of the filler is reflected in improved thermal properties (as reflected in the DSC data in Fig. 2 (right) for PP reinforced with functionalized graphene oxide) [17]. It is also seen as improved mechanical properties in PP reinforced with functionalized carbon nanotubes [18]. Other mechanical properties of the composite such as creep [19], acoustic properties [20], electrical properties [21], and gas-barrier properties often change as well due to the presence of a filler.

The efficiency of reinforcing fillers in imparting improved properties in the composite depends on a very good dispersion of the fillers in the polymer matrix. Factors in processing that control dispersion of the filler have been discussed [22, 23]. Twin-screw extruders and internal mixers are typically used to achieve high levels of dispersion. Additives such as low-molecular-weight polymers or waxes might also be used to encourage good dispersion. Improved dispersion can be achieved by surface treatment of the filler particles to improve their compatibility with the polymer matrix [24]. Covering the surface of filler particles with covalently linked functional groups that are compatible with and interact well with functionalities of the polymer results in particularly good dispersions. Successful use of inorganic-organic hybrids or organically modified inorganic oxides for this purpose has been reported [25]. Organosilanes such as vinyl or amino-alkyl

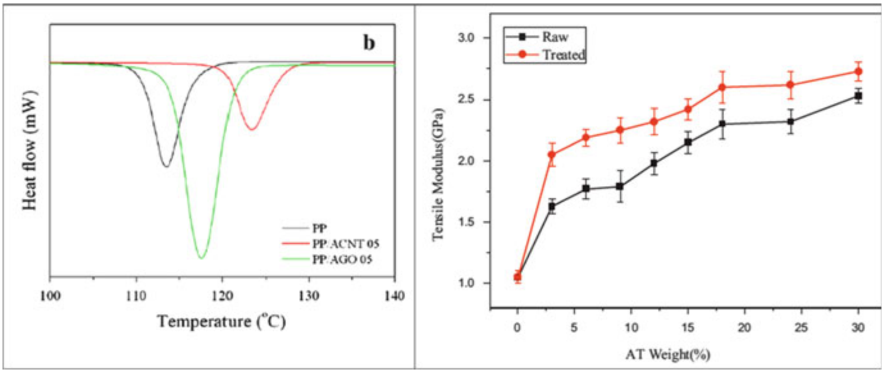


Fig. 2 (*Left*) Differential scanning calorimetry (DSC) tracings of polypropylene (PP), PP with 5 % of alkylated carbon nanotube (ACNT) filler, and 5 % alkylated graphene oxide (AGO) filler (reproduced with permission from Yun et al. [16]). (*Right*) Increase in tensile modulus with the weight fraction of asbestos tailing (AT) filler in PP (reproduced with permission from Zhai et al. [17])

silanes are used widely as a coupling agent to enhance the compatibility of the inorganic fillers with the polymer matrix.

From an environmental standpoint, however, fillers are unlikely to leach out of the plastic matrix and in any event are insoluble in water. Degradation of the surface layers of a composite during use or in litter can release the fillers into the environment [59]. For instance with rigid PVC siding or pipes with titanium dioxide filler, extensive weathering releases the filler leading to "chalking."

4.2 Plasticizers

Plasticizers are usually low-molecular-weight liquids that are mixed with the plastic to reduce their modulus (or to soften the material and increase flexibility). Plasticized PVC, for instance, is a soft, flexible plastic used in medical tubing, blood bags, automotive seat covers, shower curtains, membrane roofing, and other domestic products. Once plasticized, PVC has very different mechanical properties and feel, compared to the un-plasticized or *rigid* PVC. The latter is typically used in PVC pipes, residential siding, or window frames. Phthalates are typically used at very high weight fractions in plasticized PVC; levels as high as 60–70 % plasticizer are not unusual in soft PVC compositions.

The plasticizer molecules are dissolved in the polymer matrix and not being covalently linked to the macromolecular chains [26], can migrate freely within the resin. The exact mechanism of the action of plasticizers is not fully understood but compatible plasticizer molecules are believed to closely associate themselves with the polymer chains, creating additional free volume in the bulk plastic matrix, making it softer. This explanation is supported by the decrease in glass transition temperature Tg (°C) of plasticized polymers that (°C) is inversely related to the fractional free volume in polymer. However, this mechanism alone is often inadequate in fully explaining the plasticization in all polymer systems. Figure 3 shows the effect of plasticizer content on the glass transition temperature of PVC [27].

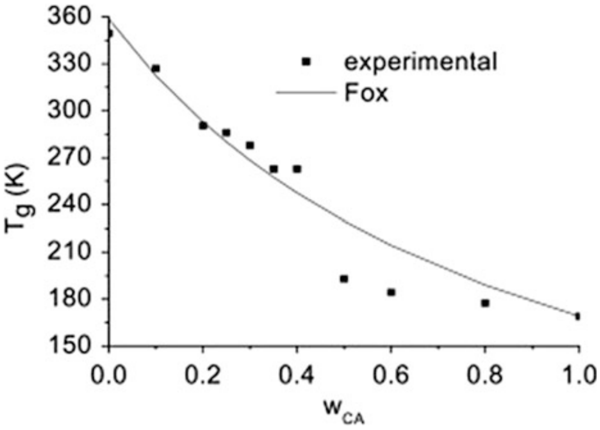
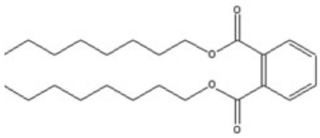
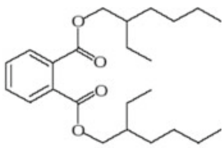


Fig. 3 The glass transition temperature of Tg (K) as a function of the weight fraction of natural plasticizer cardanol acetate (derived from cashew nut shell) in PVC. The theoretical line is from Fox equation. Reproduced with permission from (Greco et al. [26])

The best studied system is the plasticization of PVC by phthalates.

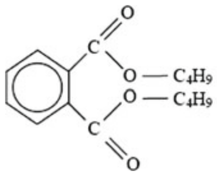


Di-n-octyl phthalate

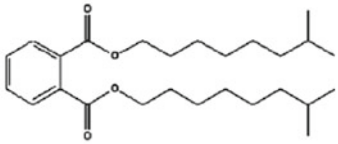


Bis(2-ethylhexyl) phthalate

Plasticizers presently account for the largest segment of the global additives market mainly because of the popularity of phthalate plasticizers. Presently, they account for nearly half the additive sales globally. Most (~94 %) of the about 6 million tons of phthalate plasticizer is used by the PVC industry [28]. Di(2-ethyl hexyl) phthalate is the most used plasticizer in PVC formulations [33]. The common phthalates used in PVC and their characteristics are summarized in Table 3.



Butyl benzyl phthalate



Diisononyl phthalate

High concentration of plasticizers in plastic products and therefore in plastic waste and litter is an environmental concern as it increases the availability of the chemical species to organisms ingesting plastics, especially in the marine environment. The phthalates with higher octanol-water partition coefficient (K_{ow}) values in Table 3 have the tendency to bio-accumulate in ingesting organisms with potential bio-magnification at higher trophic levels of the food pyramid. However, bioaccumulation may not always lead to bio-magnification. DEHP for instance does bio-accumulate but is not significantly biomagnified because organisms higher up in the food chain metabolize it efficiently. In small animals such as copepods the body concentrations reached via ingestion can be quite significant. But the potential for

Table 3 Common plasticizers used in PVC (based on [28])

Phthalate		Log $K_{(OW)}$	Water solubility (mg/L) at 25 (°C)	Boiling point (°C)
Di(2-ethyl hexyl) phthalate	DEHP	4.2–9.6	$3 \times 10^{-3} - 0.27$	384–387
Diisononyl phthalate	DINP	8.6–9.4	$10^{-4} - 0.2$	370>400
Di *n*-butyl phthalate	DBP	4.5–4.7	11.2	340
Diisodecyl phthalate	DIDP	8.8–10	$10^{-5} - 0.28$	370>400
Di-*n*-octyl phthalate	DNOP	5.2–8.5	0.22–2.9	390
Butyl benzyl phthalate	BBP	4.6–4.8	2.7–2.9	370–377

bioaccumulation in most species remains unknown. While phthalates are predominantly used, the PVC industry also uses other classes of plasticizers such as epoxidized vegetable oils. Alkyl esters of dicarboxylic acids (sebacic, azelaic, and adipic acids) and low-molecular-weight liquid polyesters are used as plasticizers as well.

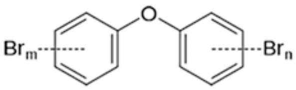
Human exposure to phthalates occurs primarily via food [29, 30] and water [31] with the plasticizer being picked up from packaging or from the environment. Concentrations in food items vary widely with lipid-rich food having relatively higher levels of phthalates. For instance, in butter (48 mg/kg of BBP) [32], peanut butter (99 mg/kg of DINP), and milk (80 mg/L DEHP) [33, 34] high levels of specific phthalates have been reported. Food packaging can of course contain much higher amounts (~10^3 mg/kg) [30], some of which leaches out, depending on the nature of contents in package. Based on data on urinary metabolite concentrations, the daily estimated intake of phthalates [35] is in the range of 0.3–4.1 (μg (kg body weight)$^{-1}$ d^{-1}).

Exposure to phthalates can result in a range of adverse health outcomes. These are primarily associated with male reproductive development and function (reduced sperm quality, increased sperm DNA damage, and altered male genital organs) [36, 37] though other effects [38] have also been reported. These concerns has led to restrictions on the use of some phthalates [29, 39], especially in toys, in the USA, European Union, and Japan in recent years. Alternatives to conventional phthalates that are less toxic, such as bis(2-propylheptyl) phthalate (DPHP) or bis (2-ethylhexyl) adipate (DEHA), are emerging, potentially "green", plasticizers. It is important, however, to ensure their relative merits in terms of toxicity of their breakdown products as well as their leachability from plastic matrices.

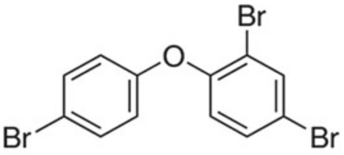
4.3 Flame Retardants

These are organo-bromine additives that are mixed into polymer formulations to control ignitability and flame propagation in the final product. They are of particular environmental interest because of their relatively high concentrations (10–20 %) in the products designed to be flame retardant and also because some of them are endocrine disruptor chemicals (EDCs). Like plasticizers, they are also dissolved or suspended in the plastic and can leach out into the environment [12, 57, 58]. Flame retardants (FR), including the polybrominated diphenyl ethers (PBDEs), are the fastest growing class of plastic additives thanks to their high-volume application in construction, transportation, and textile industries. Resins PE, high-impact polystyrene (HIPS), ethylene-vinyl acetate copolymer (EVA), and acrylonitrile-butadiene-styrene copolymer (ABS) use PBDEs as fire retardants. The additive is used in common plastic household items such as TV/computer housing, polyurethane foam, and fabric [40] as well. The global market for FR chemicals was over $7 billion in 2014 (with 2.1 MMT of the additives produced) and is expected to grow to $9.8 billion by 2020 [41].

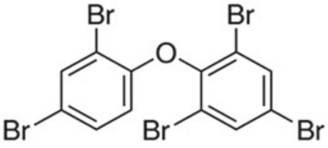
The generic formula for PBDEs below shows the available substitution sites for bromine atoms on the molecule yielding 209 theoretically possible congeners for PBDEs. As the fire-retardant mechanism relies on the availability of bromine, the deca-bromo congener is particularly effective. In case of a fire, the PBDE dissociates thermally into Br. radicals that via hydrogen abstraction from polymer forms HBr. This HBr reacts with the gaseous by-products of polymer pyrolysis and oxidation formed in the burning plastic, yielding less reactive products. This discourages the propagation of the fire.



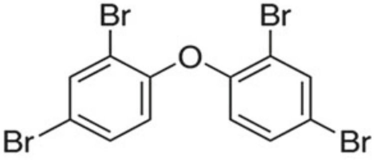
Commercial PBDE additives are mixtures of congeners (i.e., technical mixtures); the popular commercially available penta-BDE used in polyurethane foam (manufactured in the USA), for instance, is a mixture of tetra-, penta-, and hexa-congeners. PBDEs have been banned in European Union since 2003 and the penta- and octa-PBDEs are no longer produced in the USA. The deca-bromo congener is also being voluntarily phased out by the industry. The revised Stockholm Convention of 2009 restricted the production of BDE congeners with 4-7 bromines. However, some of the PBDEs manufactured in Asia can still find their way into the USA and Europe. Table 4 summarizes the characteristics of the key PBDEs used as FR additives. Some commonly used congeners of PBDEs are shown below.



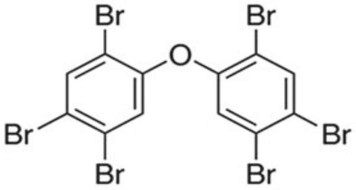
2,4,4 tri-bromo congener



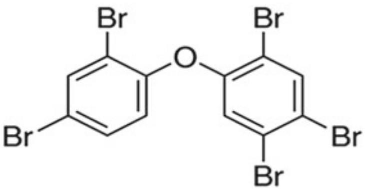
2,2,4,4,6 penta-bromo congener



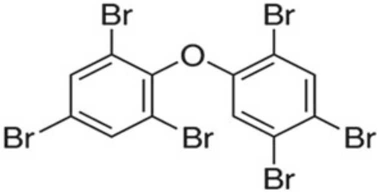
2,2,4,4 tetrabromo congener



2,2,4,4,5,5 hexa-bromo congener



2,2,4,4,5 penta-bromo congener



2,2,4,4,5,6 hexa-bromo congener

Table 4 Characteristics of the common polybrominated diphenyl ethers (PBDEs) used in plastic compositions

Congener Mix	Technical mixture	Molecular weight (g/mol)	Log K_{OW}	Water solubility (μg/L)	Boiling point (°C)
4–6	Penta-BDE	564.7	6.64–6.97	13.3	>300
6–10	Octa-BDE	801.5	6.29[a]	<1	> 330 (decomp.)
9, 10	Deca-BDE	959.2	6.27[a]	<1	>320 (decomp.)

Based on USEPA (Technical Fact Sheet January 2014). These values are for commercially available PBDEs, each of which are mixtures of several congeners

[a] Higher values of ~8 for octa-BDE and ~9.5 for deca-BDE have been reported [42]

Though no longer manufactured in most parts of the world, there is a residual environmental pool of PBDEs historically used by the industry [43]. PBDEs are classified as persistent organic chemicals (POPs) but are easily photolyzed in the outdoor environment [41, 42]. Studies carried out over a period of time show widespread environmental occurrence of the additives including presence in human plasma [43, 44, 45] and milk. For instance human milk was reported to contain ~20 μg/kg of PBDE for residents of the USA and Canada [46].

Unlike most other additives, the PBDEs are believed to be endocrine disruptor chemicals (EDCs) [44]. Furthermore, the effect of EDCs, including PBDEs, is markedly modified by the presence of other active chemicals in the system. This is sometimes referred to as the “cocktail effect.” It is a combination of these concerns as well as body of exposure data that resulted in the use of PBDEs in plastics being severely restricted. Alternative flame retardants such as alkali metal oxides are already in use; presently, aluminum hydroxide- and phosphorus-based flame-retardant alternatives dominate the market.

5 Additives Used at Low Weight Fractions

5.1 Colorants

Plastic products are colored using either dyes or inorganic pigments. Inorganic pigments popularly used include oxides, sulfides (yellow), chromates (red hues), and complexes based on metals such as cadmium, zinc, nickel, antimony, manganese, cobalt, aluminum, iron, copper, and molybdenum. Titanium dioxide (rutile) is the most widely used white pigment, especially in rigid PVC products. Black color is usually obtained with carbon black pigment. Uniformity of the color in the product is critical to consumer acceptability and depends primarily on dispersion of the pigment as fine particles (0.01–0.1 μm) in plastic. Scattering and absorption of light by the pigment particles make the colored plastic part opaque. Organic dyes dissolve in the polymer and do not scatter but only absorb light. Therefore, even at high concentrations of the dye the plastic tends to be transparent or translucent.

Unlike with textile dyes, there are limited data on potential toxicity of colorants in plastics [50]. After the phase-out of lead- and cadmium-based pigments some time back, the colorants have been used without any major query. Yet, there are isolated instances of potential toxicity as with white pigment titania [51]. With inorganic pigments the particles are generally too large to migrate to the surface of the plastic product and be released to the environment. However this can still occur with weathering degradation or ablation of the surface layer that releases the pigment over a long period of time.

5.2 Stabilizers

Thermal and thermo-oxidation stabilizers are critical to plastics industry, as all common thermoplastics would seriously degrade during processing without the protection afforded by them. They are typically used at very low levels in plastics, often ~1 wt.%, to protect the polymer from premature degradation during processing and use. Therefore, their toxicity has received little attention. Potential toxicity of stabilizers, however, is a function of both their leachability and their inherent toxicity at the relevant concentrations. If the additive is an EDC, the chemical can have serious toxicity even at very low concentrations in the plastic. As opposed to thermal stabilizers, solar UV stabilizers are used only with plastics meant for outdoor applications. These, such as the popular HALS additives, are used at very low levels (i.e., 0.1–0.5 wt.%) and some of these are macromolecular and do not leach out easily.

Some stabilizers in plastics at a high enough concentration can be hazardous to the environment and potentially toxic to humans. For instance, some benzophenones are known to be carcinogenic on the basis of rat/mice exposure studies [52]. Benzophenones are commonly used as a UV stabilizer or light absorber in transparent plastic products. Some photostabilizers in this class such as 2,2′, 4,4′-tetrahydroxybenzophenone (2-benzophenone) or 2,4-dihydroxybenzophenone (Benzophenon-1) are reported to be endocrine disruptors (EDCs) [53, 54]. Other types of stabilizers such as the benzotriazoles or hindered amines are used with thermoplastics and are found in the environment but have not been reported to be EDCs. Most of the dibutyltin-based stabilizers used in PVC and polyurethane compositions are also reported to be EDCs [55].

5.3 Lubricants

Not much is available on the potential toxicity of lubricants. But nonylphenol-based lubricants (also used as an antioxidant used in some thermoset plastics) as well as tetramethylbutyl phenol lubricants are known to be EDCs [55, 56] or may generate EDCs.

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Food Containers and Packaging Materials as Possible Source of Hazardous Chemicals to Food

Evangelia Manoli and Dimitra Voutsa

Abstract Plastics are widely used around the world as packaging material covering a wide range of applications. Plastics could be a source of chemicals into food through migration of various compounds (polymers, monomers, and processing aids) from packaging to foodstuffs. The intentionally added substances (IAS) are listed and controlled by laws and regulations from various organisations. For these authorised substances, specific migration limits (SML) have been established on the basis of migration tests performed on the plastic material using different food simulants according to the food type. These tests are based on the risk assessment of the single substance able to migrate, simulating the worst case of the foreseeable conditions, in order to ensure the safety of the final material. However, over 50 % of compounds migrating from food contact materials are non-intentionally added substances (NIAS). The European Regulation No. 10/2011 concerning plastics and multilayers recently became more strict, stating that 'the risk assessment of a substance should cover the substance itself, relevant impurities and foreseeable reaction and degradation products in the intended use'. This chapter presents the materials used in food containers and food packaging, the additives employed in different types of plastics in order to improve their properties, current legislation with emphasis on European Regulation No. 10/2011, and the migration tests and specific migration limits. In addition, there is discussion on the compounds usually found in various food categories and bottled water due to the presence of IAS or NIAS in packaging materials.

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Keywords Bottled water, Food containers, Food packaging materials, Migration, Plastics

Contents

1 Introduction

The packaging market is a highly important industrial sector with food and beverage packaging constituting more than half of all packing uses (food 41 %, beverages 14 %; [1]). Packaging plays an important role in food manufacturing process as it increases shelf life of food products by protecting them from air, loss of gas, moisture loss/incorporation, light radiation, foreign aroma compounds, microbial contamination, temperature instability, and mechanical influences. Moreover, it facilitates transport, storage, and even cooking for some foods [1]. Different materials are used to package foodstuffs: plastics, paper, cardboard, metals (aluminium foils, laminates and metalised films, tinplate, and tin-free steel), glass, regenerated cellulose, ceramics, rubbers, etc. However, the most important consumer packaging is made of plastic (38 %, both rigid and flexible plastics) [1–3]. Food packaging can interact with the packaged foodstuff by diffusion-controlled processes and various compounds may migrate into food. These compounds are starting substances used in the initial polymerisation step, like monomers or catalysts, and additives that are compounded during the manufacturing process to achieve special material properties (e.g. plasticisers). Starting substances can leach either because of incomplete polymerisation during the formation of the material or because of material degradation over time. Furthermore starting substances or additives can contain impurities, including degradation products, (non-intentionally added substances (NIAS)) which again might have leached from plastics.

Table 1 Types of plastic used

Abbreviation	Type of resin content	SPI resin identification code
PET	Polyethylene terephthalate	1
HDPE	High-density polyethylene	2
Vinyl-PVC	Vinyl-polyvinyl chloride	3
LDPE	Low-density polyethylene	4
PP	Polypropylene	5
PS	Polystyrene	6
OTHER	Mixed plastics	7

2 Types of Plastics

Various types of plastics are used for packaging purposes. The resin identification coding (RIC) system for plastic (Table 1), that has been developed by the Society of Plastic Industry (SPI) in 1988, offered a way to identify the resin content of bottles and containers commonly found in the residential waste stream [4]. There are more than 30 different types of plastics used for food packaging [5]. This chapter provides information about the main uses of the most popular of them.

Polyethylene (PE) and polypropylene (PP) are the most commonly used polyolefins. Both are flexible, durable, stable, and lightweight; have a good chemical and moisture resistance; and can be easily processed, recycled, and reused [2]. There are two types of PE products: low-density PE (LDPE) and high-density (HDPE) [6]. HDPE is used to make bottles for milk, juice, and water; cereal box liners; margarine tubs; and grocery, trash, and retail bags. LDPE is predominately used in film applications and in applications where heat sealing is necessary, e.g. for bread and frozen food bags, flexible lids, and squeezable food bottles. PP is suitable for use in hot-filled and microwavable packaging products. It is also used in yogurt containers and margarine tubs. In combination with an oxygen barrier such as ethylene vinyl alcohol or polyvinylidene chloride, PP provides the strength and moisture barrier for ketchup and salad dressing bottles [2].

Polyethylene terephthalate (PET or PETE), polycarbonate (PC), and polyethylene naphthalate (PEN) are polyesters. PET is one of the most commonly used plastics in Europe's packaging industry. Typical applications of PET include [7] (a) bottles for beverages such as soft drinks, fruit juices, and mineral waters; it is especially suitable for carbonated drinks, cooking and salad oils, sauces and dressings, and detergents; (b) wide-mouth jars and tubs for jams, preserves, fruits, and dried foods; (c) trays for pre-cooked meals that can be reheated in either microwave or conventional ovens, pasta dishes, meats, and vegetables; (d) foils for 'boil-in-the-bag' pre-cooked meals, snack foods, nuts, sweets, and long-life confectionery; and (e) other PET products with an extra oxygen barrier which are ideal for containing beer, and vacuum-packed dairy products, e.g. cheese, processed meats, 'bag-in-box' wines, condiments, coffee, cakes, and syrups. PET is widely recycled as a material, making a large contribution to the recycling targets required for plastics by the EU Directive [2, 7].

PC is used in a wide variety of common products including reusable food and drink containers [8]. Polycarbonate is mainly used as a replacement for glass in items such as large returnable/refillable water bottles and sterilisable baby bottles. PEN provides protection against transfer of flavours and odours; it is well suited for manufacturing bottles for beverages such as beer [2, 9]. PVC is the most used plastic after PE and PP. It is used as package film for food and confectionery, and also in bottles and labels [2, 10]. Polyvinylidene chloride (PVDC) is used as a monolayer film and as a thin barrier layer in multilayer film. It finds use for packaging products such as poultry, cured meats, cheese, snack foods, tea, coffee, and confectionary [2]. PS is used in protective packaging such as egg cartons, containers, disposable plastic silverware, lids, cups, plates, bottles, and food trays [2]. Polyamides are a group of plastics known also with the brand name ‘nylon’. Nylon films are used for food packaging, offering toughness and low gas permeability, and coupled with their temperature resistance for boil-in-the-bag food packaging [2].

Ethylene vinyl alcohol (EVOH) which is used in food packaging is invariably in the form of multilayer structures where an EVOH film is protected by water-resistant polymers (commonly PP) [11].

3 Additives in Plastics

Different types of additives, such as plasticisers, stabilisers, antioxidants, and anti-static and anti-blocking agents, have been developed to improve the performance either during processing and fabrication or in use of the above polymeric packaging materials. Nevertheless, there is an increased concern about the safety of foods, focused on additives that end up in the food from the packaging material, as it has been reported that some of them may cause adverse effects on human health. Additives are basically categorised by the functions that they perform rather than their chemistry [5, 12].

Plasticisers are synthetic organic molecules with low molecular weight which are added to the plastic polymers to improve properties such as flexibility, extensibility, and processability. However, they had raised the higher concern because they have high mobility and, thus, can migrate to food. Storage time and temperature may affect their migration. Diesters of phthalic acid have been the focus of several surveys and restrictions had been brought on their use, due to their potential carcinogenic and oestrogenic effect [5, 13–15]. Adipates [di(2-ethylhexyl)adipate, DEHA) and acetyltributyl citrate (ATBC), which have lower toxicity, are also commonly used as plasticisers. However, indications on the toxicity of DEHA led European Union to propose a Specific Migration Limit. Large amounts of DEHA have been observed in various types of foods wrapped with plasticised PVC films. ATBC also used as a plasticiser in flexible PVC films is not a potent multisite carcinogen, but the induction of a low incidence of a site-specific effect cannot be excluded [13, 14, 16].

Stabilisers are the second most used additives in plastics. Representative examples of stabilisers used in food packaging are organotins and epoxidised seed and vegetable oils such as soybean oil (ESBO). ESBO is a vegetable oil widely used as plasticiser and/or scavenger for hydrogen chloride liberated from PVC during heat treatment for manufacturing. PVC containing ESBO is used mainly in domestic food films (PVC cling films), as plastisols for the gaskets in lids for glass jars, and organosol can coatings [5, 16–18]. Organotins have been used for many years as heat- and light-stabilising additives or as starting substances in polymerisation. Organotins are suspected endocrine-disrupting chemicals. In the EU Regulation No. 10/2011[19], 27 different organotin compounds or mixtures are authorised for use in plastic-only food contact materials. Specific migration limits vary strongly because they are based on tin content [1, 15]. Ultraviolet (UV) stabilisers are lastly widely used (polyvinyl chloride, e.g., is usually stabilised with UV absorbers); however, technically the most important light stabiliser classes are 2-hydroxybenzophenones, 2-hydroxyphenyl benzotriazoles, hindered amines, and organic nickel compounds (used almost extensively in polyolefins) along with salicylates, cinnamate derivatives, resorcinol monobenzoates, oxanilides, and p-hydroxybenzoates. The sterically hindered amines (HALS) represent the latest development in this field and are commonly used in polyolefins [5, 12].

Antioxidants are additives commonly used in the polymer industry to prevent degradation of polymers during processing. Compounds commonly used for that purpose are polyphenols, organophosphates, and thioesters but due to their toxicity and possible migration into food their application is questionable. The presence of synthetic antioxidants in food is questioned, owing to the potential risks, and strict statutory controls are required. Alternatively, the use of natural antioxidants, particularly tocopherol, plant extracts, and essential oils from herbs and spices, is proposed [5, 13, 20].

Slip and antistat additives are compounded to reduce the surface coefficient of friction of polymers. They are key components especially of flexible packaging. Commonly used slip additives are fatty acid amides. Although amides are entrenched in most applications because of their high efficiency and good cost structure, non-migratory, high-molecular weight organic materials like siloxanes are also being used in special applications [5, 12, 21, 22].

4 Regulation

In order to protect consumers from the migration of harmful substances from packaging into food, the Commission of the European Communities (CEC) has adopted the Regulation No. 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. This is not the first regulation adopted by CEC. The first relevant CEC Directive was issued in 1976 on the approximation of the laws of the member states related to the subject. Apart from harmonized legislation, the directives proposed analytical test methods, and introduced limits upon the overall migration from plastics into food as well as food simulants and specific migration limits or composition limits for free monomers in the final article [5, 19].

It is important to note that contrary to the EU, where risk assessment and risk management are clearly separated between European Commission and European Food and Safety Authority (EFSA), the US Food and Drug Administration (FDA) carries out both risk assessment and risk management. Further the regulation of food contact materials is based on the exposure rather than on migration. The FDA enforces the Food, Drug and Cosmetic Act from 1958 which is the basic regulation on food contact materials, as well as other relevant acts. Mostly, food contact materials (FCM) are regulated in the Code of Federal Regulations (C.F.R.) under Title 21 on food and drugs, Part 176–186, and further fall under specific regulations depending on their use. Clearance is required for additives, also referred to as indirect additives, which are substances that can reasonably be expected to migrate into foodstuff. Food additives are regulated under the Food Additive Directive [23].

In addition, the Codex Alimentarius international food standards, guidelines, and codes of practice deal with safety, quality, and fairness of international food trade [24]. As a result, Codex Alimentarius deals with contaminants and toxins in food and feed, and lists the maximum levels and associated sampling plans which are recommended by the Codex Alimentarius Commission (CAC). According to Codex Alimentarius a contaminant is considered as any substance not intentionally added to food, which is present as a result of production, processing, preparation, treatment, packing, packaging, transport, and holding of food or as a result of environmental contamination. Food packaging has not received much attention within the CAC. In the Codex Alimentarius, it specifies that packaging design and materials should provide adequate protection for products to minimize contamination, prevent damage, and accommodate proper labelling. Packaging materials or gases where used must be non-toxic and not pose a threat to the safety and suitability of food under the specified conditions of storage and use.

Any substance that meets the terms of the Codex definition for a contaminant, including contaminants in feed for food-producing animals, is treated according to Standard 193-1995 [24] that provides maximum level (ML) for substances legally permitted. Particularly for the contaminants, acrylonitrile and vinylchloride monomer, that are classified by IARC as human carcinogens, and due to possible migration into food, guideline levels (GL) of 0.02 mg/kg and 0.01 mg/kg, respectively, have been established [5, 24].

4.1 European Commission Regulation

Currently the Regulation No. 10/2011 on plastic materials and articles intended to come into contact with food is used in Europe [19]. This Regulation establishes specific requirements for the manufacture and marketing of plastic materials and articles: (a) intended to come into contact with food; (b) already being in contact with food; and (c) which can reasonably be expected to come into contact with food. Plastic materials covered by the scope of the Plastics Regulation are based on synthetic polymers and synthetic or natural polymers that have been chemically modified, polymers manufactured by microbial fermentation, bio-based and biodegradable plastics if they are manufactured with synthetic polymers, as well as plastics obtained by ‘chemical recycling’ processes. The Regulation applies to materials and articles which are placed on the EU market and include:

(a) Materials, articles, and parts consisting exclusively of plastics
(b) Plastic multilayer materials and articles held together by adhesives or by other means
(c) Materials and articles referred to in points (a) or (b) that are printed and/or covered by a coating
(d) Plastic layers or plastic coatings, forming gaskets in caps and closures, that together with those caps and closures compose a set of two or more layers of different types of materials
(e) Plastic layers in multi-material multilayer materials and articles

The Plastics Regulation sets out rules concerning the authorised substances that can be used in the manufacture of plastic layers of the plastic materials and articles and restrictions—specifications for these substances regarding the parts of the plastic materials the list applies. Also this regulation sets out specific and overall migration limits for the plastic materials and articles and compliance testing requirements [25].

The list of authorised substances that may be intentionally used in the manufacture of plastic layers in plastic materials and articles contains 885 substances (Annex I) from the following categories: (a) monomers or other starting substances that are the building blocks of the polymer; (b) additives (excluding colorants); and (c) polymer production aids (PPA) excluding solvents which are used to provide a suitable medium for polymer or plastic manufacturing and macromolecules obtained from microbial fermentation [25]. Under the term ‘additive’, various categories and functions are covered such as antifoaming agents, anti-skinning agents, antioxidants, antistatic agents, dryers, emulsifiers, fillers, flame retardants, blowing agents used in the manufacture of expanded polymers like polystyrene foam, hardening agents, impact modifiers, lubricants, miscellaneous additives (extrusion aids), optical brighteners, plasticisers, preservatives (antimicrobial substances, such as surface biocides), protective colloids, reinforcements, release agents, stabilisers, viscosity or rheology, and UV absorbers.

Polymer production aids (PPA) may be present, but neither are intentionally present in finished materials or articles and they do not have a physical or chemical effect in the final material or article. Under the term PPAs, the following categories are covered: anti-foam reagents/degassing agents necessary during the manufacturing process; anti-cluster, anti-crusting agent; anti-scaling, buffering agents; build-up suppressants; coagulating agents; dispersing aids; emulsifiers necessary during the manufacturing process; flow control agents; nucleating agents; pH regulators; preservatives necessary during the manufacturing process (antimicrobial substances used

Table 2 List of food stimulants [19]

Food simulant	Abbreviation/application
Ethanol 10 % (v/v)	Food simulant A
Acetic acid 3 % (w/v)	Food simulant B (for foods which have a pH <4.5)
Ethanol 20 % (v/v)	Food simulant C (for alcoholic foods with an alcohol content of up to 20 % and those foods which contain a relevant amount of organic ingredients that render the food more lipophilic
Ethanol 50 % (v/v)	Food simulant D1 (for alcoholic foods with an alcohol content of above 20 % and for oil in water emulsions)
Vegetable oil (vegetable oil with a fatty acid distribution of <1–85 % (w/w) of methyl esters)	Food simulant D2 (for foods which contain free fats at the surface)
Poly(2,6-diphenyl-*p*-phenylene oxide), particle size 60–80 mesh, pore size 200 nm	Food simulant E (for testing specific migration into dry foods)

as process biocides); solvents; surfactants; suspension agents; stabilisers; thickening agents; and water treatment reagents. PPAs other than those included in the Union list may be used to manufacture plastics, subjected to national legislation.

4.1.1 Migration Tests

Migration tests employing various food simulants have been proposed for the evaluation of possible migration of various chemicals from plastic materials and articles into food. The Regulation defines six food stimulants (Table 2) that can be used for demonstration of compliance with migration limits for plastic materials and articles: (a) not yet in contact with food, (b) repeatedly contact with foods, (c) materials and articles intended to come into contact with different food categories or a combination of food categories. Food simulants A, B, and C are assigned for foods that have a hydrophilic character and are able to extract hydrophilic substances. Food simulants D1 and D2 are assigned for foods that have a lipophilic character and are able to extract lipophilic substances. Migration in any of the five simulants A, B, C, D1, and D2 shall not exceed 10 mg/dm^2 under the standardised testing conditions of the Plastics Regulation [19]. Water has often been used as extraction media. However, under this regulation water is considered as a food and not as a food stimulant, although testing can be performed into water only for plastic materials intended to come into contact with water.

For material or article intended to come into repeated contact with foods, the migration tests have to be carried out three times on a single sample using another sample of the food simulant on each occasion. In this case the compliance is checked on the basis of the level of the migration found in the third test. Overall migration from materials and articles intended to come into contact with different food categories or a combination of food categories is testing by a combination of stimulants based on specific characteristics of food. For examples to demonstrate compliance with the overall migration limit for all aqueous and acidic foods and alcoholic foods up to an alcohol content of 20 %, testing in food simulant C and food simulant B has to be performed [19]. EU regulation also describes the food stimulants that have to be used for testing migration from materials and articles not yet in contact with food, according to the food category or the combination of food categories. In this case most extreme conditions of time and temperature foreseeable in actual use shall be carried out in order to verify compliance of migration into foods with the migration limits [19].

The use of stimulants to identify compounds that may migrate from containers is a useful approach and the data can be compared to legislated maximum concentrations. However, they do not reflect real conditions and in subsequent steps, migration experiments additionally should be performed directly in food [13].

4.1.2 Migration Limits

Based on the safety evaluation of the authorised substances, the toxicity, and their migration behaviour, two types of migration limit have been set: (a) specific migration limit (SML, mg of substance per kg of food) which is the maximum permitted amount of a given substance released from a material or article into food or food simulants and (b) overall migration limit (OML, mg of substance per kg of food) which is the maximum permitted amount of non-volatile substances released from a material or article into food simulants. For setting the SML, it is conventionally assumed that 1 kg of food containing the substance is consumed daily by a person of 60 kg bw. Moreover, it is assumed that the 1 kg of food is in contact with a plastic material releasing the substance at the SML and that the food contact surface area is 6 dm^2/kg food. For those substances for which no specific migration limit or other restrictions are provided, a generic specific migration limit of 60 mg/kg is applied. If the toxicological evaluation results in a specific migration limit $\leq$60 mg/kg, then this is listed as SML. If the toxicological evaluation results in an SML $>$ 60 mg/kg, this is not listed as SML, as it would be above the generic SML [19].

The overall migration limit is linked to the inertness of a material. The Framework Regulation sets out that food contact materials shall not release their constituents into food in concentrations that could change the composition of the food. A release of 10 mg of constituents per 1 dm^2 surface area of plastic food contact material is established as the limit above which the migration is regarded as an unacceptable change of the food. By derogation from the previous restriction, plastic materials and articles intended to come into contact with food for infants and young children up to 3 years old (a vulnerable consumer group, as defined by Commission Directives 2006/141/EC and 2006/125/EC) shall not transfer their constituents to food simulants in quantities exceeding 60 mg of total of constituents released per kg of food stimulants (independent of the packaging size) [25].

The Regulation gives certain rules for assessing compliance with migration limits for materials and articles already in contact with food and for materials and articles not yet in contact with food. Correction factors can be applied when comparing the results from the migration test with respective limits [19]. Moreover, there are also specific provisions for multilayer materials and articles which are composed of two or more layers held together by adhesives or by other means [19, 25].

5 Hazardous Chemicals in Food and Bottled Water

A variety of chemicals may enter food at different stages of the food chain. Food packaging and other food contact materials could be sources of various chemicals in food. Due to the complex chemistry of polymers several compounds can be incorporated in the final material and potentially migrate into food. The extent of this migration and the specific toxicity of the compounds are the main factors which define the human health risk from packaging materials [26]. The substances that may migrate and affect the food obviously depend on the nature of packaging material and the type of food. Moreover, the extent of direct contact, storage time, pH, temperature, exposure conditions, common use stresses such as UV radiation in sunlight, microwave radiation, and heat via boiling may also affect the migration. The substances that can migrate into food include chemicals used as monomers, additives (antioxidants, plasticisers, clarifiers, etc.) and their degradation products, solvents, as well as inks, adhesives, and so forth in the finished product (Fig. 1). Many of these compounds may exhibit estrogenic activity and, although in

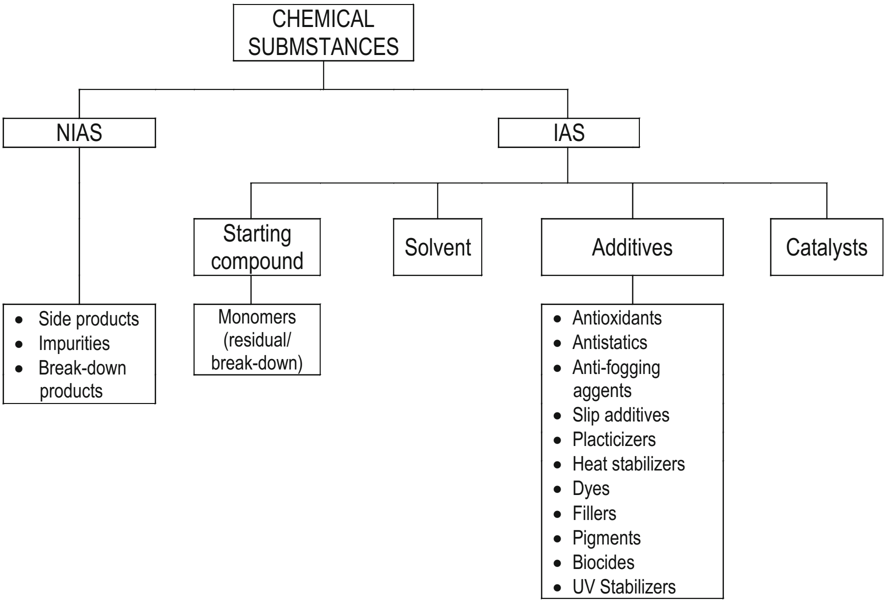

Fig. 1 Classification of possible chemical substance migrants from food packaging (modified by [1])

relatively low concentrations individually or in combination, can produce adverse effects, especially during sensitive windows of human development [1, 27]. Assessment of migration levels is usually performed by food stimulants that resemble chemical properties of the food. Analysing migrants directly into foods is difficult due to complexity of matrices. However, consumers are exposed to chemicals in actual foods, and the approximation using food simulants can over- or underestimate actual exposure levels [1].

A lot of discussion lately concerns the quality of bottled water. The consumption of bottled water has been steadily growing up in the last decades. Current regulations for bottled water require the analysis for selected microbiological and physicochemical parameters. However there is anxiety about the quality of bottled water because it is stored for longer periods and not always preserved under the recommended conditions or because containers and bottles are reused without adequate cleaning or disinfection. Many questions have been raised about possible migration of chemicals (intentionally and/or non-intentionally added substances) during long storage time especially under poor conditions (high temperatures, sun radiation, etc.) in retail stores and consumer homes. According to the legislation any container used for packaging of natural mineral waters shall be fitted with closures designed to avoid any possibility of adulteration or contamination. Therefore, the control of materials used in bottles and closures for bottled water is of special concern. Bottled water in Europe is usually available in two main sorts of packaging material: glass and plastic. About 80 % of the plastic bottles used is of poly(ethylene terephthalate) (PET) owing to the desirability of its physical and chemical properties such as strength, transparency, light weight, and easy recycling. PET is characterised by a limited range of additives and low diffusion of potential migrants in the polymer matrix. Other containers are made of polycarbonate (PC), where BPA is the key building compound, mainly in the form of reusable water carboys.

Many studies reported the presence of organic compounds in bottled water that may affect the organoleptic characteristics of the water, and pose health risk to consumers. Organic compounds could be source of carbon to inherent microorganisms which also have implications on odour and taste thresholds. The presence of xenobiotics in bottled waters represents a complex problem and the origin of several substances is not clearly established and still being debated. Bottled water can be contaminated in different phases of the production process, from supplying of the materials to handling, storing, and distribution. This includes contamination of water source in the field, during bottling process in the plant, migration from the material of the bottle or the caps to the water (monomers, catalysts, additives, or degradation products), and formation of organic compounds under deficient storage conditions.

Numerous studies have investigated the occurrence of intentionally and/or non-intentionally substances in various foodstuffs and bottled waters (Tables 3 and 4). In the following sections the occurrence of selected compounds along with conditions that may affect their migration into foodstuff is presented.

Table 3 Levels of organic compounds in food packaging and food samples

Samples	Storage material	Experimental conditions	Compounds detected (Frequency)	Concentration	Reference
Fish fillets	PVC film	2 ± 0.5°C, max contact time 360 h	DEHA	3.74 mg/dm^2 (117.6 mg/kg)	Goulas et al. [28]
Distilled water or acetic acid at 3% or ethanol at 15%	Epoxy resin, low density polyethylene (LDPE) tetrapack (Polyethylene laminate paperboard carton), high density polyethylene (HDPE), polystyrene dish, silicone teat, polycarbonate, synthetic plastic wine tops (mixed plastic foam)	Incubation at 40°C for 10 days	DMP DBP BBP DEHP OP NP BPA DEHA	85 ± 116, 6–421 363 ± 640, 25–1,948 116 ± 135, 14–355 5,086 ± 5,348, 323–17,694 6,619 ± 20,910, 6–27,956 720 ± 1,251, 18–4,185 315 ± 300, 142–973 651 ± 875, 14–2,902 All values in ng/L Plastic wine tops showed the highest level of migration	Fasano et al. [13]
1. n-Heptane 2. Distilled water, 3. 4% acetic acid, 4. Cooked rice	Polyvinyl chloride films	1. 25°C, 60 min 2. 60°C, 30 min 3. 60°C, 30 min 4. 10 g rice sample wrapped with 90 cm^2 PVC film and (a) reheated in a microwave oven (500 W, 2,450 MHz) for 1 min or (b) the sample was kept for 30 min at room temperature	4-nonylphenol	1. N.D.—1.6 μg/cm^2 2. N.D.—9.7 ng/cm^2 3. N.D.—7.2 ng/cm^2 4a. N.D.—410 ng/g 4b. N.D.—76.5 ng/g	Inoue et al. [29]

Oily food products: Pesto, eggplants, olive paste, olives, mussels, cheese garlic, artichokes, octopus, tuna, feta cheese, dried tomatoes, mango pickles, cactus leaves and tomato sauce	PVC gaskets in glass jars	Food products direct from the market and food stimulant D (olive oil) at pasteurization/sterilization conditions followed by 10 days at 40°C	ESBO DIDP DINP DEHP DEHA DEHS ATBC	10–650 mg/kg 55–705 mg/kg 15–150 mg/kg 20–430 mg/kg 80–155 mg/kg 10–20 mg/kg 225 mg/kg	Fankhauser-Noti and Grob [16]
Halawa tehineh (halva)	Polyvinyl chloride (PVC) cling-film	Kinetic study: at 25 ± 1°C 0.5–240 h contact time Penetration study: thin slices of food (1.5 mm) wrapped with film at 25 ± 1°C for 240 h contact time	DEHA ATBC	3.31 mg/dm^2 film or 81.4 mg/kg halva 1.46 mg/dm^2 film or 36.1 mg/kg halva	Goulas et al. [14]
Water, 3% acetic acid, 10% ethanol, 50% ethanol, olive oil	Polycarbonate films, plates, bars, disks, containers and bottles	Various conditions: 10 days at 40°C, 2 h at 70°C, 4 h reflux, 0.5 h at 121°C 0.5 h at 100°C followed by 10 days at 40°C	BPA	Water: 0.08–0.20 μg/dm^2 3% acetic acid: 0.11–0.41 μg/dm^2 10% ethanol: 0.09–0.87 μg/dm^2 50% ethanol: 0.22–0.45 μg/dm^2 Olive oil: 0.09–0.14 μg/dm^2	Mercea [8]
Hard and soft cheese	PVC film	Storing at 5 ± 0.5°C up to 240 h for kinetic and penetration studies	DEHA	133.9–345.4 mg/kg 7.3–18.9 mg/dm^2	Goulas et al. [30]

(continued)

Table 3 (continued)

Samples	Storage material	Experimental conditions	Compounds detected (Frequency)	Concentration	Reference
Soft drinks/ beers			BPA	bld-4.7 μg/L	Cunha et al. [31]
Soda beverages			BPA	bld	Shao et al. [32]
Soft drink in Canadian market	72 canned soft drink products		BPA	0.032–4.5 μg/L	Cao et al. [33]
Milk			BPA	bdl-0.49 μg/kg	Shao et al. [34]
Milk			BPA	0.28–2.64 μg/kg	Casajuana and Lacorte [35]
Milk infant formula			BPA	bld-0.40 μg/L	Cunha et al. [31]
Wine			BPA	bdl-2.1 ng/mL	Brenn-Struckhofova and Cichna-Markl [36]
Food simulants-hot water (leachates from commercially available bottles)			BPA	0.7–78.5 μg/L	Chang et al. [37]
Beverages and foods from Belgian market	45 canned beverages 27 canned food items Non-canned types such as PET, tetraPak, paper and plastic	1 week after purchase Stored at room temperature	BPA in	40.3 ng/g canned foods 0.46 ng/g non-canned foods Beverages and foods 1 ng/ml canned beverages <0.02 non-canned beverages	Geens et al. [38]

Food from markets in Taiwan	25 types of food	Refrigerated in their original packaging in −20°C 1 week after purchase	NP OP	5.8–123.8 ng/g Bdl-63.7 ng/g	Lu et al. [39]
Commercial infant food in Germany supermarkets	24 different categories	Stored unopened at 4°C or room temperature	4NP OP	Up 17.1 μg/kg Up 616 μg/kg	Raecker et al. [40]
Milk and milk based products			DEHP DINP DIDP BBP DBP	7–138 μg/kg <5–12 μg/kg <5 μg/kg <4 μg/kg <9 μg/kg	Sǿrensen [41]
Food contact materials Food samples	24 polysterene products Various classes of food (yoghurt, cookies, candies, etc.)		Styrene monomer	9.3–3,100 mg/kg in PS products 2.6–163 ng/g food	Genualdi et al. [42]

bld below detection limit, *DMP* dimethyl phthalate, *BP* Benzophenone, *2-PE* 2-phenoxyethanol, *4-NP* 4-nonylphenol, *BPA* bisphenol A, *BBP* benzylbuthyl phthalate, *DMIP* dimethyl isophtalate, *PEs* phthalates, *EBSO* epoxidized soy bean oil, *DINP* diisononyl phthalate, *DIDP* diisodecyl phthalate, *DEHP* di-(2ethylhexyl) phthalate, *DEHA* di-(2ethylhexyl) adipate, *DEHS* di-(2ethylhexyl) sebacate, *ELO* epoxidized linseed oil, *ATBC* acetyl tributyl citrate

Table 4 Concentrations of various substances in bottled waters

Samples	Container type	Experimental conditions	Compounds detected	Reference
Bottled water (Greece)	PET PC	Upon purchase from local markets and after exposure at outdoor conditions for 15, 30 days	BPA 4.6, NP 7.9, OP<2 ng/L DEHP 350, DBP 44, DEP 33 BPA 112–170 (PC)	Amiridou and Voutsa [43]
	PET	Solar water disinfection process (ambient sun, shade, sun and 60°C)	DEHP 100–710 ng/L	Schmid et al. [44]
	PET, HDPE caps	Continental bottled water Upon purchase	DMP 5–125, BP 14–921 ng/L DBP 25–220, BBP 77–131, NP 54	Guart et al. [45]
Bottled water	PET, PE, glass	Upon purchase and after 10 week storage up to 30°C	DBP 20–72, BBP bdl-10, DEP bdl-990 ng/L DEHP bdl-332, DMP bdl-5 BPA bdl-8, 4NP bdl-1730	Casajuana and Lacorte [46]
Bottled water (France)	PET, PC reusable, aluminum cans	29 brands from supermarkets and bottling plants	BPA 70–4,210 ng/L (in PC) 4-tertBP bdl-247 ng. L (in PC) Target compounds were not detected in PET containers or aluminium cans	Colin et al. [47]
Bottled water	PET	Different storage conditions −18 up to 40°C, 24 h, 10 days, 30 days, 45 days	DBP 79–303, BBP bdl-13 ng/L DEHP 217–917	Jeddi et al. [48]
Bottled mineral water	PET	Local market Still mineral water	BPA bdl-102 ng/L NP bdl-84	Maggioni et al. [49]
Bottled water (Italy)	PET Glass	Commercial brands of bottled water	PEs (DBP, DMP, DEP, DEHP, DiBP) 3,520 ng/L (PET) 190 ng/L (glass)	Montuori et al. [50]
	PET	Mineral water 30 days after bottling	DEHP bdl-50 μg/L DBP bdl-50, DEP bdl-1	Bošnir et al. [51]

Bottled water	–	Local market	4NP 108–298 ng/L BPA 17.6–324 TCS 0.6–9.7	Li et al. [52]
Bottled water	PET, HDPE, LDPE, PP, PE Different material of caps	Study on bottling and after 1 year of storage	BPA 32–24,200, NP 57–2,030 ng/L OP 3–128, BBP 592–3,010 DEHP 985–11,900	Guart et al. [53]
Bottled water	PET	Upon purchase and after 3 months storage	DEHP <0.02–6,800 ng/L	Leivadara et al. [54]
Bottled water	PET	Carbonated and non carbonated mineral water Exposure to sunlight-high T	FA 2.2–96.1, AA 0.9–317.8 μg/L ACE 5.1–125.6	Nawrocki et al. [55]
Bottled water	PET, glass	Carbonated waters Storage 1 day, 47, 170 days	FA 1.3–11, AA 1.0–7.4 μg/L (glass) FA 1.4–60, AA 1.3–78.1 μg/L (PET)	Dabrowska et al. [56]
Bottled water	PET	Exposure to sunlight 0, 15, 30, 63, 126 days	FA 1–44 μg/L, AA 2–6 μg/L	Wegelin et al. [57]
Bottled water Carbonate and non carbonate	PET, glass	Non-carbonated and carbonated water Storage conditions 10 days At 40, 50 and 60°C	Sb ~4–8 μg/L (worst case, 60°C, 10 days) FA ~8.5 μg/L, AA ~72 μg/L 2,4dtBP ~1.6 μg/L	Bach et al. [58]
Bottled water Boston-USA	PET, PC, HDPE, PS Various water classes (carbonated, non-carbonated, enriched)	Market-representative basket survey Storage at 23°C, 12 h/12 h light/dark for 1, 7, 30 and 60 days	Sb bdl-0.500 μg/L Br	Andra et al. [59]
Bottled water Canada-Europe	PET	Groundwater Exposure 6 months	Sb 0.566 μg/L	Shotyk et al. [111]
Bottled water USA		Commercial water at 22°C for 3 months	Sb 0.226 ± 0.160 μg/L	Westerhoff et al. [60]

(continued)

Table 4 (continued)

Samples	Container type	Experimental conditions	Compounds detected	Reference
28 countries	PET	132 brands of water	Sb 0.001–2.570 μg/L	Shotyk and Krachler [107]
EU countries	PET (hard, soft)	Ultrapure water at 2°C for 150d pH 3.5 and 6.5	Sb 0.003–0.027 μg/L	Reimann et al. [61]
Bottled water	PET	Still and sparkling mineral water Exposure at 22°C for <1 year	Sb 0.26 ± 0.160 μg/L (still) Sb 0.40 ± 0.220 μg/L (sparkling)	Keresztes et al. [62]
Bottled water	PET (different colors)	Exposure at 4, 20, 40 and 60°C For different periods up to 220 days	Sb 0.30–4.2 μg/L (short term) Sb 0.30–25 μg/L (long term)	Carneado et al. [63]

bld below detection limit, *DMP,* dimethyl phthalate; *BP* Benzophenone, *2-PE,* 2-phenoxyethanol, *4-NP* 4-nonylphenol, *BPA,* bisphenol A, *BBP* benzylbuthyl phthalate; *DMIP,* dimethyl isophtalate; *PEs,* phthalates; *AA* acetaldehyde; *FA* formaldehyde; *ACE,* acetone, *2,4dtBP* 2,4-di-tert-butuylphenol

5.1 Bisphenol A

The most prominent case of migration of plastic components to water is 4,4-dioxy-diphenyl-2,2-propane (bisphenol A, BPA), a well-known endocrine disruptor. BPA is a high-production-volume chemical. BPA applications can be divided into two categories: a first and predominant category where the chemical structure of BPA is modified or polymerised and a second minor category where BPA is used as an additive. Almost 65 % of BPA is polymerised to the resistant plastic polycarbonate. About 30 % of BPA is polymerised to epoxy resins that are mainly used as an internal coating of cans to prevent direct contact between the metal wall of the can and the food/beverage, and to protect the cans from rusting and corrosion. BPA is also used in polysulfone polymer, polyacrylates, polyetherimide, and polyester resins. BPA is used as additive in thermal paper and PVC for its antioxidant properties [64–67].

BPA has been associated with increased incidence of cardiovascular disease, diabetes, reproductive cancers, fertility problems, and other endocrine-related endpoints, even at a very low-level exposure. In January 2011, the European Commission adopted the Directive 2011/8/EU as regards the restriction of use of BPA in plastic infant feeding bottles. BPA polycarbonate infant feeding bottles have been banned. To control migration from food packaging materials into food products and based on thresholds for potential adverse health effects of BPA, a specific migration limit of 600 μg/kg has been established [19]. The European Food Safety Authority established a tolerable daily intake (TDI) of 50 μg/kg bw, which represents a safe level for daily exposure over lifetime [68]. Similarly, the Integrated Risk Information System (IRIS) of US EPA proposed a reference dose (RfD) of 0.050 mg/kg bw/day for chronic oral exposure [69].

BPA exposure through these materials can occur since a small fraction of non-polymerised, free BPA is left behind after polymerisation. Otherwise, breakdown of the polymer can occur under various conditions such as high temperatures, exposure to detergents, and alkaline conditions [70, 71]. Because the polycarbonate bond is unstable, BPA can eventually be released into food or beverages in contact with plastics. Kawamura et al. [72] reported that BPA on the surface or near the surface of polycarbonate products is easily eluted. Guart et al. [73] who studied the migration of BPA from PC material according to migration assays Commission Regulation No. 10/2011 reported that BPA was the only compound detected in PC polymers at mean concentration of 0.748 μg/kg.

The exposure to BPA occurs mainly through food contamination from polycarbonate plastics used in a wide range of applications such as water carboys, reusable milk containers, food storage vessels, and baby bottles, as well as through cans coated with epoxy resin coatings used to lacquer-coat the interior of food cans, wine storage vats, water containers, and water pipes [64, 65, 70, 71]. The concentration ranges of BPA in various products (water, beverages, wine, milk, and food simulants) are shown in Tables 3 and 4. The occurrence of BPA in food products depends on the coating/packing materials, type of food, and handling and storage conditions [33, 43, 74]. Reported BPA concentrations in canned food cover a broad range of concentrations. Canned food exhibited higher concentrations of BPA than the respective non-canned food (0.46 ng/g and <0.02 ng/mL, respectively) in the Belgian market. The concentration of BPA was higher in canned beverages than non-canned beverages (i.e. 1.0 mg/mL vs. <0.02 mg/mL) ([33, 38], and references herein). The consumption of canned food seems to be a significant source of BPA. It has been reported that BPA exposures (based on urine concentrations) were substantially reduced when the diet of participants was restricted to 'fresh foods' and food with limited packaging [75].

The occurrence of BPA in bottled water has been reported by many investigators (Table 4). BPA was among the most ubiquitous compounds in bottled waters in studies conducted by [45, 53]) concerning bottled water from the Spanish market and from 27 countries of several commercial brands from different materials (PET, PP, PC, HDPE, LDPE, glass) with a variety of caps and migration of plastic components or additives during bottling and storage. Li et al. [52] reported that BPA was present in 17 out of 21 brands of bottled waters purchased from local supermarket in Guangzhou, China, at concentrations ranging from 17.6 to 324 ng/L. Amiridou and Voutsa [43] detected low concentrations (4.6 ng/L) of BPA in PET with no significant change after 14 and 30 days of storage. However, as far as concerning PC containers (carboys) higher concentration (112 ng/L) was reported. Colin et al. [47] reported that BPA in PC bottled water ranged from 70 to 4,210 ng/L, with higher concentrations in newly manufactured bottles. The source of BPA in PET bottled water could be due to bottle closures, the water itself, or the use of recycled PET [73, 76]. The exposure of bottled water at elevated temperatures and solar irradiation increases the rate of BPA migration from polycarbonate containers into water [43, 77].

Bottled water is an additional, although minor, source of exposure to BPA. Makris et al. [78] reported a significant association between water consumption from polycarbonate containers and bisphenol A intake during harsh environmental conditions in summer. However, this route of exposure represents only a small portion of acceptable daily intake [43, 45, 47, 53] and it is unlikely to pose a significant health risk. Regarding tap water, concern was raised about the possible presence of BPA from epoxy pipe linings widely used for the rehabilitation of drinking water pipes in many countries [64, 65]; however Colin et al. [47] did not found this compound in drinking water from pipes coated with epoxy resins.

5.2 Alkylphenols

Alkylphenols such as 4-nonylphenol (NP) and octylphenol (OP) can be generated by oxidation and subsequent hydrolysis of tris(nonylphenyl)phosphite (TNPP) used as additive in plastics. TNPP is used as a heat stabiliser in various polymeric food packaging materials such as styrenes, vinyl polymers, and rubber polyolefins. TNPP is also used to maintain the colour stability, processing stability, and performance integrity of the polymers. NP is used as a starting material in the manufacture of TNPP and so it may be present as an impurity as well as a hydrolysis product. Alkylphenols in food may also be occurred due to degradation of the most widely used non-ionic surfactants polyethoxylated nonylphenols (APEOs) which are cleaning agents in bottled manufacturing [76].

There is great interest for alkylphenols (NP, OP) since these compounds can elicit endocrine disruption. However, SMLs have not been established. These compounds are listed as priority substances in the field of water policy. Moreover, NP, OP, and their ethoxylated derivatives (NPEs, OPEs) are nominated in the third contaminant list for compounds that may require regulations under the Safe Drinking Water Act [79]. For NP the limit value of 0.5 μg/L proposed for phenols in drinking water offers adequate protection against adverse health effects induced by NP or NPE [43].

Various studies reported the occurrence of nonylphenol and octylphenol in foodstuffs and bottled water (Tables 3 and 4). Kawamura et al. [80] who reported NP in different food contact materials (PVC, PS, PC, PP, etc.) presumed that this could be attributed to the degradation of TNPP antioxidant. Fernandes et al. [81] reported NP in polystyrene and PVC samples at concentrations of 64–287 μg/g, in fairly aggressive extraction conditions. Also Inoue et al. [29] found NP in PVC films, with migration depending on test conditions (solvent, temperature). NP was also detected in rice being in contact with PVC film.

Various studies reported the occurrence of nonylphenols in bottled water (Table 4). The migration of nonylphenol from plastic containers filled with distilled water was investigated by Loyo-Rosales et al. [82] that measured NP in water from HDPE, PVC, and PET containers at concentrations of 180 ng/L, 300 ng/L, and <8 ng/L, respectively. Li et al. [52] reported that 4NP was present in 21 brands of bottled water in all samples purchased from local supermarket in Guangzhou, China, at concentrations ranging from 108 to 298 ng/L; however the container type was not reported. Various studies reported the occurrence of nonylphenols in bottle water at concentrations ranging from 16 up to 465 ng/L [83]. Low levels of NP and OP were detected in bottle water by other investigators [43, 53, 73]. Casajuana and Lacorte [46] did not found alkylphenols in PET bottles after 10-week storage. Also Colin et al. [47] did not detect NP in water from PET and aluminium containers. The sources of APs in bottled water could be due to the laboratory equipment and materials, water, or container during washing steps and not directly to the water containers, especially PET bottles [76]. Recently, Takada [84] reported that plastic bottle caps could be a potential source of nonylphenol. Finally, Guart et al. [85] reported the migration of 4-NP from Tritan™, a material that has emerged as a possible substitute of polycarbonate polymer, to be used for water bottling up to 0.162 μg/kg.

5.3 Phthalates

Phthalate diesters commonly known as phthalates (PEs) represent the most important class of plasticisers. PEs are used to impact flexibility, workability, and durability to polymers but they can also be found in products such as paints, adhesives, inks, and cosmetics. About 80 % of all produced plasticisers are used in the manufacture of polyvinyl chloride (PVC). PVC is used for food wrapping and other food contact materials. The load of additives in PVC is as high as 20–50 % making migration to the foodstuffs possible. The most common PEs is DEHP which accounts for approximately 80 % of all plasticisers used in PVC. Other PEs found in PVC are also DBP, DiNP, and DiDP [86, 87]. Adipates, such as di-2-ethylhexyl adipate (DEHA) and di-isonyladipate (DiNA), are also frequently used as plasticisers in PVC products as replacement of phthalates. Possible sources of PEs in foods are PVC tubing, commonly used in milking process, food packaging materials, PVC gaskets in metallic caps for glass jars, aluminium foil paper laminates, and coatings on cookware [33, 88].

With respect to their endocrine-disrupting potential, phthalates such as BBP, DBP, DEHP, and DIBP have been found to elicit estrogenic responses in in vitro assays [86, 89, 90]. Furthermore, DEHP is possibly carcinogenic to humans (Group 2B) [91]. Due to the toxicity of several PEs and in order to reduce human exposure the European Community, through the fourth amendment to the plastics Directive [92, 93] established legislative limits for plastic and articles intended to come into contact with food. The compounds of interest are DEHP, DBP, BBP, DiNP, and DiDP where specific migration limits (SML, mg/kg food stimulant) and compositional limits in plastics (Qm, % in the plastic) have been set, depending on the single or repeated use of food contact materials. Nowadays, plasticiser migration from gaskets must respect the requirements given in the current Commission Regulation No. 10/2011 on plastic material and articles intended to come into contact with food [19]. The European Commission limited PEs in food contact material made of plastic. The proposed SML values are 0.3 mg/kg for DBP, 30 mg/kg for BBP, 1.5 mg/kg for DEHP, and 18 mg/kg for DEHA [19]. In the field of drinking water, WHO and EPA set a maximum permitted level only for DEHP (8 μg/L and 6 μg/L, respectively) [69, 94]. Simultaneously, EPA advises close screening of phthalate in drinking water at concentrations above this limit. Moreover, other compounds such as BBP, DBP, DEP, and DINP are nominated in the third contaminant list for compounds that may require regulations under the Safe Drinking Water Act [95]. It should be noted that the EPA, under the Safe Drinking Water Act, has defined the maximum contaminant level goal (MCLG) for DEHP in water as zero. The EPA has set this goal based on the best available science to prevent potential health problems.

Due to the lack of chemical bonding PEs are easily released and migrate into foods, beverages, and drinking water from the packaging or bottling materials or manufacturing processes. Owing to the ubiquitous use, PEs as an NIAS can be found even in materials that are not contained. The migration of PEs into foodstuffs from food contact materials is a well-known source of food contamination [88]. Food is considered the most important route of exposure to DEHP and PEs accounting for 80 % or more than 90 % of the daily intake of adults and can be as much as 1000 times higher than from water [86, 87, 96, 97]. It has been reported that urine concentrations, and eventually DEHP exposure, were substantially reduced when participant diets were restricted to ‘fresh foods’ and food with limited packaging [75, 87].

Various studies reported the presence of phthalates and particularly DEHP in food and food containers (Tables 3 and 4) [33, 41, 75, 86, 88, 97, 98]. They reported a broad range of contamination, showing the ubiquity of DEHP. DEHP concentrations in food are generally higher than those measured in water. The higher concentrations of DEHP are usually found in foods with high lipid content (e.g. milk products exhibited higher concentrations compared to water, wine, or beer in similar containers).

Several studies report the presence of PEs in bottled water, with DEHP usually being the prevailing compound (Table 4). A number of studies investigate directly the content of PEs in water stored in various types of containers whereas others examined the levels over time under various storage conditions (Table 4). The type of polymer and the bottling process or storage conditions are the factors that affect the presence of phthalates and other plastic components by the migration from plastic bottles [73]. Guart et al. [45, 53] studied various types of bottled water from different materials (PET, PP, PC, HDPE, LDPE, glass) with a variety of caps and migration of plastic components or additives during bottling and storage. They detect various PE compounds such as DEHP, DMP, DBP, and BBP. Montuori et al. [50] reported the presence of phthalates in water bottled in PET being significantly higher (nearly 20 times) compared to glass bottles. Cao et al. [33] reported the presence of DEP, DiBP, DBP, and DEHP in water from PETE bottles, although they did not find considerable differences in phthalate levels between PETE and PC containers, or between glass-bottled water and water in plastic containers. Moreover storage conditions and parameters such as temperature and storage period seem to affect the migration. Criado et al. [99] reported high DBP concentrations in water from PET bottles (2 μg/L) with a 20 % increase after 5-month storage. Jeddi et al. [48] detected DBP, BBP, and DEHP in bottled water as the storage time prolonged; regardless of the storage condition and brand of the bottled water, concentrations of phthalate esters increased. A pronounced increase in the concentration of phthalates was observed at 40 °C. However, other investigators did not report significant changes in PE concentrations after short exposure to ambient conditions [43, 44].

PEs are not thought to be used in the manufacture of PET bottles. Thus contamination observed is probably due to steps of production and bottling process or from the cap liner used [86]. Cross-contamination during analytical procedure due to the wide use of plasticisers is a serious problem. Generally the concentrations of PEs in bottled water were below toxic levels proposed for drinking water. However, the consumption of drinking water is among the routes of exposure to PEs. It appears that the contribution of bottled water in intake of PEs compared to the permitted total daily intake is low (<1.1 % TDI) and was considered safe even for the worst storage conditions [43, 48, 100]. Exposure through water reduces with increasing age, since children's water intake is higher compared to their body weight. In addition, the carcinogenic risk posed by the occurrence of DEHP in bottled water is low [43, 48].

5.4 Carbonyl Compounds

Formaldehyde and acetaldehyde are well-known PET degradation products. They are generated by thermo-mechanical and thermo-oxidative degradation of PET. The chemical quality of raw material, the molecular weight of the polymer, and the manufacturing technologies used in the production of PET bottles could be the reason that different aldehyde levels were generated in the PET bottle wall [76, 101]. As a result, aldehydes can migrate to bottled water. EU Regulation No. 10/2011 on food contact materials established specific migration limits (SML) for formaldehyde and acetaldehyde (15 mg/kg and 6 mg/kg, respectively) [19]. Other carbonyl compounds such as propanal, butanal, and acetone appear in positive list, but specific SMLs are not indicated.

Various studies reported the presence of formaldehyde and acetaldehyde in PET bottled waters [55, 56, 58, 102]. This migration is affected by the type of container, the storage time and the temperature, the carbonation of water, and the exposure to sunlight [55–58, 101]. Storage at high temperatures (60 °C) accelerates the migration of these compounds. This could be attributed to the fact that storage close to PET glass transition temperature (around 80 °C for semi-crystalline PET) increases the mobility of polymeric chains directly linked to the migration phenomenon [102]. Water type also affects the migration of aldehydes in bottle water. Formaldehyde and acetaldehyde were substantially present in the bottled carbonated waters probably due to relative acid pH as well as the pressure exerted on the bottle wall by carbon dioxide [56, 76, 102]. Bach et al. [103] reported that exposure to sunlight had no effect on the migration of aldehydes. However, Nawrocki et al. [55] found increased concentrations of formaldehyde and acetaldehyde in carbonated water stored in PET bottles. Formaldehyde is responsible for an off-flavour to mineral waters, deteriorating their organoleptic characteristics. Indeed, UV light exposure produced plastic-like off-odours in mineral water packaged in plastic materials.

5.5 Styrene

The presence of styrene in packaged foods is due primarily to leaching of monomer from polystyrene containers. Polystyrene (PS) is widely used in the manufacturing of food contact materials such as trays for meat, cookies, and candies with disposable plates, cups, etc. and about 50 % of the consumption of PS was related to food packaging and food service articles. During the production process the styrene monomer can become occluded in PS products and may migrate out of these materials into food [42, 104]. The rate of migration of styrene monomer from polystyrene containers depends mainly on the lipophilicity of the food, surface area of the container per volume of food, duration of contact, and food temperature.

Styrene was found in 24 food contact materials from different categories (extruded polystyrene foam, expandable polystyrene, high-impacted polystyrene) at concentrations ranging from 9.3 to 3100 mg/kg, with a mean concentration of 340 mg/kg. This concentration is below the USFDA limit for styrene in food packaging materials which are 5000 mg/kg for fatty foods and 10000 mg/kg for aqueous foods. Moreover, styrene dimers and trimers, which are also residual materials produced during polymerisation, have been detected. Styrene was found in various foods such as yoghurt, croissants, cookies, raw chicken, and raw beef held in contact with PS packaging (meat trays, cookie trays, and chocolate candy trays) at concentrations ranging from 2.6 ng/g in raw chicken to 163 ng/g in sandwich cookies [42]. Styrene is reasonably anticipated to be a human carcinogen [105]. Several international brands start to phase out polystyrene foam packaging from their products.

5.6 Antimony

Antimony (Sb) is an element usually found in bottled water from PET bottles. Antimony trioxide (Sb_2O_3) is widely used to speed up synthesis of PET because it is efficient, presents a minimal tendency to produce side effects, and does not create colour in the polymer [106]. PET typically contains Sb in the range of 170–300 mg/kg. The residual concentration of Sb remaining on the PET bottle surface may vary according to the manufacturing process [60, 62, 76]. A small fraction of the Sb contained in PET is released into water. In PET packaged food, the SML for Sb_2O_3 is 0.040 mg/ kg as total Sb [19]. The MCL for Sb in drinking water is 5 μg/L in EU and 6 μg/L in the USA and Canada.

Several studies reported the occurrence of Sb in bottled water under various storage conditions. PC, HDPE, and PS containers exhibited significantly lower Sb leaching than PET [59]. The Sb leaching from PET into water is significantly affected by storage time and temperature, water type, exposure conditions, and colour of container. An increase of Sb concentration in bottled water was observed over time by 19–90 % [59, 60, 62, 76, 107]. Temperature also highly affects the release of Sb [58–60, 62, 63, 108]. Short-term tests and long-term test of Sb migration from PET bottles into mineral water at different temperatures showed an increase of Sb migration, usually below the EU limit of 5 μg/L, at temperature <60 °C. However at harsh environments (>60 °C), Sb migration is more rapid, exceeding the limit value in a few days. Carneado et al. [63] reported that Sb (V) was the predominant species in the measured extracts, although the most toxic species, Sb (III), was also present at 40 and 60 °C. The exposure of samples in sunlight or simulated irradiation also caused a small but significant increase in Sb leaching [60, 62]. Sb migration was higher in carbonated waters; probably this migration was accelerated by carbon dioxide [58, 59, 103]. Although the influence of PET colour was also studied by several authors, its potential effect remains unclear. Various studies reported that there was no correlation between PET colour and the Sb migration potential [107]. Westerhoff et al. [60] reported an increase in Sb content in clear PET compared to blue bottles whereas others reported higher Sb migration in water stored in dark coloured than that stored in clear ones [61]. It must be noticed that a common practice of bottle reuse for refilling tap water results in increase of Sb release with each reuse cycle [109]. Drinking water could be a source of Sb. Biomonitoring studies showed an association between urinary Sb concentrations and water consumption (regarding the containers and use habits) [110].

6 Conclusions

- Packaging plays an important role in food safety. The most important consumer packaging is made of plastic.
- Food packaging and other food contact materials could be sources of various chemicals (e.g. monomers, catalysts, additives) in food.
- The migration of substances depends on the nature of packaging material, the type of food, and the exposure conditions.
- The European Regulation established specific requirements for the manufacture and marketing of plastic materials and articles intended to come into contact with food and set out rules concerning the authorised substances, the migration limits, and the compliance testing requirements.
- Consumers are exposed to chemicals in actual foods, and the approximation using food simulants can over- or underestimate actual exposure levels.
- Numerous studies reported the occurrence of intentionally and/or non-intentionally added substances in various foodstuffs and bottled waters.
- As far as the regulation is followed and the exposure conditions are carefully considered the concentrations of authorised chemicals in food are relatively low.
- However, due to the occurrence of various compounds in food, additional research is warranted to assess the magnitude and variability of human exposure through food intake as well as health risk taking into account possible additive or synergistic effects.

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Release of Additives and Monomers from Plastic Wastes

Charita S. Kwan and Hideshige Takada

Abstract Additives and monomers are integral components of plastics or polymers. Bisphenol A (BPA), nonylphenol (NP), and polybrominated diphenyl ethers (PBDEs) are the common monomer and additives used primarily to improve the quality of plastic materials. They are used as antioxidants, stabilizers, plasticizers, and flame retardants in plastics that are in turn used in the manufacture of a wide range of consumer and industrial products. In this chapter, the release of BPA, NP, and PBDEs from waste plastic materials is presented. A brief background of the physical and chemical characteristics of BPA, NP, and PBDEs, and other factors that influence the release of these monomer and additives from plastics, is also discussed. The overview of the consequential occurrence of these compounds in leachates from landfills and/or municipal solid waste (MSW) dumping sites provides evidence on the release of BPA, NP, and PBDEs from dumped plastic materials.

Keywords Additive, Bisphenol A (BPA), Monomer, Nonylphenol (NP), Polybrominated diphenyl ethers (PBDEs)

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1 Introduction

Bisphenol A (BPA) or 2,2-bis(4-hydroxyphenyl)propane is used as the constitutional monomer or the monomeric building block of polycarbonate plastics [1, 2], either by trans-esterification with diphenyl carbonate or via the interfacial process with a monohydroxylic phenol [3]. Together with epichlorohydrin, BPA is also used as a major component of epoxy resins [1]. Bisphenol A-polycarbonate plastics are in turn used in the manufacture of plastic food containers such as reusable water bottles, while epoxy resins are used as inner linings of tin cans [2]. In addition, BPA is also used as an additive in other plastics and polymers, particularly as an antioxidant or stabilizer in polyvinyl chloride, printer ink, and in some other products [1, 2].

Nonylphenol (NP) is an alkylphenol and together with its derivatives, such as trisnonylphenol phosphite (TNP) and nonylphenol polyethoxylates (NPnEO), they are used as additives in the plastic industry, e.g., in polypropylene where nonylphenol ethoxylates are used as hydrophilic surface modifiers [4] or as stabilizer during crystallization of polypropylene to enhance their mechanical properties [5]. They are also used as antioxidant, antistatic agents, and plasticizer in polymers [1, 6], and as stabilizer in plastic food packaging materials [2].

Polybrominated diphenyl ethers (PBDEs) are used as additives in many kinds of plastics and polymers to reduce the flammability or the risk of fires in many consumer products [7]. Polymer-based products may contain as much as 30% PBDEs by weight [8]. Three technical or commercial PBDE products or mixtures (i.e., penta-BDE, octa-BDE, and deca-BDE which mostly contain the penta-, octa-, and deca-BDE congeners, respectively, with some other PBDE congeners) have been manufactured since the 1970s [9]. However, the penta-BDE and octa-BDE products were banned in 2009 after the inclusion of the tetra-, penta-, hexa-, and hepta-BDEs in the list of persistent organic pollutants (POPs) under the Stockholm Convention [10], while the commercial deca-BDE product is being considered for regulation in 2017 [7].

The commercial penta-BDE product had been used in epoxy and phenolic resins, polyesters, polyurethanes, and polyvinylchloride. The commercial octa-BDE product had been used in polystyrene, polyamide, polybutylene terephthalate, and polycarbonate [11–14]. The commercial deca-BDE product is considered as a general-purpose flame retardant because it is used in many kinds of polymers [14]. Thus, PBDEs have a very wide range of applications such as in electrical and electronic (E&E) equipment as printed circuit boards, housing for computers, and other related parts [7, 9, 11–14]. They are also used in curtains and upholstery textiles as back coatings [9], and in synthetic rubber for conveyor belts, flooring and sheeting, paints, and lacquers [7, 12, 13].

With the increasing development and discovery of new products using polymers or plastics, the use of BPA, NP, and PBDEs is far ranging. In 2003, the annual output of BPA worldwide was estimated at more than 2.2 million metric tons [2]. The market volume of NP in the EU is approximately 45,000 tons/year [15]. PBDEs are estimated to constitute one-third of the world's production of brominated flame retardants [16] at 67,000 metric tons/year [7].

2 Release Mechanism of BPA, NP, and PBDEs from Plastics or Polymers

Although all the three chemicals are categorized as additives in plastics or polymers including the monomer BPA [2, 13, 14], the mechanism of release of additives and monomers from plastic or polymer materials and wastes, and their distribution in the environment, will be influenced by their physical and chemical properties, as well as by the biological processes occurring in their immediate surroundings such as in landfills and municipal solid waste (MSW) dumping sites [1, 17, 18].

2.1 Physicochemical Properties of BPA, NP, and PBDEs

BPA is fairly water soluble [19]. Its octanol–water partition coefficient, log K_{ow}, is 3.32. Due to its relatively low hydrophobicity, BPA tends to elute easily from plastics and to rapidly move into the aqueous environment where it can be adsorbed by organic matter [18, 20].

On the other hand, NP has a hydrophobic moiety in the molecule and higher log K_{ow} (4.48) than BPA. It is expected to be adsorbed to particulates in the aquatic environment [18]. PBDEs are more hydrophobic [12] and have low solubility in water [13]; therefore, they are easily removed from the aqueous environment [12]. In particular, the high log K_{ow} of BDE-209 at ~10 [21] would enable it to partition preferentially to particles in the aqueous phase [12, 22, 23]. Thus, they are expected to be present in the adsorbed rather than in the dissolved phase [24].

2.2 Release of Additives and Monomers from Plastic Materials

The release of additives from plastic materials or polymers can also be understood based on its mode of integration into the plastic materials or polymers. Additives are not chemically bonded with the polymers. They are physically dispersed [25] or usually compounded into plastics during molding [1]. The additive PBDEs are not chemically bound with the polymers [12–14]. Similarly, the additive-derived NP is incorporated within the matrix of plastics. As explained by Teuten et al. [1], additives are dispersed into the three-dimensional porous structure of the polymer. The internal pore size of the polymer and the size of the additive molecule as well as the affinity of the additives to polymers (i.e., hydrophobicity) can control both the movement of the additive molecule within the polymer and its release or migration from the polymer. Additives that fit exactly in the pores may have a small but not insignificant ability to migrate. However, smaller additives or those with lower molecular weight can move more easily through a polymer with bigger pore size. Thus, additives may leach out from the surfaces of polymers or plastics. Leaching of PBDEs from plastics has been confirmed in a leaching test by Kim et al. [26]. Differential leaching of PBDEs from polymers occurs depending on their chemical properties such as hydrophobicity and molecular size.

Monomers are the constituent molecules of polymers that are composed of carbon, hydrogen, and oxygen held together by covalent bonds, such as in BPA. Release or migration of reactively or chemically bonded monomer from a polymer will in turn require cleavage of the covalent bond(s). Cleavage of covalent bonds can occur through chemical processes such as oxidation and hydrolysis [1, 2]. The monomer BPA has been reported as a breakdown product of the BPA-based polymer (polycarbonates and epoxy resins) when exposed to acidic or basic materials over time and at elevated temperatures [2], such as the detection of BPA in the contents of baby bottles [27] and in tin cans with BPA inner linings [2]. Although present at low concentrations, BPA has also been detected in water contained in plastic water bottles [27, 28]. This has been associated to the leaching of the BPA monomer from the plastic bottles, where repeated washing of the containers may have accelerated the leaching process [2].

Another possible mechanism for the availability of free monomers is through the release of unreacted constituent monomers from the polymer [1]. The antioxidant TNP is synthesized from NP and some of the unreacted NP remains in the TNP product. Similarly, there may be some unbound BPA monomers after the polymerization of BPA. An estimated 100 tons of BPA are released into the atmosphere each year through synthesis [29]. Unreacted or unbound monomers have been found in materials stored in plastic food containers made of BPA-polycarbonate plastics. Nonylphenol has also been demonstrated to potentially migrate from HDPE into stored materials [2].

Release of BPA, NP, and PBDEs from plastic materials can therefore occur during the initial synthesis, incorporation into the polymers, and the service life of resulting plastic products.

2.3 Monomers and Additives in Landfills and/or MSW Dumping Sites

An important pathway for the release of BPA, NP, and PBDEs is during the eventual disposal of plastic products in landfills or MSW dumping sites [1, 12, 13]. Plastic disposable products have been reported to account for more than one-third of the production volume of plastics [30]. Plastic disposable products (e.g., plastic disposable eating utensils, plastic bottles for bottled water, plastic bags) have usually short useful life span in timescales of hours, minutes, or seconds [2]. This situation puts burden to landfills and MSW dumping sites since plastic materials can persist for long periods of time. Moreover, the average urban MSW generation around the world has been reported to have increased from about 0.64 kg per person per day in 2002 to 1.2 kg per person per day in 2012, and it is further estimated to increase to 1.42 kg per person per day by 2025 [31]. The amount of plastic wastes in MSW ranges from 8 to 12% [2, 31]. Thus, it can be expected that considerable amounts of plastic wastes will be continuously disposed of in MSW dumping sites worldwide.

Since plastics are made up of monomers and can contain additives, these chemicals may be released from plastics disposed in landfill and dumping sites. Rainwater can wash off the additives and monomers from the layers of disposed plastics [32, 33]. The study by Masoner et al. [34] revealed that landfills in wet environments or that receive greater amounts of precipitation (i.e., >50 cm annually) produced leachate with greater frequencies of detection and concentrations of contaminants that include BPA and NP compared to landfills in drier environments. Through hydrolysis, BPA and NP and some other plastic-derived pollutants will then be found in landfill leachates.

Landfill leachates have two phases: the aqueous or dissolved and the particulate or adsorbed phases. The fate of chemicals in the landfill sites will also be influenced by their physical and chemical properties, and by the various redox conditions and biological processes occurring through the life of the landfill [1, 17, 18]. It can be assumed that less hydrophobic substances will elute easily from the plastic wastes and rapidly move into the leachate compared to the more hydrophobic substances [20]. Among the three additives, BPA is less hydrophobic. Thus, it would likely partition into the dissolved phase. The more hydrophobic NP and PBDEs would be expected to be associated with the particulate matter in the leachate.

2.3.1 Leaching of BPA, NP, and PBDEs from Plastic Wastes

In landfill or dumping sites, plastics are exposed to an extraction solvent in the form of acidic, neutral, or alkaline leachates [1]. Formation of the different types of leachates happens during the different phases of decomposition occurring in the landfill. There is a strong relationship between the state of waste decomposition and the characteristics of the leachates [33].

During the initial aerobic phase of the landfill which lasts only for a few days, the oxygen present in void spaces of freshly dumped waste is rapidly consumed, resulting in the production of CO_2 and an increase in the temperature of the waste materials. Waste decomposition may then progress into the anaerobic acid phase [1, 33]. Leachates resulting from the release of moisture during compaction of the waste materials and the production of CO_2 have acidic pH (pH 4.5–7.5) [33] with high ionic strength [1] that may favor the decomposition of easily degradable organic compounds [33]. Polycarbonates and epoxy resins may be degraded into the constituent monomer BPA [2] at these stages due to the acidic pH of the leachate, and the high temperature and pressure of the compacted waste materials in the landfill.

Neutral leachate found in landfills in the stable methanogenic phase generally contains very high concentrations of colloidal and/or dissolved organic matter (DOM) [1, 33]. The DOM in the leachate contains a variety of organic degradation products. It can affect the leachate composition in relation to the other constituents through the complexing properties of the high-molecular-weight component of the DOM, such as facilitating the leaching and transport of hydrophobic compounds via sorption to the organic matter [1, 33].

One of the bulk parameters used to describe DOM content in leachates is dissolved organic carbon (DOC) [1, 33]. In the comparison of the DOC content in an acid-phase leachate and in a methanogenic phase leachate, higher molecular weight compounds (MW $>$ 1,000) accounted for 32% of the DOC in the methanogenic phase leachate compared to 1.3% of the DOC content in the acid-phase leachate [33].

Organic pollutants have been found to be predominantly attached to colloids and/or in the dissolved phase of the leachates [35, 36] with their occurrences generally decreasing with increasing log K_{ow} [35]. Similarly, Masoner et al. [34] observed the greatest frequency of detectable contaminants that include BPA and NP, and the highest concentrations of contaminants in leachates with the highest DOC concentrations ($>$1,000 mg/L). The DOM or DOC in the leachates may have acted as the carrier for the organic pollutants [1, 35]. The abundance of organic pollutants, including those with high hydrophobicity, e.g., NP [35] and PBDEs [37] in the dissolved phase of the leachates, would confirm the hypothesis that solubility of hydrophobic organic compounds is increased in the presence of DOM.

Similarly, alkaline leachates were found to contain high-molecular-weight organic compounds [1], such as the presence of phenols in leachates with pH values at 9.8 or more [38]. Under alkaline conditions, different modes of degradation of the polymer may occur resulting in the generation of BPA.

2.3.2 Action of Microorganisms

Unless segregation of waste (or trash separation) is strictly implemented, most landfills and MSW dumping sites receive all types of wastes including household waste with high proportions of degradable organic matter which in turn promotes the proliferation of various microbial populations in the dumping sites. These microorganisms have potentials to degrade or transform the released additives [1]. Microbial degradation or bio-decomposition of putrescible waste increases the levels of DOC. High levels of DOM in the leachate will promote elution or leaching of hydrophobic compounds from the dumped plastic waste through sorption to the organic matter [1, 17, 33, 34]. In landfills, biotic hydrolysis is considered more important than abiotic hydrolysis. Biotic hydrolysis may take place at the surface of the original plastic products, or after they have been released from the products and dissolved in the leachate, or from another surface to which they adsorbed after leaving the original resin. Biotic hydrolysis is also strongly associated to the methanogenic flora (i.e., landfills in the methanogenic phase); thus, biotic hydrolysis would likely occur in neutral leachates. Methanogenic leachates are therefore expected to be more extractive than acidogenic leachates [2].

Anaerobic microbial degradation of BDE-209, the major component of the commercial deca-BDE product to lower but more toxic congeners, has been confirmed by laboratory studies [39–41]. The underground environment of dumping sites can become anaerobic due to degradation of organic matter in the waste, as manifested by the generation of methane gas or the occurrence of methanogenic leachates. Such anaerobic conditions in the dumping sites can facilitate the debromination of BDE-209. Transformation of BDE-209 in the environment through debromination (i.e., bromine atoms are sequentially removed from the parent molecule) has an important implication because it can be a source of the lower PBDE congeners which are more toxic and bioaccumulative [12, 13, 41, 42].

Alkylphenols also appeared to be the final product in the degradation study of alkyphenol ethoxylates under methanogenic conditions [2]. Nonylphenol polyethoxylates have been reported to be aerobically degraded through the removal of ethoxy units down to nonylphenol monoethoxylate (NP1EO) which in turn will be anaerobically degraded to NP. Similarly, degradation of BPA by microorganisms has also been reported. Biodegradation of BPA was found to be effective in organic-rich sites, where the concentration of BPA decreased with time [18].

3 Evidences on the Occurrence of BPA, NP, and PBDEs in Landfill or MSW Leachates

3.1 BPA and NP

Results from analyses of landfill leachates suggest that the additive or unreacted BPA is readily released from its polymer during the early age of a landfill, i.e., under acidogenic conditions being more hydrophilic [20]. This has been supported by leaching studies with water-containing acetic acid and ethanol to mimic acidogenic leachates [1]. Similarly, BPA was found mainly in the dissolved form rather than bound to macromolecular organic substances in leachates [18]. Only an average of 1% up to a maximum of 7% BPA was observed in the solid phase of ($n = 8$) leachate samples [20].

Based on available data, the concentrations of BPA and NP measured in leachate samples collected from various landfill sites of some countries are summarized in Table 1. Detection of BPA and NP in landfill leachates has been reported in Japan [20, 38, 44–46]; in selected tropical Asian countries, Cambodia, India, Lao PDR, Malaysia, the Philippines, Thailand, Vietnam [1], Denmark [6], Germany [47], the USA [34, 49], and Sweden [35]; and from various sources as reviewed by Kjeldsen et al. [33]. The BPA concentrations ranged from <0.01 μg/L (Sweden) [35] to as high as 17,200 μg/L (Japan) [46]. The concentrations of NP ranged from less than detection limit (Denmark) [6] or 0.05 μg/L (Japan) [20] to 98 μg/L (Cambodia) [1].

The highest detected concentration of BPA at 17,200 μg/L is four orders of magnitude higher than the proposed water quality objective of 5 μg/L BPA for surface water [43]. The highest detected concentration of NP at 98 μg/L is one order of magnitude higher than the maximum acceptable concentration of 2 μg/L NP for surface water [48], and three orders of magnitude higher than the proposed water quality objective of 0.04 μg/L NP in surface water [43]. The upper range concentrations of BPA and NP in the different leachates collected from landfills or dumping sites of various countries generally exceeded the water quality standards, indicating that leachates are significant sources of BPA and NP in receiving bodies of water such as rivers and lakes, and therefore may potentially contaminate surface and ground waters. Thus, provisions for collection and treatment of leachates before discharging to the aquatic environment are very important components in the operations of landfills or dumping sites.

The concentrations of BPA in the leachates were generally higher than the concentrations of NP. Among the phenols analyzed in leachates from four landfills in Sweden [35], BPA was detected with the highest total concentrations (<0.01–107 μg/L), followed by 4-*t*-BP (0.027–8.1 μg/L) and 4-NP (<0.1–7.3 μg/L). Similar trends were also observed in the leachates obtained from the dumping sites of tropical Asian countries: BPA > NP > OP [1]. Kurata et al. [38] observed high detection rates and wide concentration ranges of BPA and NP in landfill leachates in Japan, i.e., in all the leachate samples obtained from 38 MSW landfill sites. Asakura et al. [20] also detected alkylphenols including NP in approximately 80%

Table 1 Concentrations of bisphenol A and nonylphenol in landfill leachates from various countries

Additive or monomer	Country	No. of landfills	No. of leachate samples	Concentration range (μg/L)	Surface water quality standard (μg/L)	References
Bisphenol A					5[a]	[43]
	Lao PDR	1	4	0.18–26		[1]
	Cambodia	2	6	6.6–55		[1]
	Vietnam	3	6	2.3–34		[1]
	India	1	3	19–205		[1]
	Thailand	1	3	160–570		[1]
	The Philippines	2	3	8.3–1,100		[1]
	Malaysia	3	8	63–4,300		[1]
	Japan	5/8 (sites)[b]	8	0.15–12.3		[44]
	Japan	7/11 (sites)[b]	11	6.3–2,980		[45]
	Japan	10	10	<0.5–17,200		[46]
	Japan	2	8	0.07–228		[20]
	Japan	38	41	0.009–3,600		[38]
	Germany	4	2[c]	67.9–85.6		[47]
			2[d]	24.8–146		
	Sweden	4	8	<0.01–107		[35]
	USA	19	19	0.1[e]–6,380		[34]
	Unspecified			200–240		[33]
Nonylphenol					0.04[a]	[43]
					2[f]	[48]
	Lao PDR	1	4	0.74–2.1		[1]
	Cambodia	2	6	3–98		[1]
	Vietnam	3	6	0.18–4.6		[1]
	India	1	3	3.5–4.6		[1]
	Thailand	1	3	2.2–30		[1]
	The Philippines	2	3	0.89–7.6		[1]
	Malaysia	3	8	8–54		[1]
	Japan	2	8	0.05–0.07		[20]
	Japan	38	41	0.027–6.4		[38]
	Denmark	10	10	<Detection-7		[6]
	Sweden	4	8	<0.1–7.3		[35]

(continued)

Table 1 (continued)

Additive or monomer	Country	No. of landfills	No. of leachate samples	Concentration range (μg/L)	Surface water quality standard (μg/L)	References
	USA	19	19	8–320		[34]
	Unspecified			6.3–7		[33]

[a] Proposed water quality objective in mg/m^3 (Canada)

[b] Ratio of the number of landfills with BPA detection to the total number of landfills investigated

[c] Dump water

[d] Compost water

[e] Reporting limit

[f] Maximum acceptable concentration (European environmental quality standard)

of raw leachates. BPA was among those most frequently detected in landfill leachates collected from 19 landfill sites in the USA [34].

Further, Kurata et al. [38] observed higher detection rates of BPA in leachates with pH slightly higher than 7 up to less than pH 9. Leaching of BPA from polycarbonate plastics was found to be accelerated above pH 8 which indicated that BPA polymer is easily dissociated to BPA under alkaline conditions [50]. BPA has a pKa of 9.59–11.30 and will therefore be dissociated under environmental conditions of high pH [19]. Thus, plastic wastes in a high-pH environment would likely favor the presence of BPA in the leachates [18].

3.2 PBDEs

In the study by Kwan et al. [37] that examined the types of PBDEs in the leachates ($n = 24$ samples) collected from MSW dumping sites of eight tropical Asian countries (Lao PDR, Cambodia, Vietnam, India, Indonesia, Thailand, the Philippines, Malaysia), the congener profiles in the leachates reflected the basic composition of the technical PBDE mixtures. Deca-BDE (BDE-209) was predominant in most of the leachate samples. The other predominant congeners were BDEs 99, 47, 206, 203, 183, 153, 196, 208, 207, 154, and 49. These congeners have been identified as components of the commercial penta-BDE mixture, octa-BDE mixture, and deca-BDE mixture [14, 51]. This is an indication of the release of PBDEs from plastic and synthetic textile fiber wastes disposed of in landfills or dumping sites.

Occurrence of PBDEs in landfill leachates has also been reported in the USA [52], Canada [53, 54], Sweden [55], Japan [24], Indonesia [56], and South Africa [57, 58]. The concentrations of some PBDE congeners that have been detected in landfill leachates from various countries are summarized in Table 2. In general, the concentrations of PBDEs in the leachates from the MSW dumping sites of most tropical Asian countries are higher than those reported in other countries. The total

Table 2 Concentrations of selected PBDE congeners in raw landfill or municipal solid waste leachates from various countries [37]

Country	Sample	Concentration (ng/L)						References
		BDE-33/28	BDE-47	BDE-66	BDE-85	BDE-99	BDE-100	
Lao PDR	MSW adsorbed + dissolved	ND[a]	0.151–0.391	ND-5.62	ND-2.71	<LOD[b]-0.351	ND-0.073	[37]
Cambodia	MSW adsorbed + dissolved	0.640–1.20	43.9–44.4	1.60–3.97	1.20–3.10	71.5–79.7	2.74–4.86	[37]
Vietnam	MSW adsorbed + dissolved	ND	0.803–2.65	ND-<LOD	ND	<LOD-157	<LOD	[37]
India	MSW adsorbed + dissolved	27.9	31.4	6.19	0.177	8.14	0.457	[37]
Thailand	MSW adsorbed + dissolved	ND-1,280	1.57–18,800	ND-1,380	ND-66.6	2.05–1,590	0.238–75.2	[37]
The Philippines	MSW adsorbed + dissolved	0.074–0.441	0.346–13.1	<LOD-0.415	ND-0.912	0.375–24.1	0.039–2.71	[37]
Malaysia	MSW adsorbed + dissolved	0.459–2.83	23.5–48.5	0.898–3.82	0.219–2.97	33.9–72.8	4.55–11.0	[37]
Japan	MSW overall	<0.008–0.97 (28)	<0.008–2.2	<0.008-<0.5		<0.008–1.8	<0.008–<0.5	[24]
South Africa (1)	MSW overall	0.1–3.3 (28)	1.470–9.790	ND-4.020		ND-5.190	ND-2.162	[57]
South Africa (2)	MSW overall	ND-42.4(28)	0.05–2,990		ND-1.240	0.10–2,160	0.06–1,180	[58]
Canada, North	Landfill total		BMDL[c]-6.200			BMDL-2.460	BMDL-2.587	[53]
Canada, South	Urban landfill total		BMDL-194			BMDL-500	BMDL-100	[53]
USA	Landfill[d]		<5,000			<8,000	<2,000	[52]

(continued)

Table 2 (continued)

Country	Sample	Concentration (ng/L)						References
		BDE-153	BDE-154	BDE-183	Tetra[e]-BDEs	Penta[f]-BDEs	Hexa[g]-BDEs	
Lao PDR	MSW adsorbed + dissolved	ND	ND	ND-<LOD	0.151–6.01	<LOD-3.13	ND-<LOD	[37]
Cambodia	MSW adsorbed + dissolved	10.5–20.6	6.68–9.12	2.11–4.59	67.0–68.7	75.4–87.7	18.2–30.2	[37]
Vietnam	MSW adsorbed + dissolved	ND	ND	ND-<LOD	1.62–3.04	<LOD-1.57	ND-<LOD	[37]
India	MSW adsorbed + dissolved	<LOD	<LOD	<LOD	44.4	8.77	<LOD	[37]
Thailand	MSW adsorbed + dissolved	0.304–429	0.231–77.7	ND-189	1.97–2,180	2.38–1,980	0.626–515	[37]
The Philippines	MSW adsorbed + dissolved	0.109–7.45	<LOD-5.65	<LOD-6.62	0.422–16.5	0.414–27.7	0.11–13.3	[37]
Malaysia	MSW adsorbed + dissolved	15.6–31.9	5.73–9.28	7.27–21.8	26.4–60.0	40.3–81.8	22.3–47.5	[37]
Japan	MSW overall	<0.008–<0.5	<0.008–1.2					[24]
South Africa (1)	MSW overall	ND-0.875	ND-2.18	8.39–54.8				[57]
South Africa (2)	MSW overall	ND-7,990	ND-713	ND-5,890				[58]
Canada, North	Landfill total	BMDL-3.850	BMDL-2.400	BMDL-28.4				[53]
Canada, South	Urban landfill total		BMDL-81.7					[53]
USA	Landfill[d]	<1,000	<1,000					[52]
Sweden[h]	MSW total				8.5–7,100	1.7–7,000	<LOD-2	[55]

Country	Sample	Concentration (ng/L)						References
		Hepta[i]-BDEs	Octa[j]-BDEs	Nona[k]-BDEs	BDE-206	BDE-207	BDE-209	
Lao PDR	MSW adsorbed + dissolved	0.137–0.356	6.22–8.55	0.399–3.82	0.207–2.89	0.156–0.192	0.776–1.02	[37]
Cambodia	MSW adsorbed + dissolved	7.45–12.9	9.14–19.9	51.7–52.0	17.2–26.8	12.3–17.1	53.6–148	[37]
Vietnam	MSW adsorbed + dissolved	ND-1.42	<LOD-1.14	6.36–7.87	3.06–4.80	2.04–2.21	29.1–34.6	[37]
India	MSW adsorbed + dissolved	5.5	12.2	339	227	27	37	[37]
Thailand	MSW adsorbed + dissolved	0.341–261	3.12–1,560	2.99–5,560	0.778–3,060	1.26–1,700	12.5–97,800	[37]
The Philippines	MSW adsorbed + dissolved	<LOD-6.70	0.505–15.4	0.686–11.8	0.261–5.61	0.228–3.96	1.49–116	[37]
Malaysia	MSW adsorbed + dissolved	11.5–31.7	26.5–36.5	22.3–34.8	6.73–11.6	6.34–9.08	22.3–31.2	[37]
Japan	MSW overall						<0.800–<50	[24]
South Africa (2)	MSW overall						ND-6,380	[58]
Canada, North	Landfill total				ND-4.41	ND-7.310	ND-104	[53]
Canada, South	Urban landfill total					BMDL-21.3	BMDL-460	[53]
USA	Landfill[d]					<2,000		[52]
Sweden[h]	MSW total	<LOD-5	<LOD-56	<LOD-1,100			<LOD-4,200	[55]

[a] Not detected
[b] Limit of detection
[c] BMDL: Below method detection limit
[d] Upper range concentrations estimated from the figure presented [52]
[e] Tetra-BDEs = ∑BDEs 47, 49, 66, 71, 75, 77
[f] Penta-BDEs = ∑BDEs 85, 99, 100, 116, 118, 119, 126
[g] Hexa-BDEs = ∑BDEs 138, 153, 154, 155, 166
[h] BDE congeners for each homologue were not specified
[i] Hepta-BDEs = ∑BDEs 179, 181, 183, 188, 190 [55]
[j] Octa-BDEs = ∑BDEs 196, 197, 202, 203
[k] Nona-BDEs = ∑BDEs 206, 207, 208

concentrations of 46 PBDE congeners from mono- to deca-BDEs in the leachates from the tropical Asian countries range from 3.7 to 133,000 ng/L. The highest concentration of BDE-209 at 97,800 ng/L was obtained in the leachate from a dumping site in Thailand [37].

In the study by Kwan et al. [37], the congener profiles of the PBDEs were found to be highly variable among the MSW dumping sites and even among samples taken from the same sites. A number of studies also reported that PBDE concentrations in landfill leachates were scattered over a wide range, with some of the PBDE congeners in the thousands of nanograms per liter range [24, 52, 53, 55, 57, 58]. The variability may be caused by the heterogeneous nature of the MSW, the different composition of the flame retardants in consumer products, or the different processes occurring in the landfills, e.g., biodegradation of PBDEs through anaerobic debromination and the amount and distribution of precipitation in the landfill.

Possible transformation of BDE-209 by debromination to lower PBDE congeners with higher toxicity (i.e., tetra-, penta-, hexa-, and hepta-BDEs) was demonstrated by the occurrence of congeners that are not contained in the commercial PBDE products (e.g., BDEs 202, 179, 188, 37, 32, 15, 12/13, 8, 7, 3, 2, and 1) in the leachate samples from tropical Asian countries [37]. Further, congeners that are present in trace proportions in the commercial mixtures (e.g., BDEs 208, 207, 206, 49, 28, and 17) were observed to be proportionately more abundant in the leachates [37]. Anaerobic debromination of BDE-209 may have occurred in the dumping sites. Degradation of labile waste materials to methane and CO_2 occurs under anaerobic conditions [33], where the pH of the leachates (i.e., in the methanogenic phase) ranges from 7.5 to 9 [59]. The pH values of the leachates obtained from the tropical Asian countries were within the range for landfills in the methanogenic phase [37], suggesting anaerobic conditions of the MSW dumping sites, thus facilitating the anaerobic debromination of BDE-209.

Another mechanism for the transformation of deca-BDE to lower BDE congeners is through photolytic debromination by either UV light [13, 60, 61] or natural sunlight [62, 63]. BDE-202 which is not contained in commercial PBDE products [51] has been proposed as a debromination marker through photolysis of BDE-209 [61]. Photolytic debromination of higher brominated PBDEs, such as BDE-209, may occur in landfill sites of countries that receive strong and prolonged solar radiation. The detection of BDE-202 in the leachates collected from the dumping sites of tropical Asian countries [37] could indicate the occurrence of photolytic debromination in MSW dumping sites.

Examination on the partitioning of PBDEs in the leachates showed that PBDEs were predominantly found in the adsorbed phase which is reasonably based on their hydrophobic character [37]. However, considerable amount of PBDEs were also found in the dissolved phase. Dissolved organic matter may have contributed to the dissolution of the PBDEs in the aqueous phase and this was confirmed by higher concentrations of DOC (i.e., 596–964 mg/L) as compared to particulate organic carbon (i.e., 29–55 mg/L) in the leachates [37]. Dissolution of PBDEs by DOM may facilitate their dispersion or transport to the aquatic and terrestrial environments especially in the absence of a proper system for leachate collection and treatment.

3.3 Socioeconomic Factors Influencing the Occurrence of Plastic-Derived Contaminants in Landfills and/or MSW Dumping Sites

The preceding discussions demonstrated that additives and monomers are released from plastic wastes to ambient environments through landfill leachates. The amounts and composition of the wastes control the concentrations of the plastic-derived chemicals in the leachates and in the receiving waters. However, the amounts and composition of the wastes are also largely affected by socioeconomic factors. High population growth rates, rapid urbanization, and greater prospects for industrialization will likely result in higher waste generation and leachate production in the landfill or MSW dumping sites [64]. These factors will then promote the occurrence and transport of pollutants to the environment. In the case of BPA (Table 1), relatively higher concentrations were reported in the leachates from industrialized countries such as Japan [38, 45, 46] and the USA [34]. Higher concentrations of BPA were also found in the leachate samples from Malaysia, the Philippines, Thailand, and India [1] which are more industrialized [65] and/or more populated [66] than Lao PDR and Cambodia.

Relatively higher concentrations of PBDEs (e.g., BDE-209; Table 2) were also found in the leachates from MSW dumping sites of countries that are more industrialized and/or more populated. However, relatively high concentrations of PBDEs were also obtained in the leachates from Cambodia (Table 2) which is not highly industrialized. Importation of E&E waste (or e-waste) may be one of the possible causes for the relatively higher concentration of PBDEs in the leachates in Cambodia. Some tropical Asian countries or developing countries may be recipients of used e-products and e-waste. E-waste has been identified as one the fastest growing waste streams worldwide due to the high obsolescence rate of E&E equipment [67]. Importation of e-waste to other countries, although illegal under the Basel Convention [68] may be considered as a cheaper alternative to the costly treatment of regulated substances including the PBDEs, and possibly seen as the solution to the strict environmental regulations of other countries. Thus, importation of e-waste can be a potential source for the release of PBDEs during usage of used discarded e-products, recycling operations, and disposal of e-waste in landfills or MSW dumping sites especially in developing countries.

In addition, dumping together of plastic wastes with highly degradable organic waste will result in highly anaerobic conditions in the MSW dumping sites and generation of more dissolved organic matter. This will then facilitate the leaching of the additives and monomers, including the transformation of deca-BDE and other higher brominated PBDE congeners to more toxic congeners. Thus, segregation of biodegradable organic waste (e.g., kitchen waste, paper, and other similar organic waste) from plastic waste by providing separate landfills or dumping sites each for the degradable organic waste and for plastic-containing waste may help prevent the release of BPA, NP, and PBDEs to the environment. However, segregation of waste is not vigorously practiced in most developing countries. Instead, most of the wastes are dumped altogether in the MSW dumping sites, thus possibly contributing to the high concentrations of plastic-derived contaminants in landfill leachates.

4 Conclusions and Recommendations

Additives and monomers can leach out from plastics. BPA, NP, and PBDEs are widely detected in landfill leachates. Although the concentrations in the leachates may be considered low as they are usually in the range of less than 1 mg/L, the concentration levels sometimes exceed water quality standards, e.g., for surface waters that have been set for the protection and preservation of aquatic life. The release of BPA, NP, and PBDEs from plastics is influenced by their physical and chemical characteristics, the conditions in the landfill or MSW dumping sites, as well as economic and social factors. To mitigate the impact of these pollutants, e.g., contaminating the groundwater and other bodies of water, dumping sites must be properly designed with provisions for collection and treatment of landfill leachates. Another simple option would be to reduce the anaerobic conditions in the dumping sites through segregation of highly degradable organic waste from plastic wastes. On a larger scale, international regulations such as the Basel Convention should be respected and/or strictly implemented so as not to burden the limited resources of developing countries in handling these toxic and hazardous waste. Finally, each individual can also help reduce the proliferation of these pollutants in the environment by limiting the use of plastic products to only those that are very essential and with no other alternative products.

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Degradation of Various Plastics in the Environment

Kalliopi N. Fotopoulou and Hrissi K. Karapanagioti

Abstract It is very important to understand the interaction between plastics and environment in ambient conditions. The plastics degrade because of this interaction and often their surface properties change resulting in the creation of new functional groups. The plastics after this change continue to interact with the environment and biota. It is a dynamic situation with continuous changing parameters. Polyethylene, polypropylene, and polyethylene terephthalate (PET) degrade through the mechanisms of photo-, thermal, and biodegradation. The three polymers degrade with different rates and different pathways. Under normal conditions, photo- and thermal degradation are similar. For polyethylene, photo-degradation results in sharper peaks in the bands which represent ketones, esters, acids, etc. on their infrared spectrum. The same is true for polypropylene but this polymer is more resistant to photo-degradation. The photo-oxidation of PET involves the formation of hydroperoxide species through oxidation of the CH_2 groups adjacent to the ester linkages and the hydroperoxides species involving the formation of photoproducts through several pathways. For the three polymers, interaction with microbes and formation of biofilms are different. Generally, biodegradation results in the decrease of carbonyl indices if the sample has already been photodegraded by exposure to UV. Studies with environmental samples agree with these findings but the degradation of plastics is very subjective to the local environmental conditions that are usually a combination of those simulated in laboratory conditions. For example, some studies suggested that fragmentation of plastic sheet by solar radiation can occur within months to a couple of years on beaches, whereas PET bottles stay intact over 15 years on sea bottoms.

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Contents

1 Introduction

Plastic is the largest component accounting for 50–80% of debris that contaminates marine habitat at global scale [1]. Plastic waste once released to the environment should be classified as hazardous [2]. It is known that virgin polymers are hydrophobic and inert towards aqueous cations. However, polymers such as polyethylene (PE) and polypropylene (PP) sorb persistent organic pollutants and metals from seawater after they are exposed to environmental conditions [3, 4]. Microplastics potentially sorb pollutants not only from water but also from air and soil [5]. According to Ioakeimidis et al. [6], the majority of the waste in the bottom of the Eastern Mediterranean and Black Seas is plastics, at a percentage up to 95% of total marine litter items. Furthermore, plastic particles in the ocean have been shown to contain quite high levels of organic pollutants (e.g., [7–11]). The plastics are persistent in the environment [12], sorb pollutants [13], and when cut into smaller pieces sorb from the atmosphere, seawater, and sediment [5].

The most widely used plastics are polyethylene [PE; high density (HDPE), low density (LDPE), and linear low density (LLDPE)], polypropylene (PP), PET, and polyvinyl chloride (PVC). The European demand for these plastics is up to 13,000 kt for PE, 8,000 kt for PP, 3,000 kt for PET, and 5,000 kt for PVC per year [14].

2 Degradation

Any change of the physical or chemical properties is called degradation and it could be due to chemical, physicochemical (photo-degradation, thermal degradation, and mechanical degradation), or biological processes (Fig. 1). The primary polymer degradation mechanisms either due to chemical or biological causes are hydrolysis and oxidation [15].

Photo-degradation is the process of decomposition of the material by the action of light, which is considered as one of the primary sources of damage exerted upon polymeric substrates at ambient conditions. Most of the synthetic polymers are susceptible to degradation initiated by ultra violet (UV) and visible light. Normally, the near-UV radiations (400–290 nm) in the sunlight determines the lifetime of polymeric materials in outdoor applications. The near-UV light quanta (400–290 nm) have energies from 3.1 to 4.3 eV which corresponds to 72–97 kcal/mol. This means that these UV quanta have energy for breaking the most chemical bonds [16]. Under normal conditions, photo- and thermal degradation are similar [17].

Biodegradation is governed by different factors that include polymer characteristics, type of organism, and nature of pretreatment. The polymer characteristics such as its mobility, tacticity, crystallinity, molecular weight, the type of functional groups and substituents present in its structure, and plasticizers or additives added to the polymer all play an important role in its degradation [18]. The initial breakdown of a polymer can result from a variety of physical and biological forces [19]. Biodegradation is defined by several steps that could be identified by specific terminology [20]. The first step of biodegradation is the biodeterioration that includes the combined action of microbial communities. Deterioration is a superficial degradation that modifies the mechanical, physical, and chemical properties of a given material [21]. The second step is the depolymerization which is characterized by the cleavage of polymeric molecules into oligomers, dimers, or monomers by catalytic agents secreted by microorganisms. The next step is the assimilation, and the last step is the mineralization. Assimilation refers to the integration of molecules transported in the cytoplasm in the microbial metabolism to produce energy, new biomass, storage vesicles, and numerous primary and secondary metabolites. Mineralization refers to the excretion of simple and different salts, and complex metabolites that reach the extracellular surroundings [20].

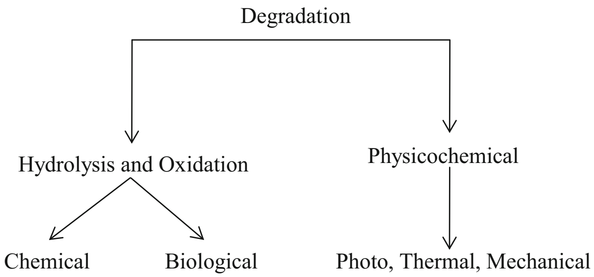

Fig. 1 Degradation pathways

Biodegradable plastics were originally developed in order to solve specific waste issues related to agricultural films or to the collection and separation of food waste. Biodegradation always follows photo-degradation and chemical degradation [22].

3 Polyolefins

Polyolefins are the largest group of thermoplastic materials. They are polymers of simple olefins such as ethylene, propylene, and butenes. Polyolefins consist only from carbon and hydrogen atoms and they are nonaromatic. The two most important and common polyolefins are polyethylene and polypropylene. According to Plastics Europe [14], the European demand for polyolefins (HDPE, LDPE, and PP) was up to 22,000 kt among 44,000 kt of all the polymers in Europe.

The photo-degradation of polyolefins is due to a variety of impurities. These impurities could be carbonyls and hydroperoxide groups which are formed during the fabrication or processing of the polyolefin products [23]. The susceptibility to photodegradation is dependent upon the nature of absorbing impurities and, consequently, is wavelength dependent. The oxidation susceptibility of polyolefins can be listed as follows: (isostatic) iPP $>$ LDPE $>$ LLDPE $>$ HDPE [24]. The first product of the oxidation is the hydroperoxide groups which are thermally and photolytically unstable. It decomposes to produce two radicals, each of which can participate in a chain reaction process. The presence of carbonyl groups in a degraded polymer indicates that oxidation has taken place and also, means that the material is vulnerable to further degradation since these groups are photolabile [25].

It is reported that there is a synergetic interaction between photo-oxidation and biodegradation [25]. Photo-oxidation of the polyolefins changes the high hydrophobic surface area to less hydrophobic, decreases molecular weight, decreases tensile strength, and, thus, favors biodegradation. On the other hand, as the polyolefins surface is hydrophobic in nature, it has been suggested that the more hydrophobic the bacterial cell surface, the higher the interaction with the polyolefins [26].

3.1 Degradation of Polyethylene (PE)

Polyethylene (PE) is a thermoplastic polymer consisting of long hydrocarbon chains. PE is used in a number of applications including flexible film packaging produced by the blown film process. Significant differences in physical properties have been observed in linear low density polyethylene (LLDPE), low density polyethylene (LDPE), and high density polyethylene (HDPE) blown films. Structural parameters, such as density/crystallinity, molecular weight and its distribution, short chain branching (SCB)/long chain branching (LCB) length and amount, and crystalline morphology are the key factors that control the properties. HDPE is the most crystalline PE, since its chains are linear and contain very little branching [27]. There are many intrinsic factors affecting polymer degradation. Such factors include the number of branching of the polymer, the molecular weight, the hydrophobicity/hydrophilicity ratio, the crystallinity, and the morphology of the polymer [15]. There are several publications that study the degradation of PE [28, 29] and the alteration of plastic surfaces in the laboratory or under controlled conditions in the field [30–34].

3.2 Photo- and Thermal Degradation of PE

At present, the mechanism of photo-degradation accounting for the main routes of degradation of PE is well understood and can be summarized as shown in Fig. 2 [35]. Light absorption by chromophoric defects results in the formation of radicals, which can react following different pathways: abstraction of a hydrogen atom from the macromolecular chain, addition to an unsaturated group (cross-linking reaction), or addition to oxygen [36]. Hydroperoxides are formed as primary photoproducts. Once they are formed, they can decompose by the scission of the weak O–O bond, which gives a macro-alkoxy and a hydroxyl radical HO. The alkoxy macroradical is the key intermediate in the reaction. This radical can react by several routes: b-scission with cleavage of the main chain to form aldehydes, abstraction of hydrogen without

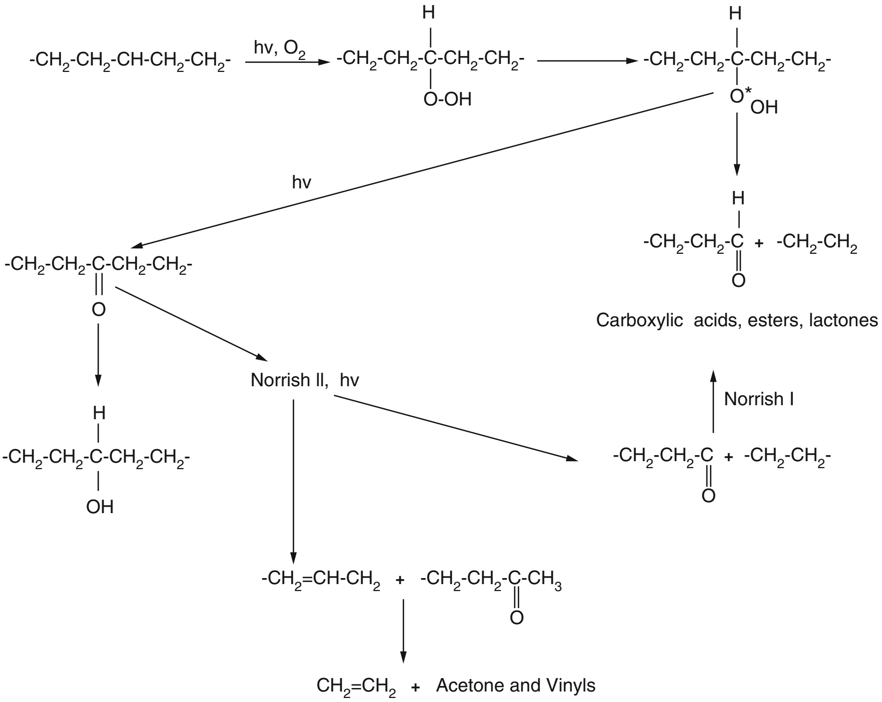

Fig. 2 The photo-degradation of PE [35]

cleavage of the chain to form hydroxyls, cage reaction between the pair of the radicals formed, i.e., macro-alkoxy radical and hydroxyl radical HO^1. The latter reaction produces chain ketones. It is worthy to recall that it has been recently proposed that ketones could be formed by a reaction that does not involve the decomposition of hydroperoxides. Ketones photochemically react by Norrish type I or type II reactions [37].

In the case of photo-degradable plastics, the materials are constructed with the incorporation of light-sensitive chemical additives or copolymers that weaken the bonds of the polymer in the presence of ultraviolet radiation. Photo-degradable plastics are designed to become weak and brittle when exposed to sunlight for prolonged periods. Photosensitizers used include diketones, ferrocene derivatives (aminoalkyferrocene), and carbonyl-containing species. These plastics degrade in a two-stage process, with UV light initially breaking some bonds leaving more brittle lower molecular weight compounds that can further degrade from physical stresses such as wave action or scarification on rocks [22]. It seems that degradation does facilitate the formation of microplastics which are initially the same polymer as the bigger item but with some of their sides degraded.

In the case of nonlight absorbing polymers such as PE, the absorption of light is attributed to unidentified chromophores that can vary from one PE to another. For PE, it is acceptable that the oxidized species are formed during processing. Initially, UV irradiation is absorbed by the chromophoric defects which lead to radical formation. Eventually, the radicals are added to oxygen and hydroperoxides are formed. The final products are carbonyl groups. Additional exposure to UV irradiation causes the carbonyl groups to undergo Norrish type I and/or Norrish type II reactions [25]. The Norrish type I reaction is the cleavage of a-C–C bond to form two free radicals, one of which is a carbonyl radical, which then participates in side reactions that result in further fragmentation of the chain. In the Norrish type II reaction, the excited carbonyl causes removal and acceptance of a c-hydrogen to form a diradical moiety to the molecule chain, which then gives two new smaller chains. The most damaging UV wavelength for a specific plastic depends on the bonds present, and the maximum degradation therefore occurs at different wavelengths for various types of plastics, e.g., it is around 300 nm for polyethylene (PE) [17].

There are many studies showing the photo-degradation of PE and the change on the surface functional groups. For example, Roy et al. [38] studied the photo- and thermal degradation of LDPE films under accelerated conditions. Fourier transformation infrared spectroscopy (FTIR) showed that the band representing the carbonyl index is more incisive for thermal and photo-degradation. Benitez et al. [39] studied the abiotic degradation of LLDPE and LDPE formulated with pro-oxidant additives under accelerated and environmental conditions. The FTIR showed a sharp increase in bands between 1,800 and 1,650 cm^{-1}.

In most of the studies, photo-degradation results in sharper peaks in the bands which represent ketones, esters, acids, etc. on infrared spectrum. Table 1 shows the main changes in the surface functional groups of PE under different photo-degradation conditions as were observed using FTIR.

Table 1 Main changes in the surface functional groups on PE surface after exposure to different conditions

Wavenumber cm^{-1}	Functional group	Degradation mode	Reference	Type of PE
1,733–1,743	Aldehydes or ester	UV-Xenon lamb	[31]	HDPE, LDPE, and LLDPE
	Carbonyl band	Xenon lamb	[40]	LLDPE
	Ester	Electron beam and gamma	[30]	HDPE
	Ketones and acid	Natural	[41]	HDPE
	Aldehydes	Accelerated environmental conditions	[39]	LDPE and LLDPE
	Esters and lactones	Photo-oxidation thermo-oxidation	[35]	PE with vinyl and *t*-vinylene groups
	Esters	Environment	[42]	Environmentally beached PE pellets
1,712–1,723	Ketones	UV-Xenon lamb	[31]	HDPE, LDPE, and LLDPE
	Acid	Xenon lamb	[40]	LLDPE
	Ketones	Electron beam and gamma	[30]	HDPE
	Ketones and acid	Natural	[41]	HDPE
	Carbonyl	Natural	[43]	HDPE
	Ketones	Accelerated environmental conditions	[39]	LDPE and LLDPE
	Carbonyl	Natural	[44]	HDPE
	Ketones and acid	Photo-oxidation thermo-oxidation	[35]	PE with vinyl and *t*-vinylene groups
	Ketones	Environment	[42]	Environmentally beached PE pellets

3.3 Biodegradation of PE

Plastic debris provides a substrate for marine life that lasts much longer than most natural floating substrates and has been implicated as a vector for transportation of harmful algal species. Biofilm formation varies with season, substrate, and location. A piece of plastic weighing 1 g and possessing 6% microbial biomass harbors nearly an order of magnitude more microbial biomass (in terms of carbon content) than 1,000 l of open ocean seawater [45].

The high hydrophobic level and the high molecular weight of PE make it non-biodegradable [46]. To make PE biodegradable requires modifying its crystalline level, molecular weight, and mechanical properties that are responsible for PE resistance towards degradation [47]. This can be achieved by improving hydrophilic level of PE and/or reducing its polymer chain length by oxidation to be accessible for microbial degradation [48]. Biodegradation of PE is known to occur by two mechanisms hydro-biodegradation and oxo-biodegradation [49].

Over the past 50 years, there are many studies showing that a number of strains interact with different kinds of PE causing some kind of deterioration. Microorganisms able to colonize the surfaces of polyethylene have diverse effects on its properties; seven different characteristics are usually monitored for change in order to establish the extent of biodegradation of the polymer: functional groups on the surface, hydrophobicity/hydrophilicity, crystallinity, surface topography, mechanical properties, molecular weight distribution, and mass balance [29]. Table 2 shows the changes in the surface functional groups and Table 3 shows the changes in the characteristics of different types of PE.

In general, it is accepted that in the presence of microorganisms, the concentration of the surface functional groups will decrease, which is commonly reported as a decrease in the carbonyl indices. This happens because microorganisms are commonly attached to the carbonyl groups [25, 26, 57].

Biofilms are sessile communities of microorganisms developed on a surface that can be composed of individuals from the same or different species [58]. Complex biofilm communities comprised of different microorganisms have been detected on polyethylene surfaces once they were exposed to different biotic environments. Studies on microorganism attachment to polyethylene have identified that the main limitation of the colonization process is the relatively high hydrophobicity of the polymer in contrast to the regularly hydrophilic surfaces of most microorganisms [26, 53]. It has been proposed that strains with more hydrophobic surfaces can play an important role in the initial colonization of the polymer. As PE surface is hydrophobic in nature, it has been suggested that the more hydrophobic the bacterial cell surface, the higher the interaction with the PE [26]. The other metabolic adaptation that can be important in polymer colonization is the production of surfactants which are molecules that can mediate the attachment process of microorganisms to the hydrophobic surface. Harshvardhan and Jha [28] stated that marine bacteria (*Kocuria palustris* M16, *Bacillus pumilus* M27, and *Bacillus subtilis* H1584), the

Table 2 Main changes in the surface functional groups for PE after exposure to different biodegradation conditions

Wavenumber cm^{-1}	Functional group	Degradation mode	Reference	Type of PE
1,733–1,743	Ketones	Marine bacteria	[28]	LDPE
	Esters	Monitor environment after 10 years in soils	[25]	LDPE
	Decrease in ester	Exposed to *B. sphericus* for 1 year	[50]	LDPE
1,712–1,723	Acids	Marine bacteria	[28]	LDPE
	Ketones	Monitor environment after 10 years in soils	[25]	LDPE

Table 3 Changes found in the literature for PE after exposure to different biodegradation conditions

Reference	Type of PE	Environment	Parameter	Changes
[25]	LDPE after UV irradiation	LDPE mixed with natural soils for 10 years	FTIR	UV irradiation increased carbonyl index, peak at 905–915 cm^{-1} due to biodegradation
[49]	PE with TDPA	*Rhodococcus rhodochrous*, *Cladosporium cladosporioides*, and *Nocardia asteroides*	SEM FTIR Molecular weight	Surface physically weak, readily disintegrated under mild pressure Band at 1,088 cm^{-1} due to polysaccharides Increased carbonyl index, decreased molecular weight Reduction in molecular weight
[28]	LDPE with 60 marine bacteria from Arabian sea	Monitor environment	FTIR Crystallinity	Peak at 905–915 cm^{-1} Reduction in crystallinity
[51]	LDPE mixed with different natural soils	Monitor environment	FTIR Weight loss Tensile strength Elongation brake	Peaks at 1,448–1,470, 2,800–300 cm^{-1} Weight loss due to biodegradation Tensile strength decreased Elongation brake decreased
[52]	LDPE with 12% starch	*P. chrysosporium* in soils with LDPE with 12% starch	FTIR	1,650–1,860 carbonyl compounds 900–1,200 peaks due to biodegradation
[53]	LDPE	*Pseudomonas* sp. AKS2	AFM Weight loss Tensile strength	Rough surface with cracks and grooves Time dependent weight loss Reduction in tensile strength
[54]	PE food plastic bags	Monitor environment (PE in 2 m depth in the sea)	Hydrophobicity	Decreased hydrophobicity
[55]	HDPE and LDPE	Monitor environment	Hydrophobicity AFM FTIR Weight loss	Decreased hydrophobicity Increased surface roughness Decreased carbonyl index

(continued)

Table 3 (continued)

Reference	Type of PE	Environment	Parameter	Changes
				Weight loss with higher rates for LDPE
[56]	HDPE, LDPE, and LLDPE	*Rhodococcus rhodochrous* ATCC 29672 after UV irradiation	Molecular weight FTIR SEM	Reduction in molecular weight Increased at 1,712 for pre-photo-oxidized samples HPDE film behaves differently than the LDPE and LLDPE and was not so favorable for microbial metabolism

microorganisms, use the PE surface as a carbon source. This is the first step of PE biodegradation and, simultaneously, a reduction in molecular weight happens. Once the size of the molecule is reduced, oxidation is required in order to transform the hydrocarbon into a carboxylic acid that can be metabolized by means of β-oxidation and the Krebs cycle [25].

3.4 Degradation of Polypropylene (PP)

PP is a thermoplastic material used in a wide variety of applications including packaging, labeling, textiles, etc. Due to high processability and low cost, PP is one of the most extensively produced polymers, especially, for auto industry. Pristine PP is resistant to photo-oxidation and thermal oxidation at moderate temperatures. However, PP is sensitive to various external aging environments (such as heat, light, and radiation), and, hence, has a relatively low service temperature. When PP is exposed to high temperatures or to an irradiation environment, the tertiary hydrogen atoms present in PP chains are susceptible to be attacked by oxygen [59]. It is well known that PP oxidation depends on both light and temperature in outdoor aging conditions. PP can also be photo-degraded because several molecular chains are affected in the wavelength range from 310 to 350 nm [60].

3.5 Photo- and Thermal Degradation of PP

PP is resistant to photo-oxidation at moderate temperatures. However, PP is sensitive to various external aging environments (such as heat, light, and radiation) and hence has a relatively lower service temperature. When PP is exposed to a high temperature or to an irradiation environment, the tertiary hydrogen atoms present in PP chains are susceptible to be attacked by oxygen [59]. The wavelengths of the sunshine at the earth's surface that are over 290 nm are enough to initiate the degradation and cause discoloration, chalking, and embrittlement of PP. Thus, evaluation of the service life of PP in a natural environment is a well-established practice [20]. There are many studies showing the accelerated degradation conditions for PP. Ultraviolet (UV) irradiation will cause a serious degradation of the material and, consequently, weaken its strength when it is exposed directly under sunlight. Many attempts have been made to investigate the results of photo-oxidation of the material in order to provide a good estimation to its long-term service performances. Two methods have commonly been used for this purpose. One is the outdoor weathering test, the other one is the accelerated weathering test [61]. Table 4 shows the studies for degradation of PP under different accelerated or environmental conditions.

The photo-oxidation of PP as described by Ranby [16] is presented in Fig. 3. The photo-degradation of polyolefins is due to a variety of impurities. The susceptibility to photo-degradation depends upon the nature of absorbing impurities and, consequently, is wavelength dependent. These traces of impurities and extraneous groups in the PP absorb UV light and form alkyl radicals on the chains by hydrogen abstraction.

3.6 Biodegradation of PP

Degradation of polyolefins in nature is a very slow process which is first initiated by environmental factors and followed by microorganisms [50]. PP being highly hydrophobic with high molecular weight, lacking active functional groups, and with continuous chain of repetitive methylene units shows resistance to biodegradation [68] since the formation of biofilm or attachment of microorganism on PP is very poor [69]. To make polyolefins biodegradable requires improving hydrophilic levels or reducing its polymer chain length by oxidation to be accessible for microbial degradation. Several studies have been done to improve these properties and to determine the effect of additives in the biodegradation process [70, 71]. Treatments including UV, thermal, and chemical lead to the oxidation of the polymer surface and the formation of carbonyl, carboxyl, and ester functional groups. This decreases the hydrophobicity of the surface and hence favors biodegradation. Limited studies have been done for the biodegradation of PP. Table 5 shows different studies for the biodegradation of PP under various conditions.

4 Polyesters

Aromatic polyesters such as PET constitute an important class of polymers with widespread applications such as fibers, films, and beverage containers. PET is considered to be one of the friendliest synthetic polymers used for food packaging. However, the presence of PET residues in the waste stream is substantial because of its extremely high resistance to atmospheric and biological agents [75]. PET is an aromatic polyester and

Table 4 Changes found in the literature for PP after exposure to different biodegradation conditions

Reference	Environment	Parameters	Changes
[62]	Accelerated and outdoor weathering	FTIR Molecular weight SEM	Different carbonyl products formed during degradation Reduction in molecular weight Increasing cracks in the surface with increasing exposure
[63]	Thermal	FTIR chemiluminescence spectroscopy	Initial peak wavelength of chemiluminescence emission at 490 nm remained constant during the early stages of thermal degradation New emissions developed with time in the red spectral region (i.e., 490, 660, and 740 nm) over an extended oxidation period
[64]	Xisha tropical environment	Macroscopic morphology Chromatic aberration Tensile strength Elongation break	Macroscopic cracks observed after 9 months of exposure Rapidly increasing chromatic aberration, the sample becomes darker with the exposure Reduction in tensile strength due to oxidation Dramatic decrease in elongation break. The toughness of the polymer is more sensitive than the strength
[65]	Electron irradiated aging in autoclave	Weight and geometry Tensile strength FTIR-ATR	No significant changes in geometry Reduction of tensile strength proportional to temperature Ether and carbonyl species due to oxidation
[66]	Accelerated photo-thermal aging	FTIR DSC Molecular weight	Different carbonyl species, hydroperoxides, and hydroxyl species due to exposure Reduction in crystallinity, for samples containing nanocomposites increasing crystallinity Reduction in molecular weight
[61]	Outdoor weathering and accelerated conditions	Tensile strength Intrinsic viscosity FTIR	Reduction in tensile strength Reduction in intrinsic viscosity The carbonyl contents increased with increasing exposure
[67]	Outdoor weathering and accelerated conditions	Tensile strength FTIR	Reduction in tensile strength Carbonyl concentration rose with the irradiation time and the increasing rate depends on UV content

like all aromatic polyesters provides excellent material properties and, hence, is commercially used. To date, these polymers are considered resistant against microbial attack [76, 77].

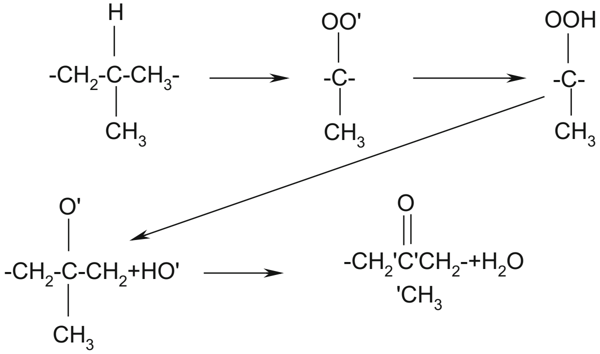

Fig. 3 The photo-degradation pathway for PP [16]

4.1 Polyethylene Terephthalate (PET)

The first stage to produce PET is the reaction of ethylene glycol with terephthalic acid or dimethyl terephthalate [78]. After the initial reaction, two or three polymerization steps are then performed, depending on the required molecular weight [79]. The chemical structure of PET is composed of repeated units as shown in Fig. 4. Each unit has a physical length of about 1.09 nm and a molecular weight of ~200 [80]. As it is shown in Fig. 4, PET monomer consists from an aromatic ring coupled with a short aliphatic chain that makes PET a stiff molecule as compared to other aliphatic polymers such as polyolefin or polyamide. The lack of segmental mobility in the polymer chains results in relatively high thermal stability. A textile grade polymer will have an average number of 100 repeat units per molecule so that the extended length of the typical polymer chain is about 100 nm with a molecular weight of ~20,000. Higher levels of polymerization produce higher strength fibers but the melt viscosity and stability of the melt to even tiny amounts of moisture causes hydrolytic degradation [80].

Zheng et al. [27] observed that in most cases, polymers with pure carbon backbones are particularly resistant to most methods of degradation, but polymers that include heteroatoms in the backbone (e.g., polyesters and polyamines) show higher susceptibility to degradation. While this is often true, there is, however, a secondary qualifier in the latter case; aromatic polymers tend to be resistant to degradation, despite the presence of bonds that are normally readily hydrolyzed [81]. PET is a classical example of such a polymer, i.e., although the ester bond that is part of PET can be easily broken, PET is resistant to degradation due to its aromatic group.

4.2 Photo-Thermal Degradation of PET

Photo-degradation of PET occurs after exposure to near-ultraviolet light resulting in either chain scission by Norrish I and II reactions. Cross-linking also takes place

Table 5 Changes found in the literature for PP after exposure to different biodegradation conditions

Reference	Environment	Parameter	Changes
[68]	PP and thermally treated PP in soil consortia for 12 months	FTIR Surface energy Mechanical properties	Carbonyl index increased due to thermal treatment Carbonyl index decreased due to biodegradation Crystallinity increased, tensile strength decreased
[72]	PP and UV irradiated PP in four different soil consortia	FTIR Surface energy Weight loss	Carbonyl index increased due to thermally treatment Carbonyl index decreased due to biodegradation Decreased hydrophobicity, highest weight loss for UV irradiated samples
[73]	Thermal and photochemical treatment for PP and then mixed with *R. rhodochrous* ATCC 29672	FTIR Molecular weight SEC	Increase in carbonyl index due to abiotic treatment The loss in molecular weights is lower in the case of additive-free PP *R. rhodochrous* cells were able to use the oxidized polymer films as carbon source
[71]	PP/starched based materials aged in soil	TGA	The kinetic parameters dependent on: (a) the influence of the atmosphere in which the experiment was carried out, (b) the composition of the blend, and (c) the process of degradation in soil
[74]	PP photo-degraded and then biodegraded	Molecular weight ^{1}H NMR	Decreased molecular weight Biodegradation occurred anaerobically

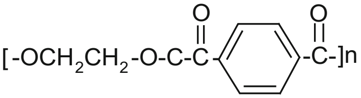

Fig. 4 Chemical structure of PET monomer

and polymer becomes brittle, discolored, and with uneven surface [37]. PET when exposed to UV light degrades rather rapidly leading to deterioration in physical and mechanical properties and develops intense yellow color [82]. It has been suggested that the photo-oxidation of PET involves the formation of hydroperoxide species through oxidation of the CH_2 groups adjacent to the ester linkages and the hydroperoxide species involving the formation of photoproducts through several pathways. The ester moieties in the terephthalate moiety as well as CH_2 groups are strongly involved in the photo-degradation of PET [83]. The vinyl ester ends also act as crosslinkers and gelling agents. They polymerize and the polymers thermally degrade to give yellow or brown polyenes that discolor the final polymer. The formation of highly conjugated species is catalyzed by carboxyl groups. The formation of colored species is followed by increase of more carboxyl terminated species. Hence, the product having higher carboxyl value is subject to more discoloration [80]. Furthermore, as the carboxyl content increases, the thermo-oxidative stability decreases. The carboxyl end groups act as catalysts for further degradation [48].

Venkatachalam et al. [80] suggest that the initial stage of thermal degradation is a random scission of the in-chain ester linkage resulting in the formation of a vinyl ester and carboxyl end groups. Transesterification of the vinyl ester then occurs to give the vinyl alcohol, which is transformed immediately to acetaldehyde. Limited studies have been done for the environmental degradation of PET. Djebara et al. [84] study PET after irradiation by MeV He^+. They observed that the colorless samples become brittle and a yellow color is observed as a function of irradiation. Decrease in the natural bonds of the polymer after irradiation was observed.

4.3 Hydrolytic Degradation of PET

The mechanism for the hydrolysis of PET is not fully understood and at least four different kinetic schemes have been proposed. It is thought that the water diffuses into the amorphous regions of the polymer and hydrolysis occurs there. The rate will obviously depend on the polymer morphology and its degree of crystallinity, and on relative humidity and temperature [85]. There are only a few studies about the hydrolytic degradation of PET. Kint et al. [75] study the hydrolytic degradation of PET copolymer containing nitrated units. The experiments revealed that the PET copolymers containing nitrated units degraded faster than semicrystalline and amorphous PET and the degradation rate increased with increasing content in nitrated units. Sammon et al. [85] study the effect of hydrolytic degradation on the structure of PET. They observed a dramatic change in the ν(C–H) band due to degradation. This was interpreted as resulting from a change in the environment of the aliphatic methyl groups and subsequent extensive hydrogen bonding, due to an increase in the numbers of hydrophilic end groups.

5 Environmental Degradation of Polymers

Limited studies exist on the evaluation of polymer degradations under environmental conditions in real world. Some of them are discussed in this section.

Gregory [86] used scanning electron microscopy (SEM) to determine the degradation of beached plastic pellets. Based on the SEM observations, he suggested that relative inertness is generally emphasized but also some degradation and oxidative aging is evident in the plastic pellets collected. This can ultimately lead to complete disintegration of the plastic pellets and dispersal as dust. Based on previous references, he suggests that some degradation occurs while the granules float at sea but most deterioration appears to take place after they have stranded on the beaches due to exposure to UV.

Orhan and Buyukgungor [52] tested the degradability of PE (starch blended LDPE) bags in soil. For 90 days, the bags did not degrade even with the starch. Only when the soil was inoculated with fungi, some degradation was observed. In a later study, after 5 months of soil burial, the starch peaks seemed to disappear in the FTIR spectra and microplastic pieces of bags were formed [87]. The order of decreasing susceptibility of the examined films was as follows: starch blended PE >>> LDPE > HDPE.

Endo et al. [3] studying the sorption properties of plastic pellets suggested that the degree of discoloring can be an index of residence time of the pellets in the seawater. Additives, especially phenolic antioxidants, are the major reason for discoloration. Based on the literature, phenolic antioxidants quench free radicals generated by exposure to UV light, high-temperature polymerization, nitrogen oxides in the air, etc., preventing the polymer from oxidizing. The sacrificial reaction of phenolic antioxidants forms byproducts having quinonoidal structures that cause yellowing of the polymer. They also used the carbonyl index to estimate the degree of weathering of plastic resin pellets. This is the absorbance of carbonyl moieties relative to the absorbance of reference peaks in IR spectra. It is frequently used for measuring light induced photo-oxidation of PE, since it normally increases with increasing exposure time. The carbonyl index values of the examined pellets in this study ranged from 0.00 to 0.89.

Basfar and Idriss Ali [88] study the natural weathering of films made using various formulations of LDPE and LLDPE. Natural (outdoor) weathering of PE or plastic films is generally carried out in accordance with ASTM 1435 D on suitable racks facing at 45° to south. The results showed that the UV stability of films strongly depends on the nature of stabilizers and light absorbers added. For all samples tested that were thin polyethylene films of 0.06 mm, the reduction in tensile strength less than 50% ranged between 30 and 590 days.

Ojeda et al. [43] studied LLDPE, HDPE, and PP film degradation under environmental conditions and more specifically under solar light. Film thickness varied from 15 to 80 μm. In less than a year, they observed a substantial reduction in molar mass and an increase in content of carbonyl groups, and the mechanical properties of the polymers decreased virtually to zero. PP was strongly oxidized at a much higher rate than those observed for HDPE and LLDPE. The main factors influencing the degradability were the frequency of tertiary carbon atoms in the polymer chain and the presence of a pro-oxidant additive. PP showed the most rapid loss of mechanical properties and started fragmentation in the second month of exposure whereas the mechanical strength of PP was negligible after 48 days. The mechanical strength of HDPE fell to zero in about 2 months of exposure, contributing to the subsequent disintegration. Initial fragmentation of LLDPE was observed after 3 months, and the mechanical properties were virtually nonexistent by 5.5 months.

Fotopoulou and Karapanagioti [42] studied environmentally degraded plastic pellets made from PE and PP. Based on SEM pictures, PE surface seemed to be chemically altered whereas PP was physically broken and not chemically altered as suggested by Ojeda et al. [43]. PE was further characterized with FTIR and surface functional groups were observed due to the oxidation of the surface.

Fotopoulou and Karapanagioti [89] studied environmentally degraded HDPE, PET, and PVC in the coastal zone. Degraded HDPE demonstrated an altered surface topography, color, and new functional groups. Degraded PET surface was uneven, yellow, and, occasionally, colonized by microbes. A decrease in FTIR peaks was observed for degraded PET suggesting that degradation had occurred. For degraded PVC, its surface became more lamellar and a new IR peak was observed.

Ioakeimidis et al. [90] studied degraded PET from the bottom of the Aegean Sea (~150–350 m depth). They used expiration dates on the bottles to determine the age of the plastic. They have found that PET surface remains unchanged for almost 15 years. After that, the surface functional groups which are present in the virgin polymer disappear and new surface functional groups are created. The surface of PET bottle samples collected from another sea (Ionian Sea) was also characterized in the same manner. The FTIR spectra of the bottles from Ionian Sea were compared with the FTIR spectra of the bottles from the Aegean Sea. The bottle ages that were estimated based on the FTIR comparison agreed well with the expiration dates on the bottles. Thus, degradation patterns were similar for bottles collected from both seas but less intense compared to the ones observed for samples collected from the beach in Fotopoulou and Karapanagioti [89]. Nevertheless, the degradation of plastics is very subjective to the local environmental conditions that are usually a combination of those simulated in laboratory conditions.

6 Conclusions

Only for the last 20 years, there have been studies on the degradation of plastics in the environment and only a few of them have been performed in the natural environment. Although there have been some steps towards the understanding of the degradation of plastics in the environment, there are still many questions to answer. How the changes caused by the environment in plastic can affect the environment? How we can classify the degraded plastics? How long it takes for each plastic to degrade? How smaller pieces of plastics (microplastics) interact with environment? Since these questions are many and unanswered at the moment, it is wise to suggest that the correct and rational management of plastics is our future.

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Occurrence of Marine Litter in the Marine Environment: A World Panorama of Floating and Seafloor Plastics

Christos Ioakeimidis, François Galgani, and George Papatheodorou

Abstract The marine environment is directly linked to human life. Healthy oceans have always been important to mankind as all life depends on them. Nowadays, marine litter, mainly plastic, is found widespread in the environment, in all sea compartments, posing one of the major threats for the marine environment. To date, the fate of this litter is still questionable and the identification of areas where litter permanently accumulates is a major challenge.

In the present chapter, a world panorama is given in respect to the occurrence of floating and seafloor plastics. Information on floating micro-, meso-, and macro-plastics is given, as well as information on plastics of size bigger than 10 mm lying on the seafloor (shallow waters, continental shelf, deep-sea environments) of world's seas.

Keywords Floating, Hot-spots, Plastic, Seafloor

Contents

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1 Introduction

Marine litter originating from many unspecified sources was initially identified as an aesthetic problem. Nowadays, it is one of the most serious, rapidly developing and worsening global environmental problems [1–3]. In 2012, the global production of waste had reached 1.3 billion tons and this figure is expected to double by 2025, while about half of this amount concerns non-biodegradable materials (i.e., plastics and metals) [4]. It is an evident fact that much of this waste escapes management schemes and finally ends up in the environment.

The global plastic production reached up to 280 million tons in 2012 [5], of which approximately 4.8–12.7 million tons are entering into the oceans every year [6]. The imprudent use of plastics in our everyday life [7, 8] elevated plastics into the major pollutant component of the world seas and oceans [9]. Plastics are ubiquitous in the marine environment, in vast quantities [10], and are present even on the most remote areas of the planet [11]. This is evident in certain areas of the globe (Fig. 1) for which plastics can be found in excess, consisting more than 80% of the recorded marine litter items. Such areas (hot-spots) can also be found in the Mediterranean Sea (Fig. 2). Especially for the Mediterranean coast, recent studies [12] have revealed that may be more affected than the oceanic gyres.

Once the plastics (synthetic polymers) are released into the oceans, the breakdown process (fragmentation) is initiated. The synthetic polymers when reaching the oceans are extremely persistent, which makes the degradation process significantly low. This is mainly due to physical factors and to photo-degradation [13]. Plastics can last in the marine environment for decades or even hundreds of years when in surface [14, 15]; likely far longer when in deep sea [8]. Most polymers (polyethylene, polypropylene) are buoyant in waters while others (high-density polyethylene, polyethylene terephthalate) may sink [16].

Both plastics [17, 18] and micro-plastics [19, 20] have adverse effects on marine biota, may be used as substrate from microorganisms, invertebrates, and microbial communities [21, 22], or even form plastiglomerates [23]. Microplastics are certainly the most numerically abundant within floating litter items [24], while larger plastics items (macro-plastics) seem to prevail in tonnage (approx. 233,500 T; [12]). On the contrary, several studies dedicated on seafloor marine litter [25–29] are highlighting plastics as an important stock deposited on the world seafloor. The behavior and interaction of plastics with the deep marine environment is yet unidentified.

Fig. 1 Worldwide plastic seafloor hot-spots areas, where plastic exceed 80%

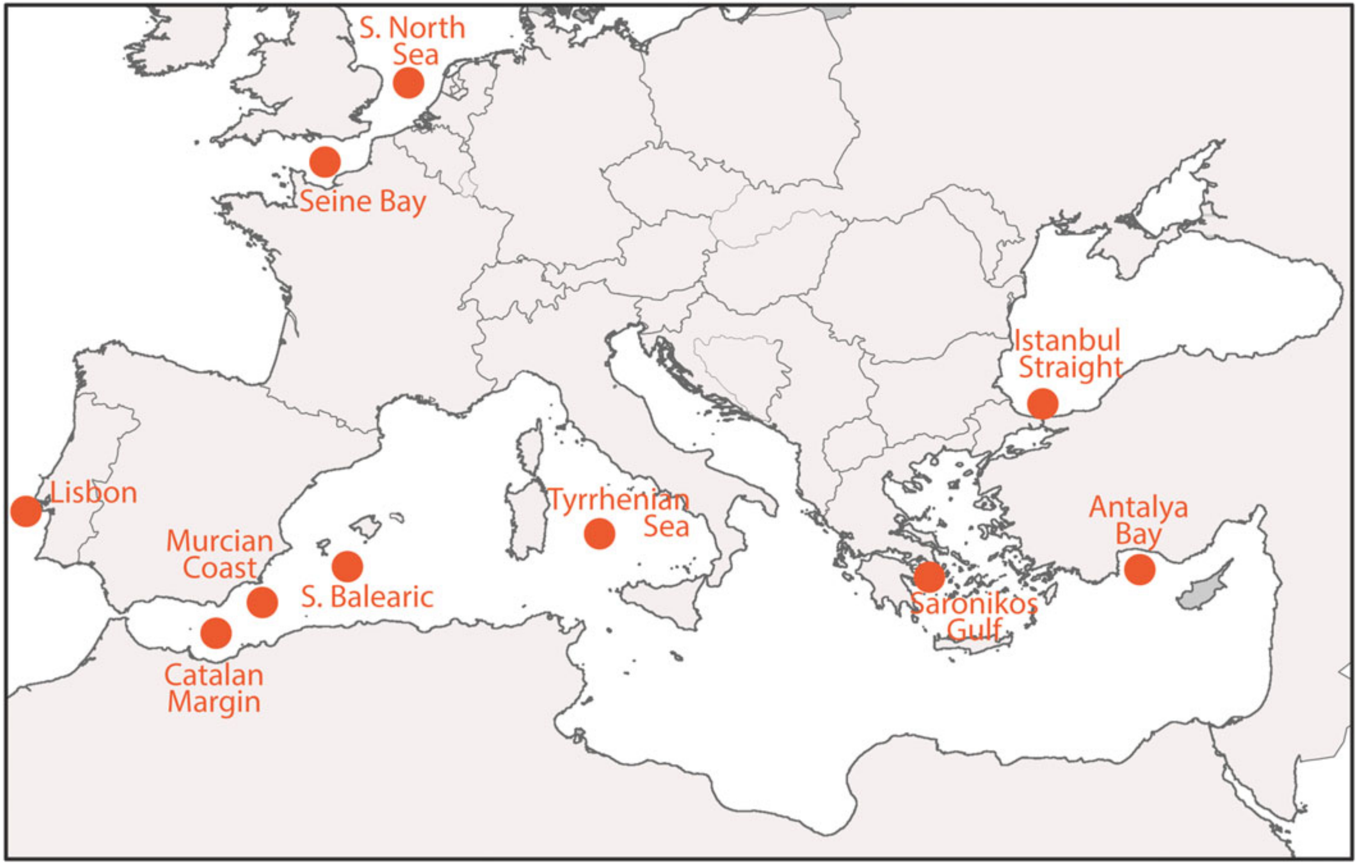

Fig. 2 Plastic seafloor hot-spot areas (≥80%) in the Mediterranean and other European Seas

2 Floating Plastics

One of the first reports of floating marine litter was conducted back in 1983 by Dixon and Dixon [30], where they assessed floating marine litter in the North Sea. In their study, plastic bottles, cups, and sheets were the main marine litter items, which had the biggest share (79%). Nowadays more studies exist (Fig. 3) regarding floating micro-, meso-, and macro-plastics. However the picture is still fragmented and even more coordinated studies are needed towards the identification of accumulation zones and plastic "hot-spot" areas.

2.1 Floating Microplastics

In the Mediterranean Sea, only a few studies exist on floating microplastics. Collignon et al. [31] found plastic particles present within the neuston in 74% of the samples, with an annual average of the abundance on the surface layer of total plastic particles ($<$10 mm) being at 6.2 particles per 100 m^2. The large microplastic particles (2–5 mm) were found to be the most abundant, representing 54% of the total amount of plastic particles with an annual average abundance of 3.4 particles per 100 m^2. In 2015, Cózar et al. found plastic debris in all surface net tows carried out in different sampling areas throughout the Mediterranean Sea. Five different types of plastic items were identified (pellets/granules, films, fishing threads, foam, fragments), with the majority of the items being fragments of initially larger items (87.7%, e.g., bottles, caps) and thin films (5.9%; e.g., pieces of bags or wrappings). In total, 83% of the total collected marine litter items were microplastics. In the same study [32], when comparing the proportion of plastic marine litter in the Mediterranean Sea to that of the open ocean, they found that the small plastic items ($<$2 mm) were less in the Mediterranean Sea, with larger items ($>$20 mm) being more abundant. Plastics in the Mediterranean Sea weighted from 22 to 1,934 g km^{-2} with a mean value of 423 g km^{-2} (243,853 items km^{-2}). The vast majority of the sampling sites (92%) gave significant high concentrations ($>$50 g km^{-2}), while the mean abundance of plastics is comparable to the one found in the five subtropical gyres (281–639 g km^{-2}).

In Southwest England, in the Tamar Estuary [33] floating microplastics were found at approximately 82% of floating items with the following relative proportions: polyethylene (40%), polystyrene (25%), polypropylene (19%), polyvinyl chloride (7%), polyester (6%), and nylon (3%). In respect to sizes, the 1–3 mm size-category was the most abundant at approximately 70% of the samples containing all different types of polymers. Polyethylene was present in a similar proportion (approx. 20%) across all the different size-categories ($<$1, 1–3, 3–5, and $>$5 mm), while PVC was present only in the 1–3 and 3–5 mm; and nylon only in the $<$1 and 1–3 mm size-categories. Plastic items (i.e., polyvinyl chlorides) that are heavier than seawater and that are found floating in seawater may trigger hypothesis

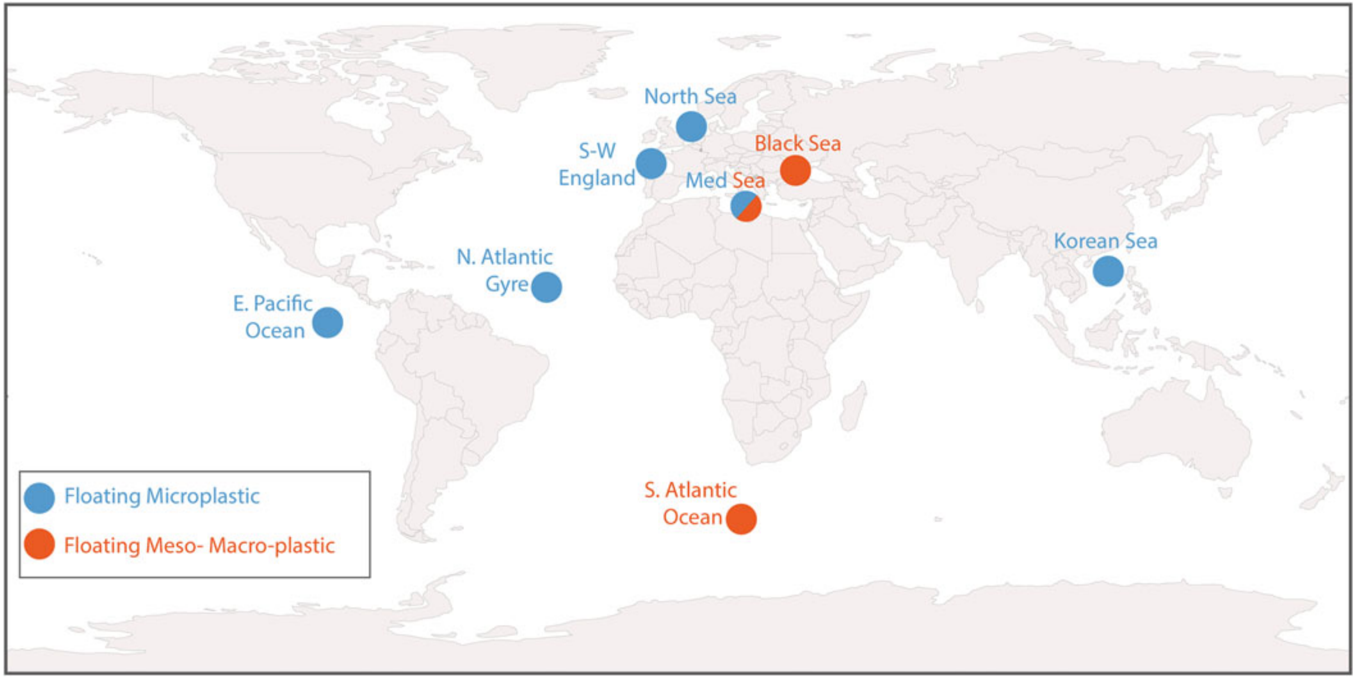

Fig. 3 A panorama of the world floating micro-, meso-, and macro-plastic surveys

that the transportation of plastic particles in the water column is not only controlled by factors such as the density. Turbulent mixing activated by wind and tidal currents may be one of the factors influencing the re-suspension of these heavier plastic particles in the water column, especially in shallow and turbulent waters in estuaries, or even through the introduction of these particles into the shorelines from sewage outlets [33, 34].

In the North Atlantic Gyre [35], floating marine litter was found in abundance at approximately 1.69 items m^{-3} (1.60 mg m^{-3}), mainly consisting of fragments of polyethylene (84.7%) and polypropylene (15.3%) items. Hard plastics (46.6%) and sheets (45.4%) were predominant, while plastic lines (7.9%), pellets (0.05%), and foams (0.008%) showed a much lower presence. For the same area, when investigating the mass (kg), plastics were more abundant in the surface than in deeper layers.

An 11-year data-set of surface plastic marine litter in the Eastern Pacific Ocean [36] recorded plastic abundance at a percentage of 42% with the industrial resin pellets constituting 2% of total pieces. The mean plastic abundance within the accumulation zone was 104 items km^{-2}, while outside the zone the mean abundance was 0 items km^{-2}. Moreover, the 92% of all samples taken within the accumulation zone gave plastic abundance greater than 50,000 items km^{-2}.

In the Southeastern coast of Korea [37], the abundance of floating marine litter items ranged between 0.62 and 57 items m^{-3} before the rainy season (May) and 0.64–860 items m^{-3} after the rainy season (July). In terms of size, the maximum abundance of particles was recorded for the 2–5-mm size class (48–857 items m^{-3}), while smaller items (<2 mm) were less abundant (9–52 items m^{-3}). The larger floating items (5–25 and >25 mm) ranged only between 0.39 and 0.08 items m^{-3}. Styrofoam was the most abundant (20–52%) polymer type for all size classes (<2, 2–5, and 5–25 mm), followed by paint particles (19–49%), fibers (17.5–35.5%), and hard plastic (18–23%). In the Southern Korean coast (Geoje island; offshore environment) [38], polymers had the biggest share (81%) followed by poly(acrylate/styrene) (11%). The mean abundance of floating microplastics was 195 ± 114 items L^{-1}, while the mean abundance of plastics was 16 ± 14 items L^{-1} (13 ± 11 items m^{-2}).

2.2 Floating Meso/Macro-Plastics

Only few studies exist in respect to the assessment of larger floating plastic marine litter items (meso-, macro-plastics). In the Central-Western Mediterranean Sea [39], anthropogenic floating litter items were observed in 87% of the transects with a mean total abundance of 25 ± 2.4 items km^{-2}. The Adriatic Sea (52–55 items km^{-2}) has the highest floating marine litter abundance, followed by the Algerian Basin (53 items km^{-2}), the Central Tyrrhenian Sea (5 items km^{-2}), and the Sicilian Sea (6.3 items km^{-2}). In all areas, the mean abundance of anthropogenic marine litter ranged between 11 and 31 items km^{-2}. Plastics consist approximately 82% of the recorded floating litter items, mainly consisting of fragments, bottles, containers, wraps, packaging, and shopping bags. Styrofoam accounted for 13.6% mainly consisting of fragmented fish boxes. In the Adriatic Sea, the 59% of all litter items was styrofoam. In terms of size class, the vast majority (86.7%) of the recorded floating litter items were smaller than 50 cm; 52.9% were between 10 and 50 cm; 34.7% were <10 cm; 10.4% were between 50 and 100 cm, and only 2% accounted for litter items >1 m.

In the North-Western Black Sea [40], the recorded man-made floating litter items represented only 24.5% of all sighted objects, with mean abundance at 31 ± 7 items km^{-2} and a maximum of 136 items km^{-2}. Plastic litter items accounted for 89%, mainly consisting of fragments, bags, containers, and packaging. In the South Atlantic "garbage patch" [41], the abundance of floating litters ranged between 3 items km^{-2} and 67 items km^{-2}, with plastics being predominant (97%). Within plastic, packaging was found to be the most abundant floating litter item, with its proportion being greater in coastal than in oceanic waters. Fisheries-related items were also present (i.e., pieces of fish trays) with its proportion being greater offshore. In terms of color, most recorded floating litter items were white (46%) or clear (18%), blue (10%), yellow (8%), orange/red/pink (6%), green (5%), and black (1%) or grey (<1%). In the African sector of the Southern Ocean, between Cape Town and Dronning Maud (Antarctica) [42], plastic accounted for approximately 96% of the recorded floating litter. Among plastic litter, packaging was the most common litter item (58%) with its proportion being greater in temperate waters than in sub-Antarctic and Antarctic waters. Fishery-related items (mainly floats) were more abundant in the Antarctic than in temperate waters.

3 Plastics on the Seafloor of World Seas and Oceans

3.1 Plastics in Shallow Waters

There are only a few studies investigating marine litter in shallow waters (Table 1) mainly surveyed by scuba divers. Unlike what is found in the continental shelf and the deep-sea environments, plastics in shallow waters do not exceed 50% of the total marine litter. Only one study recorded marine litter in the Mediterranean Sea in selected study areas in Greece (Saronikos Gulf, W. Crete, S. Peloponnese, Santorini isl., W. Greece), in depths ranging from the shoreline (0 m) to 25 m [43]. Plastics accounted for 52% (4,749 items km^{-2}) of the marine litter collected in Santorini island (9,133 items km^{-2}); 47% (14,880 items km^{-2}) in the Saronikos Gulf (31,660 items km^{-2}); 47% (6,592 items km^{-2}) in S. Peloponnese (14,025 items km^{-2}), and 45% (8,525 items km^{-2}) in W. Crete (18,944 items km^{-2}). Several studies have been conducted in the Atlantic Ocean [44–46, 48–50] with plastics being less abundant ranging from <5% (591 items km^{-2}) in Florida Keys Archipelagos (USA), 37.9% (5,458 items km^{-2}) in Arvoredo island (Brazil), and

Table 1 Review table of the plastics found on the seafloor in shallow waters worldwide

Geographical area		Country	Year	Seafloor morphology	Depth (m)	Abundance (items km^{-2})	Surveyed area	Plastics (%)	Reference
Mediterranean Sea	Saronikos Gulf	GRC	2003	Shallow coastal waters	0–25	31,660	1,600 m^2/dive	47	[43]
	W. Crete isl.					18,944		45	
	S. Peloponnese					14,025		47	
	Santorini isl.					9,133		52	
Western Atlantic	Florida Keys Archipelagos	USA	2001	Coral reef	0–15	11,825	0.0252 km^2	<5	[44]
	NW Hawaii (Lisiaki, Pearl, and Hermes island)	USA (Hawaii)	2000	Coral reef	0–10	20–40	1–1.3 km^2	–	[45]
	Arvoredo island	BRA	2004	Coral reef	0–15	14,400 (17,000–19,600)	0.011176 km^2	38	[46]
	NW Hawaii (Kure island)	USA (Hawaii)	2000	Coral reef	0–10	165	1–1.3 km^2	–	[47]
	Gray's Reef National Marine Sanctuary	USA (Hawaii)	2004–2005	Coral reef	16–20	5,200 (0–10,000)	0.0179 km^2	51	[48]
	SE USA	USA	1996–1998	Coral reef	0–10	3.4–66.2	1.1 km^2	–	[49]
	S. Caribbean	CUW (Dutch Caribbean)	2000	Reef terrace	10	370,000 (200,000–660,000)	–	–	[50]
Red Sea	Gulf of Aqaba	JOR	2003–2004	Coral reef/ sand	0–10	2,800,000	0.00375 km^2	42	[51]

(continued)

Table 1 (continued)

Geographical area		Country	Year	Seafloor morphology	Depth (m)	Abundance (items km^{-2})	Surveyed area	Plastics (%)	Reference
Pacific Ocean	Majuro Lagoon	MHL		Coral atoll	3–5	200.26	0.0079 km^2	8	[52]
					8–10				
					≤3	234.24	0.0033 km^2		
	Ahe Atoll Lagoon	PYF	2013	Oyster aquaculture site	0–45	–	–	–	[53]
Indian Ocean	Kawau island	NZL	1995	Rocky and muddy substrata	≤10	–	–	–	[54]

50.5% (2,626 items km^{-2}) in Gray's Reef (Hawaii). In the Pacific Ocean [52, 53], plastics accounted only 8% (≈17 items km^{-2}) in the Majuro Lagoon (Marshall islands), while in the Red Sea [51], plastics accounted approximately 42% of the total litter abundance.

3.2 *Plastics in Shelf Environments*

The continental shelf of the world seas and oceans has been extensively studied in respect to the abundance and distribution of marine litter (Table 2). Today, much of the existing data on seafloor marine litter comes from trawl surveys conducted by commercial or experimental trawl fishery vessels, with numerous studies using this method; from the Arctic, the major oceans, the Black Sea, the European north seas, and the Mediterranean Sea. However, all these studies have been using different cod-end mesh size ranging from 38 to 10 mm. Thus, a critical question rises regarding the comparability of these results, which remains to be clarified.

The first recorded study was conducted by Bingel et al. [96] in the Eastern Mediterranean Sea. In the early 1990s, June (1990) assessed marine litter in the Pacific Ocean. Thereafter, several studies have been conducted, using several approaches, protocols, and units (items km^{-1}, items km^{-2}, kg km^{-2}, kg h^{-1}) in which plastics was the most abundant marine litter item. In the Mediterranean Sea, no more than 15 studies exist (Fig. 4), dedicated on the assessment and accumulation of seafloor marine litter with the use of otter-trawlers.

Plastics have been found widespread in the continental shelf, exceeding in some areas the 80% ("hot-spots") of marine litter. In the Western Mediterranean Sea, plastics were recorded in the Gulf of Lions [25, 62] at a range of 64% (1996–1997) up to 77% (1994–1995) with the mean marine litter concentration ranging among the different studies, i.e., 633–1935 items km^{-2} (1993–1994); 3,900 items km^{-2} (1996); and 143 items km^{-2} (1996–1997). In the same geographical area, plastics accounted in the Catalan Coast for 60% with a mean marine litter density of 7,003 ± 6,010 items km^{-2}; while in the Murcian coast plastics were excessive (84%) with a mean marine litter density of 4,424 ± 3,743 items km^{-2} [60].

In the Central Mediterranean Sea, Sanchez et al. [60] also found high percentage of plastics (87%) (5,200 items km^{-2}). Relatively high percentages of plastic (77%) were found in Corsica [62], while in the Maltese islands (47%) and the North-Central Adriatic Sea (24–62%), plastics were moderate in abundance [63, 65].

The Eastern Mediterranean is the least studied compartment of the three compartments (western, central, eastern) of the Mediterranean Sea. Galil et al. [55] found plastics at 36% during a big survey in the Eastern Mediterranean Sea (Italy, Greece, Egypt, Cyprus, Israel) with the mean marine litter density ranging from 200 till 8,500 items km^{-2}. More targeted studies conducted in the Eastern Ionian Sea by Stefatos et al. [56] and Koutsodendris et al. [28] assessed plastics percentages in the Gulf of Patras and the Echinades Gulf at 81 and 56%, respectively. A more recent study, conducted in 2013–2014 by Ioakeimidis et al. [26], found

Table 2 Marine litter and plastic abundance and distribution in the continental shelf and deep-sea environments worldwide

Geographical area		Country	Year	Method	Cod-end mesh size	Stations	Seafloor morphology	Depth (m)	Abundance	Surveyed area	Plastics (%)	Reference
Eastern Mediterranean	Eastern Med	ITA, GRC, EGY, CYP, ISR	1993	Trawl	1 cm	17	Continental shelf, deep sea	194–4,614	200–8,500 items km^{-2}	–	36	[55]
	Gulf of Patras	GRC	1997–1998	Trawl	1.5 cm	3	Continental shelf	80–120	240 items km^{-2}	1.2 km^2	83	[56]
	Echinades Gulf					2		247–360	89–240 items km^{-22}	1.2 km^2	79	
	Gulf of Patras	GRC	2000–2003	Trawl	1.5 cm	54	Fishing grounds/ continental shelf	15–320	165 items km^{-2} (72–437)	20 km^2	56	[28]
	Gulf of Corinth											
	Echinades Gulf											
	Lakonikos Gulf											
	S. Cretan	GRC	2007–2010	Trawl	40 mm, 12 mm	10	Margin and deep basins	1,200; 2,000; 3,000	0.02–3,264.6 kg km^{-2}	N.d.	–	[57]
	S. Ionian Sea					5				N.d.	71	
	Saronikos Gulf	GRC	2013	Trawl	50 mm	41	Continental shelf	50–350	1,211 ± 594 items km^{-2}	3.1 km^2	95	[26]
	Gulf of Patras		2013		50 mm	18		20–150	641 ± 579 items km^{-2}	2.9 km^2	60	
	Echinades Gulf		2013		50 mm	10		50–200	416 ± 379 items km^{-2}	1.9 km^2	67	
	Limassol Gulf	CYP	2013		50 mm	9		60–400	24 ± 28 items km^{-2}	2.1 km^2	67	
	Argolikos Gulf	GRC	2014	Trawl	20 mm	8		150–750	360 ± 193 items km^{-2}	0.8 km^2	75	[58]
	Saronikos Gulf	GRC	2014	ROV	–	2	Continental shelf	94–115	4,460,193 items km^{-2}	0.007 km^2	55	[27]
	Antalya Bay	TUR	2012	Trawl	24 mm	32	Bottom/ bathyal	200–800	115–2,762 items km^{-2}	270–820 km^2/ haul	81	[59]

	Eastern Ionian	GRC	2009	Trawl	10 mm	6	Fishing grounds	40–80	2,300 items km^{-2}	0.09 km^2	77	[60]
	Mersin Bay	TUR	2010–2012	Trawl	24 mm	132	Fishing grounds	19–178	0.01–5.85 kg h^{-1}	–	73	[61]
Central Mediterranean	Gulf of Lion	FRA	1994	Trawl	55 mm	69	Continental shelf	–	–	0.0444 km^2	–	[62]
	Corsica					19		–	633–1,935 items km^{-2}		77	
	Bay of Marseille		1993	Trawl (Boc73)	10 mm	6		–	–	0.0278 km^2	–	
	East-Corsica	FRA	1998	Trawl	10 mm	20	Continental shelf	–	229 items km^{-2}	–	≈46	[25]
	Adriatic Sea	ITA	1998	Trawl	20 mm	10		–	378 items km^{-2}	–	≈69	
	Central Tyrrhenian	ITA	2009	Trawl	10 mm	6	Fishing grounds	40–80	5,950 ± 3,023 items km^{-2}	0.09 km^2	87	[60]
	Maltese islands	MLT	2005	Trawl	20 mm	44 Stations	Continental shelf	49–697	97 ± 78 items km^{-2}	3.5 km^2	47	[63]
	Tyrrhenian	ITA	2010–2012	ROV	–	10 Transects	Fishing grounds (Rocky Banks)	70–280	–	0.0029 km^2	–	[64]
Central Mediterranean	Adriatic Sea (North and Central)	ITA, HRV, SVN	2011–2012	Trawl	40 mm	67	Fishing grounds	0–30	170.6 ± 35.8 kg km^{-2}	4.3 km^2	≈42	[65]
								30–50	65.4 ± 21.6 kg km^{-2}		≈62	
								50–100	47.9 ± 23.4 kg km^{-2}		≈24	
	Campania (Tyrrh. Sea)	ITA	2010	ROV	–	15	Rocky coral assemblages	30–300	120,000 items km^{-2}	6.03 km^2	89	[66]
	Sardinia (Tyrrh. Sea)	ITA	2011			37			30,000 items km^{-2}		92	
	Sicily (Tyrrh. Sea)	ITA	2011			17			90,000 items km^{-2}		96	

(continued)

Table 2 (continued)

Geographical area		Country	Year	Method	Cod-end mesh size	Stations	Seafloor morphology	Depth (m)	Abundance	Surveyed area	Plastics (%)	Reference
Western Mediterranean	Gulf of Lions	FRA	1994–1995	Trawl	10 mm	141	Continental shelf and canyons	40–1,442			72	[67]
	Gulf of Lions	FRA	1996	Trawl	10 mm	15	Canyons – bathyal plain	500–1,600	3,900 items km^{-2}	0.71 km^2	–	
	Marseille – Nice	FRA	1995	SUBV	–	16	Canyon	<100	1,623 items km^{-2}	–	86	
	Gulf of Lion	FRA	1996–1997	Trawl	10 mm	24	Continental shelf	–	143 items km^{-2}	–	≈64	[25]
	NW Mediterranean	FRA, ITA	1997	SUBV	–	35	Bathyal plain	–	1,935 items km^{-2}	–	–	
	Murcian Coast	ESP	2009	Trawl	10 mm	6	Fishing grounds (sand)	40–80	4,424 ± 3,743 items km^{-2}	0.09 km^2	84	[60]
	Catalan Coast		2009	Trawl	10 mm	6	Fishing grounds (sand)		7,003 ± 6,010 items km^{-2}	0.09 km^2	60	
	Catalan Margin (Blanes Canyon)	ESP	2007–2010	Trawl (Otter Trawl, Agassiz Trawl)	40 mm, 12 mm	11 Stations (292 tows)	Bathyal/ abyssal (sand)	900–2,700	0.02–3264.6 kg km^{-2}	–	–	[57]
	Southern Balearic					12 Stations (6/6)	Margin and deep basins	1,200; 2,000; 3,000	–	–	–	
	French Mediterranean	FRA	2009	ROV	–	101 Dives	Canyons	180–700	3.01 items km^{-1} (0–12)	159.3 km (width:1 m)	12	[68]
	North-Catalan Continental Margin	ESP-FR	2011	ROV	–	26 Dives	Canyons	140–1,731	15,057 items km^{-2}		72	[69]

Black Sea	W. Black Sea	TUR	2007–2008	Trawl	22 mm	14	Continental shelf	49–77	128–1,320 items km^{-2}	–	90	[70]
	Istanbul Strait							21–25; 58				
	E. Black Sea							76–103				
	Constanta Bay	ROU	2013	Trawl	20 mm	16	Continental shelf	20–60	291 ± 237 items km^{-2}	0.7 km^2	45	[26]
Baltic Sea	West Baltic Sea	–	1996	Trawl	20 mm	5	Continental shelf	–	126 items km^{-2}	–	≈36	[25]
North Sea	S. North Sea	–	1998	Trawl	20 mm	80	Continental shelf (sand)	0–200	156 items km^{-2}	4.8 km^2	48	[25]
	S. North Sea	BEL	2010	Trawl	10 mm	5 Sites (3 tows/ site)	Continental shelf	10–30	3,125 ± 2,830 items km^{-2} (1,250–11,227)	0.041 km^2	96	[71, 72]
	W. North Sea	UK	1992–2012	Trawl	20 mm	44 Surveys (74–441 stations/ year)	Continental shelf (sand)	0–200	115 items km^{-2} (0–14,550)	0.15 km^2/station	72–82	[73]
	East English Channel	–	1998	Trawl	20 mm	83	Continental shelf	–	17.6 items km^{-2}	–	–	[25]
Eastern Atlantic	Seine Bay	FRA	1993	Trawl	55 mm	8	continental shelf	–	1–4 items/station	–	80	[74]
	Biscay Bay	FRA	1992–1993	Trawl	55 mm	165	Continental shelf	<100	142 items km^{-2}	0.155 km^2	62	[74]
	Biscay Bay	FRA	1994	SUBV	–	10	Continental shelf (sand)	0–200	142 ± 25 items km^{-2}	10.95 km^2	62	[25]
	Seine Bay	FRA	1993	Trawl	20 mm	8			7,200 items km^{-2}	–	–	
	Celtic Sea	–	1998	Trawl	20 mm	50			528 items km^{-2}	7.5 km^2	30	
	Lisbon	PRT	2007	ROV (2 m width)	16 Dives	1	Canyon	1,602	1,616 items km^{-2}	60 km	86	[75]
	Setubal					1		2,194	2,463 items km^{-2}		30	
	Cascais					1		4,574	1,058 items km^{-2}		54	
	Nazare					13		741–4,385	0–2,030 items km^{-2}		25	

(continued)

Table 2 (continued)

Geographical area		Country	Year	Method	Cod-end mesh size	Stations	Seafloor morphology	Depth (m)	Abundance	Surveyed area	Plastics (%)	Reference
	Condor Seamount	PRT	2010–2011	ROV	–	45	Seamount (Rocky)	185–265	1,439 items km^{-2}	0.031 km^2	89	[76]
	Condor Seamount					3		297–1,092	397 items km^{-2}	0.025 km^2	50	
	Gorringe Bank	PRT	2011	ROV	–	4 Dives	Seamount	60–3,015	1–4 items km^{-2}	80.6 km	10	[77]
	Portuguese Coast	PRT	2013	Trawl	55–80 mm	135	Continental shelf	90–349	17.3–78.7 items km^{-2} (max: 179 items km^{-2})	56.2 km^2	76	[78]
	São Vicente	PRT	2011	ROV	–	3 Dives	Canyon	93–553	0.58–3.31 items 100 m^{-1}	8.1 km	≈90	[79]
Western Atlantic	Rio de la Plata	ARG	1996–2001	Trawl	102 mm/ cod-end	296 Sites	Estuary (sand/mud)	0–23	513 items km^{-2} (0–1,509)	0.027–0.056 km^2	77	[80]
	US West Coast	USA	2007–2008	Trawl	38 mm	535	Fishing grounds (shelves/ sand)	55–183	30 items km^{-2}	36,399 km^2	23	[81]
						439	Fishing grounds (slopes)	184–549	59 items km^{-2}	29,997 km^2		
						373	Fishing grounds (slopes/ bathyal)	550–1,280	129 items km^{-2}	69,142 km^2		
	N. Gulf of Mexico	MEX	2000–2002	Trawl	3.8 cm stretch mesh	40 Hauls	Slopes/ abyssal	250–3,650	140 items km^{-2} (0–6,500)	–	44	[82]

Eastern Pacific	Oregon Coast	USA	<1990	Trawl	32 mm	70 Stations	Continental shelf (slopes/ sand)	100–675	149 items km^{-2}	2.7 km^2	26	[83]
	Kodiak island	USA [AK]	1994	Trawl	40 mm	114	Soft bottom; fishing grounds	Near Shore	138 items km^{-2}	2.36 km^2	49	[84]
						86		Off Shore	20 items km^{-2}	1.92 km^2		
			1995			115		Near Shore	151 items km^{-2}	2.42 km^2	59	
						93		Off Shore	44 items km^{-2}	2.07 km^2		
			1996			117		Near Shore	130 items km^{-2}	2.49 km^2	47	
						100		Off Shore	29 items km^{-2}	2.23 km^2		
	Monterey Bay	USA	1993–1994, 1997–1998	SUBV	–	210 Video transects	Continental shelf – canyon	20–365	17 items km^{-1}	26.7 km	97	[85]
			2002		–	321 Video transects			2 items km^{-1}	121.7 km	41	
			2007		–						95	
	Monterey Bay (California)	USA	1989–2011	ROV, SUBV	–	1,149 Videos	From margin, slopes (0–40°) to abyssal	25–3,971	632 items km^{-2}	2,429 km^2	33	[86]
N. Pacific	Gulf of Alaska	USA	1975	Trawl	–	58 Stations	Continental shelf	–	–	–	–	[87]
	Bering Sea	USA	<1990	Trawl	32 mm	541	Continental shelf (slopes/ sand)	20–500	7.5 items km^{-2}	26.2 km^2	51	[83]
W. Pacific	Tokyo Bay	JPN	1995–2000	Trawl	(NOAA Protocol)	–	Continental shelf (sand)	0–200	185–338 items km^{-2}	96.4 km^2	51.2	[88]
	E. China Sea	KOR	2002–2005	Trawl	60–65 mm	20 Stations	Continental shelf	15–200	30.6 kg km^{-2}	–	5	[89]
	S. Korea Sea	KOR	1996–1997			19 Stations			109.8 kg km^{-2}	–	10	
	South China Sea	CHN	2009–2010	Trawl	–	4 Stations	Soft sand bottom	3–9	1,135 items km^{-2}	0.092 km^2	42	[90]
				Dive	–	1 Dive		0.5	3,282 items km^{-2}	0.0036 km^2	86	

(continued)

Table 2 (continued)

Geographical area		Country	Year	Method	Cod-end mesh size	Stations	Seafloor morphology	Depth (m)	Abundance	Surveyed area	Plastics (%)	Reference
	Sankiru Bay	JPN	Jamstec Databank	ROV, SUBV	–	3 Dives	Abyssal	400; 1,147; 1,682	15.9 items h^{-1}	–	42.8	[91]
Arctic	Fram Strait 79°N	–	1999, 2003	ROV	–	10 Dives	Abyssal plain	2,500–5,552	56 items km^{-2} (0–220)	5,200 m (1999) 2,602 m (2003)	65.2	[92]
	N. Antarctic Peninsula, Scotia Arc	–	2006	Trawl	10 mm	32	Slopes and bathyal	200–1,500	2 items only	–	50 (1item)	[8]
	Antarctica	–	2008	Trawl	10 mm	37	Slopes and bathyal	472–3,213	0	–	–	[93]
	Hausgarten Observatory (Fram Strait 79°N)	–	2002, 2004, 2007, 2008, 2011	ROV	–	1 Transect/year (2,878 pics)	Abyssal plain	2,500	3,635 (2002) 7,719 (2011) items km^{-2}	8,570 km^2	59	[94]
Caribbean	South Caribbean	NLD	2000	SUBV	–	24 Transects	Deep sea	80–900	2,700 items km^{-2}	0.072 km^2	29	[95]

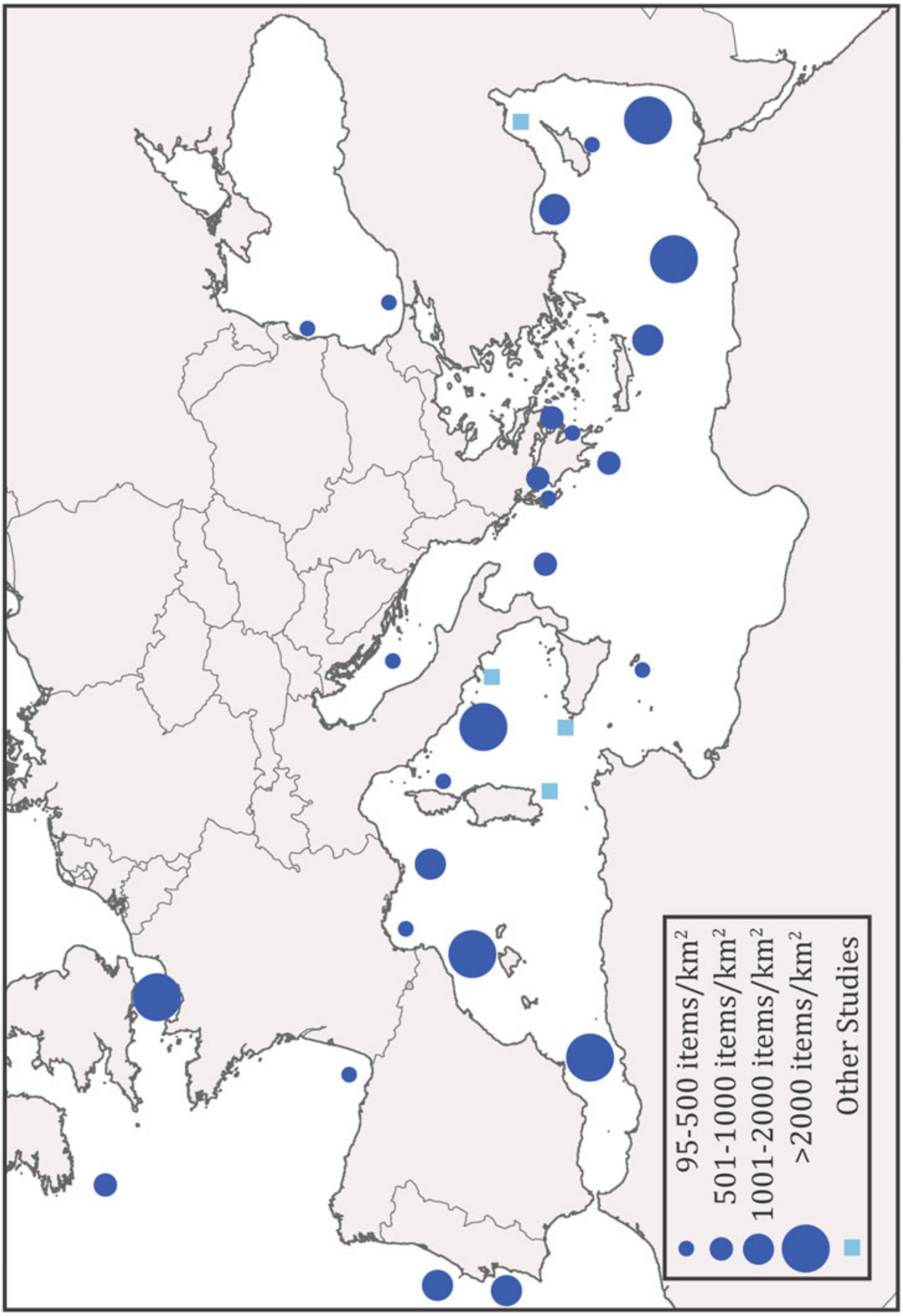

Fig. 4 Seafloor marine litter distribution in the Mediterranean and other European Seas

plastic percentages in the same areas at 60% (Gulf of Patras) and 67% (Echinades Gulf). Albeit the fact that the marine litter abundance was increased in the Gulf of Patras (1997–1998: 240 items km^{-2}; 2000–2003: 313 items km^{-2}; 2013–2014: 641 items km^{-2}) and the Echinades Gulf (1997–1998: 89–240 items km^{-2}; 2000–2003: 313 items km^{-2}; 2013–2014: 416 items km^{-2}), the plastic percentage seems to follow more or less similar pattern. High quantities of plastic litter were also found in Antalya (81%) and Mersin (73%) bays [59, 61], while in Cyprus (Limassol Gulf) plastics were found in more moderate quantities (59%) from Ioakeimidis et al. [26]. By far the most plastic-associated area is the Saronikos Gulf (Greece), with plastic percentages at the extreme of 95%, while in the Argolikos Gulf (W. Aegean) plastics accounted for 75% of the total recorded marine litter [26].

In the Black Sea, plastic percentages were found in excess (90%) by Topçu et al. [70], while in Constanta Bay (Romania) plastics did not exceed 75% [26]. In the other European Seas, plastic percentages were found at 36% (≈45 items km^{-2}) in the Baltic Sea (46 items km^{-2}) [25] and at a range of 72–96% in the North Sea [71–73].

In the East Atlantic Ocean, the French Part of Seine Bay gave an extreme of 80% for plastics, Biscay Bay 62% (≈88 items km^{-2}) [25, 74], while along the Portuguese coast plastics accounted for 76% [78]. The Celtic Sea gave more moderate plastic percentage at 30% (≈158 items km^{-2}) [25]. In the West Atlantic, in Argentina (Rio de la Plata), plastics were also high in percentage at 77% (≈395 items km^{-2}) [80].

In East Pacific Ocean, plastics accounted for 26% (≈39 items km^{-2}) in Oregon coast [83], 46.5–59% in Kodiak island (Alaska) [84] and 51% (≈4 items km^{-2}) in Bering Sea [83]. In West Pacific Ocean, plastics ranged between 42 and 86% (≈477–2,822 items km^{-2}), in the South China Sea [90], in Tokyo Bay plastics were moderate at 51% [88], while in East China Sea and South Korea Sea plastics ranged between 5 and 10% [89].

3.3 Plastics in Deep-Sea Environments

The use of observation tools, i.e., Remote Operated Vehicles (ROVs) and Submersible Vehicles, is a possible approach for deep-sea environments. Unfortunately, these methods require considerable means but are of great use for non-accessible areas by other means. The use of observation tools helped scientists assess marine litter far beyond the commonly used fishing grounds (sandy bottoms) and the continental shelf and extend the assessment of marine litter in bathyal and abyssal environments, reaching in depths up to 4 km. It was really surprising to find unexpected high marine litter densities (or unexpected marine litter items) at abyssal depths, where human activities are totally absent. The ageing of plastics at such depths is not well investigated and the sinking of plastics to the seafloor began long before specific scientific investigations started in the 1990s [8]. Despite the considerable means needed, there are several dedicated studies investigating marine litter in deep-sea environments (Table 2).

In the Mediterranean Sea, the first assessment of marine litter with deep-sea observation tools was done back in 1995 by Galgani et al. [67] in the marine Canyon of Marseille-Nice (1,623 items km^{-2}) in which plastics were surprisingly found in a high percentage (86%). Nowadays, in the Mediterranean Sea such data exist also for the Western Mediterranean [25, 67, 68] with plastic percentages ranging from 12 to 86% and the Central Mediterranean Sea (Tyrrhenian Sea: 30,000–120,000 items km^{-2}) in which plastic percentages ranged from 82 to 93% [64, 66]. No relevant data exist for the Eastern Mediterranean Sea, and thus, such research efforts should be promoted in this area.

A few studies also exist for the Atlantic Ocean. In the Eastern Atlantic Ocean, being adjacent to Europe; in the São Vicente submarine canyon (SW Portugal), plastic percentage exceeded 90%, in the Lisbon Canyon an extreme of 86% was observed, while the Setubal (30%), Cascais (54%), and Nazare (25%) canyons had moderate plastic presence [75, 79]. On the contrary, Gorringe Bank in Portugal gave much lower plastic abundance at approximately 10% [77] and Condor Seamount 50% [76]. In the Pacific Ocean the Monterey Bay has been extensively studied, with fluctuations regarding the plastic percentage; 33% by Schlining et al. [86], and 41–97% by Mordecai et al. [75]. The abyssal Plato off Sanriku (Japan) in Western Pacific is another area that has been investigated for marine litter with plastics accounting for 43% [91]. In the South Caribbean, plastics accounted for 29% ($\approx$783 items km^{-2}) [95].

Scientists have reached even the most remote areas of the globe; assessing marine litter in the Arctic. In the Hausgarten Observatory (Fram Strait 79°N), marine litter ranged from several items up to 7,719 items/km^2 with plastics ranging in moderate percentages of 59–65% [92, 94], while in Antarctica no or insignificant amounts of litter were found [8, 93].

4 Discussion

It is now evident that plastics are present from the shallow water, the continental shelf, till the abyssal plains, in all different sea compartments and basins and thus, posing an important problem for the marine environment. From the oceanographic and chemical perspectives, the distribution of marine litter and the degradation processes of plastic are important parameters that affect their impacts on marine life and local contamination. Unfortunately so far, we do not have a clear picture regarding the areas where the accumulation of plastics is significant although several ongoing studies try to give a clearer picture. Apart from the five subtropical gyres, the so-called garbage patches, there are also other highly affected areas like the Mediterranean Sea with comparable abundance rates (especially for microplastics). The Mediterranean Sea is very peculiar as there are no areas where marine litter permanently accumulates. Instead, there is a constant circulation. For other sea basins like the Black Sea, there is lack in baseline assessment data. The picture is fragmented as only through nonrecurring studies information becomes available and this is not enough to drawn safe results or even to partially assess the situation.

It is evident that an important stock of marine litter lies on the world seafloors with great spatial heterogeneity, roughly estimated at a range of 71.5–116 billion large plastic litter items [97]. The assessment of the corresponding tonnage may result in very impressive figures. It is important to note that these figures do not take into consideration the small plastic particles that are accumulating in the deep-sea sediments [71, 72, 98]. Therefore, the deep seafloor is believed to be the final global sink for marine litter. This might also be the case of the Mediterranean Sea [25, 26, 29] where the presence of accumulation areas on the seafloor has been demonstrated and mapped in the present chapter. The fact that the shelves are not extended and the deep-sea environments may be easily affected by coastal locations of canyons further supports this hypothesis. The geomorphology together with the steep inclination of the seafloor seems to highly affect the already described canyons.

In the Mediterranean Sea, plastic litter is mostly accumulating on the seafloor of the Western and Eastern basins. This might be linked to the fact that the Western Mediterranean Sea is where we have the main input of water masses from the Atlantic Ocean and the Eastern Mediterranean Sea is where the currents are attenuating and are not strong enough to loop-back the plastic masses. For the rest of the world, the picture is rather incomplete and especially, for the deep ocean compartments as well as the Black Sea, more dedicated studies should be strongly encouraged.

The information regarding the floating plastic is scarcer than that available for the seafloor marine litter. The heterogeneity of the spatial abundance is high in many studied areas worldwide, in terms of weight and size [12]. Plastic and microplastic particles are moving and accumulating throughout seas and oceans, mainly depending on wind-driven and non-wind-driven surface currents. Especially for the Mediterranean Sea, the variable plastic distribution can be attributed to the variability of the Mediterranean surface circulation that is not creating well-established accumulation zones [20]. Nonetheless, Cózar et al. [20] clearly demonstrated that the abundance of the Mediterranean Sea in plastics is absolutely comparable to the ones found in the five subtropical gyres.

More studies are definitely needed worldwide in the area of floating marine litter. The Mediterranean Sea together with the Black Sea are the two basins, which are probably less studied among the world seas and oceans. A better view of the surface plastic litter abundance together with the seafloor data might trigger some hypothesis regarding the floating and benthic litter proportion. Special attention should be also given to the removal processes of plastic litter that can be sustainably applied in terms of cost, effort, and habitat destruction.

Overall a harmonized worldwide marine litter assessment should be strongly supported for the different kinds of marine litter items, which are present in the marine environment (i.e., mainly for floating and benthic litter). The worldwide assessment should include all depth ranges, from the really shallow coastal waters up to the deep submarine canyons, all different sampling techniques (Experimental Trawlers, Commercial Trawlers, ROVs, Submersible Vehicles, Manta Net), and should be implemented on a constant basis in a monitoring-shaped framework.

From a chemical perspective, some important questions are still remaining. What is the lifespan of plastic marine litter items in the marine environment? Ioakeimidis et al. [99] have given a first hint on the degradation potential of plastic PET bottles in the marine environment and it seems that initial degradation could be faster than usually expected. The same sort of information should also become available for the rest, commonly recorded plastic marine litter items. There is also an increased concern regarding persistent, bioaccumulative (PBT), and toxic chemicals such as polycyclic aromatic hydrocarbons (PAH) and pesticides absorbed onto plastics, which then become vectors for these highly toxic pollutants. The link between distribution of plastic at sea and the release of toxics must be determined. High densities of plastic able to desorb toxic compounds may lead to pollution of coastal waters. Mapping the distribution of plastics will enable to better locate "hot-spots" of pollution and a better risk assessment. The relationship between plastic particle size and toxicity has also been observed but remains highly debated in the ecotoxicological community. As a distinct effect, it remains to be conclusively shown, especially for nanoparticles. Risk assessment method needs to better define "no effect" and "effective" concentration as well as distribution for various litter types. The development of models to predict the degradation and subsequent harm (release of contaminants, toxicity) should be based on a better knowledge on plastic distribution. From a management and policy point of view, a better knowledge on plastic distribution will enable us to determine the sources of plastic pollution and support reduction measures.

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Sources, Distribution, and Fate of Microscopic Plastics in Marine Environments

Richard C. Thompson

Abstract Microplastics are pieces of plastic debris <5 mm in diameter. They enter the environment from a variety of sources including the direct input of small pieces such as exfoliating beads used in cosmetics and as a consequence of the fragmentation of larger items of debris. A range of common polymers, including polyethylene, polypropylene, polystyrene, and polyvinyl chloride, are present in the environment as microplastic particles. Microplastics are widely distributed in marine and freshwater habitats. They have been reported on shorelines from the poles to the equator; they are present at the sea surface and have accumulated in ocean systems far from land. Microplastics are also present in substantial quantities on the seabed. A wide range of organisms including birds, fish, and invertebrates are known to ingest microplastics and for some species it is clear that a substantial proportion of the population have microplastic in their digestive tract. The extent to which this might have harmful effects is not clear; however, the widespread encounter rate indicates that substantial quantities of microplastic may be distributed within living organisms themselves as well as in the habitats in which they live. Our understanding about the long-term fate of microplastics is relatively limited. Some habitats such as the deep sea may be an ultimate sink for the accumulation of plastic debris at sea; indeed, some recent evidence indicates quantities in the deep sea can be greater than at the sea surface. It has also been suggested that microplastics might be susceptible to biodegradation by microorganisms; however, this is yet to be established and the prevailing view is that even if emissions of debris to the environment are substantially reduced, the abundance of microplastics will increase over the next few decades. However, it is also clear that the benefits which plastics bring to society can be realized without the need for emissions of end-of-life plastics to the ocean. To some extent the accumulation of

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microplastic debris in the environment is a symptom of an outdated business model. There are solutions at hand and many synergistic benefits can be achieved in terms of both waste reduction and sustainable use of resources by moving toward a circular economy.

Keywords Contamination, Harm, Microplastic, Policy, Pollution, Solutions

Contents

1 Definitions

The term microplastic is used to describe small pieces of plastic debris. There is no universally recognized definition. Small fragments of debris were first reported at the sea surface in the early 1970s [e.g., 1, 2] and Ryan and Moloney described the abundance of fragments on shorelines in the 1980s using the term microplastic [3]. In 2004, evidence of widespread occurrence of truly microscopic pieces of plastics was presented by Thompson et al. who also used the term "Microplastics" to describe these pieces, but no formal definition was presented [4]. Research interest in the topic of microplastics increased dramatically thereafter (Fig. 1). In 2008, NOAA hosted the first international workshop on the Occurrence, Effects and Fate of Microplastics [5] and a working group of the assembled participants made a somewhat pragmatic decision to define microplastic as small pieces less than 5 mm in diameter. One reason for this was that they considered particles of this size might behave differently in the environment and present different types of hazards to those that were already widely recognized for larger items, where entanglement is a major concern [6, 7]. While 5 mm is widely accepted as an upper bound for the definition of microplastics, the lower bound is much less clearly defined.

Particles as small as 20 μm have been reported in the environment and it seems likely that even smaller particles of plastic debris in the nanoparticle size range are also present in the environment. However, at present the limit of detection, which relies on particle identification by spectroscopy, is around 20 μm [8]. The ability to capture very small particles such as these is also directly affected by the type of sampling equipment used. For example, collection from the water column will often utilize plankton nets which are typically made of 333 μm mesh. Whereas, microplastics are often extracted from sediments via a density gradient and flotation subsequently collecting the buoyant particles over filter paper which can be capable

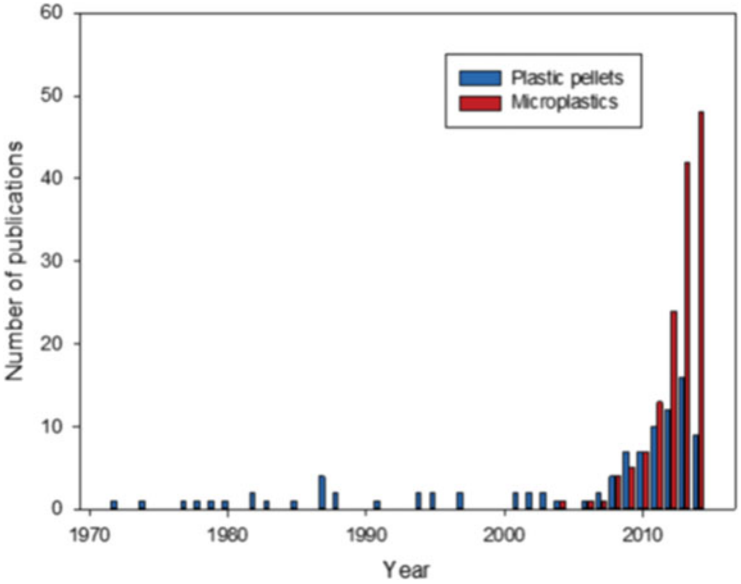

Fig. 1 Publications by year 1970 – July 2015. Using the search terms "plastic pellets" and "microplastics." Compiled by Sarah Gall, Plymouth University. Reproduced from [9] with permission

of capturing much smaller particles. Hence, at present there is no universally accepted size range or methodology for the collection of microplastics. A recent report by GESAMP, an advisory body to the United Nations, adopted the working definition of microplastics from 1 nm to <5 mm [9]. However our knowledge about environmental quantities of particles at the lower end of this size range is completely lacking. Within the EU, there is currently work to promote greater harmonization for future monitoring [8]; however, at present, it is difficult to make formal comparisons between data collected by different research teams since methodologies vary. This is important because it fundamentally limits our ability to describe distributions and also to accurately assess abundance which is of fundamental importance not just in order to monitor changes in the levels of contamination but also to indicate the likely frequency of encounter by biota which is necessary to inform risk assessment.

2 Sources

A wide variety of polymers are used to make a diverse array of plastic products, many of which bring considerable societal benefit. All of the most common polymers have been identified as microplastic particles. These include, in order of frequency of studies reporting: Polyethylene (PE), Polypropylene (PP), Polystyrene

(PS), Polyamide (Nylon) (PA), Polyester (PES), Acrylic (AC), Polyoximethylene (POM), Polyvinyl alcohol (PVA), Polyvinyl chloride (PVC), Polymethyl acrylate (PMA), Polyethylene terephthalate (PET), Alkyd (AKD), and Polyurethane (PU) [10]. However, knowledge of the type of polymer found as a microplastic particle in the environment does little to help confirm the source of the particle since a single polymer can be used in a very diverse array of applications. Microplastics have been reported in the environment in a wide variety of colors, shapes, and sizes [10, 11]. Collectively this information on polymer type, shape, and color may, to a very limited extent, help to indicate possible sources according to original usage; for example, fibers from rope/netting, versus fibers from clothing/carpets. However, this information is of little use in identifying the geographic sources of origin. Microplastics can be described in two very broad categories which reflect their potential sources and usage; these are "primary" and secondary microplastics.

Primary microplastics are particles which enter the environment as litter of microplastic (<5 mm) size. That is to say, the release of pieces that are manufactured for use as microplastic sized particles. Sources of primary microplastics include spillage of pre-production pellets (~4 mm in diameter, sometimes called "mermaids tears" or "nurdles") or powders (>1 mm in diameter such as those used in roto-molding) which are being transported prior to being converted into plastic products. In addition, release of plastic particles which are used as shot blasting media, particularly in the cleaning of softer metals such as aluminum [12]. Primary microplastics also include the release of exfoliant microbeads used extensively in the cosmetics industry. For example, microbeads typically around 250 μm in diameter are used in a wide range of skin cleansers, shower gels, and toothpaste. When used, there is nothing the consumer can do to prevent the release of these microplastic particles into waste water and it is considered likely that a substantial proportion will then pass through waste treatment into the environment [13]. Quantities can be considerable with millions of individual plastic particles in a single 150 mL container of cosmetic [14].

By contrast, secondary microplastics are microplastic sized particles that have arisen as a consequence of the fragmentation, in the environment, of larger items of debris, such as packaging, rope, sanitary related products. With secondary microplastics, it is logical to assume that quantiles should broadly reflect the quantities of larger, identifiable, items of debris collected in routine monitoring. Such studies typically report single-use disposable items of packaging, sewage related debris, together with rope and netting as being some of the most common types of litter on shorelines. A further and potentially substantial input of microplastic to the environment is the release of fibers from textiles, for example, as a consequence of machine washing. Fibers have been reported in residues from sewage treatment on land [15] and at elevated quantities around former sewage sludge dumping grounds in the marine environment [16]. While these fibers can in effect enter the environment as pieces that are already microplastic in size, since they were not manufactured as microplastics they are generally considered as a secondary input.

3 Distribution

The distribution of microplastics can be considered from several perspectives. The most obvious is perhaps the geographic distribution and this can be evaluated at a range of spatial scales from less than a few meters, for example, within a beach [e.g., 17], to scales of several kilometers between beaches in a region, for example, to global scale patterns between countries or continents [16, 18]. Distribution can also be categorized between environmental compartments, for example, the quantity of microplastic at the sea surface, in the water column, on the sea bed (both subtidal and intertidal, e.g., [4]) and quantities in biota, for example, that have accumulated via ingestion [19, 20].

Since there are no universally recognized protocols for collection, sampling methods vary considerably among researchers, and this will have a strong influence on both the ability to detect microplastics as well as the types, sizes, and abundance of microplastics recorded [10]. The potential for bias is likely to increase as the size of the particles being investigated decrees. For example pieces <1 mm in diameter can typically be identified as plastic with a high degree of confidence by unaided visual examination. However, smaller particles will require visualization via microscopy and to be certain will also need formal identification using either Fourier transform infrared (FT-IR) or Raman spectroscopy [10]. These spectroscopic approaches require expensive capital equipment and are time consuming, hence are not universally applied. Yet in my experience of the submillimeter particles that appear “unusual” and look sufficiently like they might be plastic for them to be subjected to formal spectroscopic identification actually only about one third are confirmed as plastic. Despite these difficulties several studies do present information on geographic patterns of distribution. Thompson et al. [4] use standard approaches and FT-IR spectroscopy to illustrate the presence of microplastics at sites around the United Kingdom and, working near Plymouth, UK, also show greater abundance in subtidal sediments compared to intertidal sediments (Fig. 2). Using the same approach this team went on to sample intertidal sediments on a global scale, reporting the presence of microplastic on each of more than 20 shorelines sampled. Spatial variation among sampling sites was relatively low indicating the ubiquity of microplastics in the intertidal [16]. A much more extensive study spanning more than 20 years of routine data collection by volunteers shows the relative abundance of debris captured by plankton nets in the Atlantic Ocean. Here, there was no routine formal particle identification analysis, but the pieces recorded were typically 1 mm. A key finding from this study was substantial evidence of spatial patterns. Interestingly, the debris was most abundant in locations far from land indicating the importance of transport, of example away from human population centers. Indeed, the relative abundance showed a good level of predictability based on patterns of ocean circulation which appeared to be causing debris to accumulate in oceanic gyres (Fig. 3). Recent work in the Mediterranean has also shown elevated abundance near to population centers implicating them as potential sources and the shoreline study by Browne et al. also indicated a weak correlation

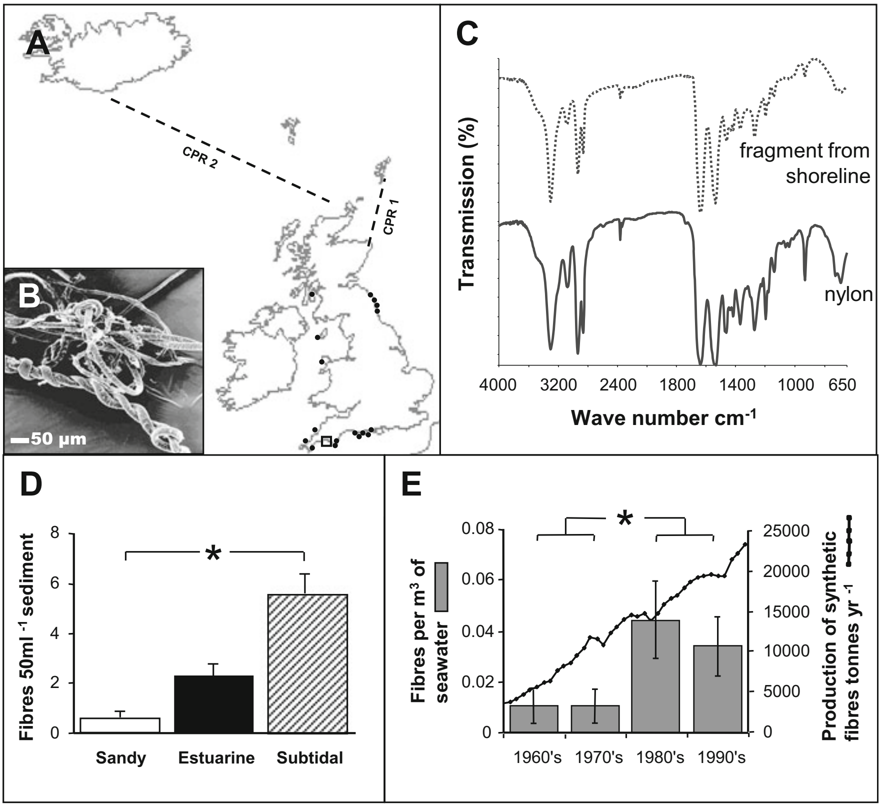

Fig. 2 (**a**) Sampling locations in North-East Atlantic: Location of sites near Plymouth used to compare the abundance of microscopic plastic among habitats, *square* (see Fig. 2D). Other shores where similar fragments were also found, *circle*. Routes sampled by Continuous Plankton Recorder (CPR 1 and 2) since 1960 and used to assess changes in the abundance of microplastics, *dashed lines*. (**b**) One of numerous microscopic fragments found among sediment from beaches and identified as plastic using FT-IR spectroscopy, bar = 50 µm. (**c**) FT-IR spectra of a microscopic fragment matched that of nylon. (**d**) There were significant differences in abundance of microplastics between sandy beaches and subtidal habitats (ANOVA on $\log_{10}(x+1)$ transformed data, $F_{2,3} = 13.26$, $P < 0.05$, $* = P < 0.01$), but abundance was consistent among sites within habitat type. (**e**) Accumulation of microscopic plastic in CPR samples revealed a significant increase in abundance when comparing the 1960s and 1970s to the 1980s and 1990s (ANOVA on $\log_{10}(x+1)$ transformed data, $F_{3,3} = 14.42$, $P < 0.05$, $* = P < 0.05$). Approximate figures for global production of synthetic fibers overlain for comparison. Microplastics were also less abundant along the oceanic route CPR 2 than CPR 1 ($F_{1,24} = 5.18$, $P < 0.5$). Reproduced from [4] with permission

between abundance and the human population at a regional scale [16]. In summary, these studies have demonstrated the wide spread distribution of microplastic on shorelines and at the sea surface, with evidence of elevated abundance near to population centers and also in locations where ocean circulation causes floating items to become trapped in surface gyres [21] or possibly where particles sink to the

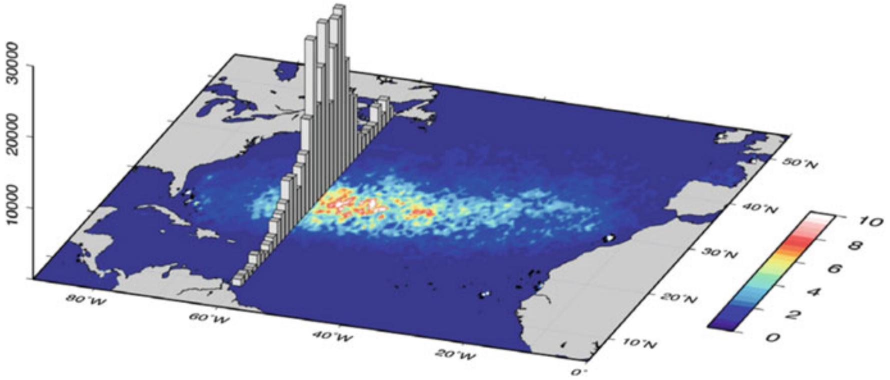

Fig. 3 Average plastic concentration as a function of latitude for data shown in Fig. 1 of [21] (bars, units of pieces km-2), and concentration, *C* (color shading), of initially homogeneous ($C = 1$) surface tracer after 10-year model integration (S2). Averages and standard errors were computed in one-degree latitude bins. The highest plastic concentrations were observed in subtropical latitudes (22–38°N) where model tracer concentration is also a maximum. Reproduced from [21] with permission

seabed [11]. There is a considerable challenge in scaling up from individual studies, especially considering the lack of consistency in sampling, in order to produce global estimates of marine debris and even more challenging global estimates of plastic distribution [22]. However, numerical models based on floating macroplastic debris have been developed [23–25] and no-doubt models to estimate the distribution of microplastic will be evolved. Such models can be invaluable in helping to formulate predictions and to help frame hypotheses about the sources and ultimate sinks for marine debris and, hence, also inform our understanding of encounter rate with marine organisms.

In addition to the studies above some of which were designed to make spatial comparisons of microplastic using standardized protocols, there have been numerous pioneering studies demonstrating the accumulation of microplastics in specific locations and environmental compartments. In terms of habitats, microplastic has, to my knowledge, been reported in every location so far examined. In addition, to the sea surface and intertidal, substantial quantities of microplastics have been reported in marine sediments. This includes substantial quantities in shallow water sediments. For example, quantities in excess of 2,000 items per kilogram dry weight have been reported from sediments in the Venice Lagoon [26]. Recent work suggests that quantities per unit volume in the deep sea sediment may be greater than per unit volume of water collected at the sea surface (although sampling these habitats unavoidably requires different methodology) possibly implicating the deep sea as an ultimate sink for microplastic accumulation [11]. Elevated quantities have also been reported in sea ice collected in the Arctic. Here, it appears that the process of ice formation may provide a mechanism leading to the concentration of particulate plastic from the nearby water column [27]. It should be noted that while this chapter focuses on the marine environment, there is growing evidence of widespread accumulation in freshwater lakes and rivers [28]. Microplastics have also been widely reported in biota. A recent review indicated around 10% of all papers describing encounters between debris and species described encounters with microplastics [7]. For example, microplastics have been reported in commercially important species of fish [19, 20] and shellfish [29]. Although quantities per individual are low, typically one or two items per individual, data indicate that a substantial proportion of the individuals in some populations are contaminated with microplastics. For instance, Murray et al. showed that over 80% of the individuals for a population of Dublin Bay prawns contained microplastics [29]. The most extensive data on ingestion of plastic debris comes from the work of Jan van Franeker who has been sampling populations of the Northern Fulmar in European waters for over 30 years. At the outset, his surveys did not explicitly categorize microplastics, however many of the items in these birds were within the microplastic size range. He has shown that in some parts of Europe more than 90% of individuals contain plastic debris. Indeed, the quantities in some birds are substantial, and despite some of the debris being regurgitated or defecated it appears that seabirds are retaining plastic debris. Jan van Franeker has estimated that in the North Sea region Fulmars probably process by ingestion around 6 tonnes of plastic annually translating to about 0.6 tonnes contained within the living population at any given time (van Franeker, personal communication). Once a bird dies and its body tissues decay then any plastic it did contain will be released back to the environment [30].

4 Fate

Plastics have only been mass produced for around 60 years; however, it is clear that in this time, plastic debris has contaminated habitats and biota on a global scale. This is equally true of microplastics which have accumulated on shorelines from the poles to the equator at the sea surface and in the deep sea; they have also accumulated in wildlife. There are few data on temporal trends in the abundance of plastic debris and the data that do exist tend to show considerable temporal variability rather than a trend of increasing abundance as might be expected based on plastic production statistics. Microplastic is a potential exception to this with some data illustrating an increase in abundance over time. Data collected by the continuous plankton recorder in Scottish waters showed significant increases in microplastic abundance when comparing between the 1960s and 1970s with the 1980s and 1990s. Hence it has been suggested that one of the reasons an increasing trend in the abundance of macroplastic is not evident from monitoring data is that larger items (i.e. macroplastics) are progressively fragmenting into smaller items that have not been captured in routine monitoring studies. It is also clear that microplastics are accumulating in inaccessible and relatively under-sampled locations such as the deep sea [11] and within arctic sea ice [27] and biota [7]. Microplastics have also accumulated in beach sediments more than a meter beneath the sediment surface [31]. More generally during microplastic sampling, all protocols require a visual discrimination step. This means that microplastics that resemble natural particulates, for example, white or translucent relatively spherical particles will be hard to distinguish from sand when compared to brightly colored fibrous shaped pieces. Hence there are a variety of factors that all result in environmental monitoring under sampling microplastics.

Plastics are very durable and are resistant to degradation. Ultraviolet light weakens plastic and coupled with mechanical action, for example, from wave energy, this can cause large items to fragment into microplastics. Hence, it is possible that the ultimate fate of all of the plastic in the environment is as microplastic sized pieces. In term of quantities, microplastics are substantially more abundant than macroplastics in some locations. However, by mass macroplastics are still by far the dominant size faction in the environment [17]. Therefore even if we were able to prevent additional inputs of plastic debris to the sea with immediate effect the quantity of microplastics would still continue to increase over time as a consequence of the fragmentation of legacy items already present in the environment (Fig. 4). It is also clear that there is no effective means of removing microplastic once it is in the ocean. Hence, in addition to further research to quantify the abundance of microplastics and consider their potential effects on biota and the environment, it is essential to focus on developing measures to reduce the inputs of debris. This is a pressing priority because even if we were able to initiate this action today it could take decades before this was translated into a substantial reduction in the rate of accumulation of microplastics.

From the perspective of the longer term fate of microplastics in the ocean, polymer chemists consider that all of the conventional plastic (i.e., nonbiodegradable) that has ever been produced is still present on the planet in a form that is too large to be biodegraded [32]. The exception to this is plastic that has been incinerated. Like all solid items in aquatic habitat plastic debris including microplastics readily becomes colonized by microorganism and microbial assemblages have been shown to vary according to plastic type [33, 34]. Some consider that biodegradation of conventional plastics is ultimately possible however there is little clear evidence of this. If biodegradation is occurring, it would appear that rates are incredibly slow, to the extent at least, that we should not rely on biodegradation to have any meaningful effect on the quantities of debris in our oceans when considered in relation to the substantial inputs of plastic marine debris [35].

5 A Personal Perspective on the Solutions to This Global Environmental Problem

Is the long-term fate then that our planet will become contaminated with exponentially increasing quantities of microplastics? From a personal perspective it seems that the warning signs are apparent and recent papers outline some of the concerns

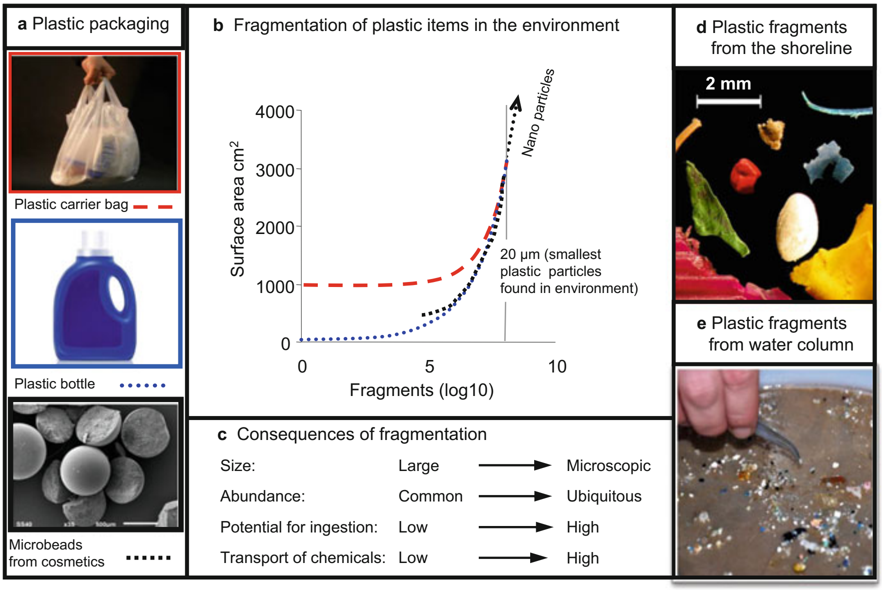

Fig. 4 Sources and accumulation of microplastics. (**a**) Microplastics can be generated from the breakup of large (macroplastic) items in the environment. These items include plastic packaging such as carrier bags and bottles. Microplastics formed in this way are described as secondary microplastics ((**a**) *top two photos*). Microplastics also enter the environment as a consequence of direct inputs of microplastics sized particles. Such particles are described as primary microplastics ((**a**) *bottom photo*, a plastic microbead from a cosmetic product, Courtesy of Adil Bakir and Richard Thompson, and Plymouth University Electron Microscopy Unit). (**b**) Once in the environment plastic items will progressively fragment into smaller and smaller pieces. Here, we see the relationship between the number of fragments formed by breakdown of the items shown in (**a**, *red line* = carrier bag, *blue line* = bottle, and *black line* = microbeads from a cosmetic product) and the total surface area of plastic. (**c**) This fragmentation will lead to formation of smaller particles and be associated with increased abundance, increased potential for ingestion, and increased surface area and hence increased potential for chemical transport. (**d**) Microplastic fragments recovered from the Tamar Estuary, Plymouth Courtesy of Mark Browne, Plymouth University and (**e**) Microplastic fragments recovered from surface waters in the North Atlantic (courtesy of Kara Lavender Law, SEA Foundation)

relating to microplastics in the environment including the potential for physical damage [36] as well as toxicological harm [37]. Is it inevitable that quantities of plastic and microplastic will increase? Yes it is inevitable, unless steps are taken to reduce inputs of debris to the ocean.

Thinking more broadly about inputs of plastic to the environment, there are several important additional considerations [38]: (1) From the perspective of sustainable use of resources, it has been estimated that we use around 8% of world oil production to make plastic items, yet around a third of these items are discarded within a short time frame. Plastics are inherently recyclable, so by recycling end-of-life plastic it is possible to reduce the accumulation of debris while at the same time reducing our demand for fossil carbon [39]. (2) Plastic items are important to society; however, there is something fundamentally different between the problem of plastic marine debris and several other current environmental problems. Unlike turning on an electric light or taking an aeroplane journey, the emission, in this case of debris to the oceans, is not directly linked to the benefit. So we can, in theory, obtain the benefits from plastic items without there being a need for emissions of end-of-life plastics to the oceans. (3) Together with other scientists, representatives from industry, policy makers, and NGOs, I frequently attend meetings focused on marine debris problems and solutions. While there may be discussion and sometimes disagreement about the relative importance of the various impacts, there is typically universal consensus to reduce inputs of debris to the ocean – in essence, I do not meet "marine debris deniers." From a broad perspective, we already know that marine debris is damaging to the economy, to wildlife, and the environment, it is wasteful and unnecessary and (as far as I am aware) we are agreed that it needs to stop. That being the case, then, what are the problems that retard progress?

In my opinion, the problems that retard progress relate to prioritizing solutions: who should take the action and if there are costs, who should pay [for further discussion see [38]]? The solutions are well known; they principally lie on land rather than at sea and in decreasing order of merit are: (1) reduce material usage – any reduction in the amount of new plastic produced will reduce the quantity of end-of life material that results and hence reduce the potential for formation of microplastics, (2) reuse items – this will directly reduce the need for new plastic items and so also reduce the quantity of end-of-life plastic material, (3) dispose of end-of-life items properly; ideally, recycle them, (4) recycle, since turning end-of-life material back into new items in a closed loop will reduce the accumulation of waste and simultaneously reduce the demand for fossil carbon, and (5) energy recovery via incineration – where items cannot easily be re-used or recycled, should be considered as a poor alternative to (1)–(4). Finally, but because it is overarching potentially most important we need to redesign, so for every plastic product consider, at the design stage, the hierarchy of options above in order to maximize the overall environmental footprint, i.e., reduce the use of fossil carbon and reduce the accumulation of waste, for example, by designing so that the eventual end-of-life products can readily be used as raw material for new production. Such principles are gaining momentum, for example, within the EU, there is considerable interest in the philosophy of circular economy [40]. There is public interest and response from industry, for example, some manufacturers have voluntarily opted to reduce the use of microbeads in their cosmetics [14]. Public interest and concern has also translated into policy actions, for example, to reduce the number of single-use plastic carrier bags. There are also industry led initiatives which unless used appropriately could work against these goals, for example, use of bio-based carbon from agriculture is seen as a sustainable alternative to fossil carbon. However altering the carbon source does nothing to reduce marine debris, and where land is at a premium for food housing or natural habitats, a more efficient and arguably more sustainable solution is to supply the required carbon by recycling end-of-life plastic. Similarly designing plastic products so that they degrade/disintegrate more rapidly can compromise the potential for product re-use, contaminate recycling, and lead to rapid accumulation of fragments in the environment [39]. What is needed is policy-led coordination of actions, supported by sound science, to utilize the measures above to achieve change as efficiently and rapidly as possible. This will likely involve voluntary actions, incentives, taxes, and education [41]. In particular there is a need to re-educate, thus far my lifetime has been spent in a world with rapidly increasing production of disposable short-term products and packaging, and of durable goods that cannot be repaired or renewed. In short, we are in a growing culture of throw-away living; there is an urgent need to recognize there is no such place as "away." Marine litter and in this case microplastics are in effect symptoms of an outdated and inefficient business model; there are choices that need to be made now in order to be more sustainable and to reduce the environmental impacts that otherwise will be left to challenge future generations.

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Nature of Plastic Marine Pollution in the Subtropical Gyres

Marcus Eriksen, Martin Thiel, and Laurent Lebreton

Abstract The abundance and distribution of plastic debris in the marine environment show patterns of near- and offshore generation, migration toward and accumulation in the subtropical gyres, fragmentation, and redistribution globally. Ecological impacts in the subtropical gyres include invasive species transport and rampant ingestion and entanglement; yet plastics have also created substantial new habitat, resulting in population increases in some species. Though estimates of surface abundance and weight indicate over a quarter million tons and particle counts in the trillions, there is also a rapid removal of microplastics from the sea surface. Recent studies show widespread occurrence of these microplastics throughout the vertical column and in benthic and coastal sediments. It is likely that sedimentation is the ultimate fate for plastic lost at sea. Before microplastics sink, they likely cause significant impacts to marine food chains and ecosystems. In the open ocean, plastics are mingled with marine communities, making removal at sea prohibitive. This new understanding informs mitigation efforts to divert attention away from open-ocean cleanup. Similar to the way societies dealt with widely distributed particulate contamination in the air above cities, the "smog" of

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microplastics destined to pass through marine ecosystems before finally settling on the seafloor is best addressed with preventative measures.

Keywords Garbage patch, Marine debris, Plastic debris, Subtropical gyre

Contents

1 Tracking Plastic in the Gyres

There are 11 gyres described in the world's oceans [1], 2 subpolar gyres below the Arctic Circle, 3 in Arctic waters, the circumpolar gyre around Antarctica, and the 5 subtropical gyres (Fig. 1). Plastic debris has been observed worldwide, with variation in the distribution and abundance following predictions from current models. This hydrodynamic flow, coupled with seasonal trends and variation in human inputs, influences the spatial variability of anthropogenic debris. Much attention is directed toward the subtropical gyres because of their propensity to accumulate floating debris. Here, the behavior of floating plastics in the gyres is reviewed with emphasis on the movement, characterization, some ecological characteristics, and fragmentation and fate of microplastics.

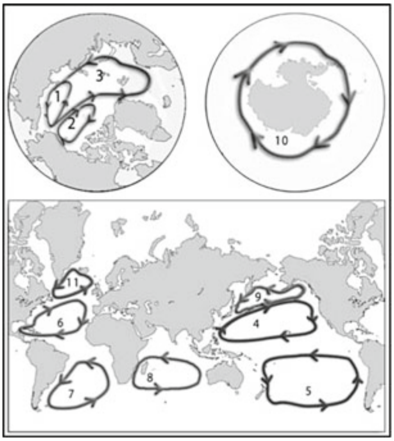
1.1 Defining a Gyre

The subtropical gyres are large-scale systems of wind-driven surface currents, flowing counterclockwise in the southern hemisphere and clockwise in the north, caused by the Coriolis effect, a force which tends to move wind and water currents to the right in the northern hemisphere and to the left in the south, creating cyclonic atmospheric and ocean movements.

Westward equatorial currents, on both sides of the equator, split when they reach continents. One branch flows toward the equator to join equatorial countercurrents. The other branch flows away from the equator, forming the western boundary currents of the subtropical gyres. These currents turn when they reach colder waters and flow eastward across the ocean again until reaching another continent, where they split again. In the northern hemisphere, one branch flows north toward the subpolar gyres, while the southern branch forms the eastern boundary currents of the North Atlantic and North Pacific subtropical gyres. In the southern hemisphere, these eastward currents also split, with one branch forming the eastern boundary current of the three subtropical gyres. The other branch continues east around Cape Horn, Cape of Good Hope, and south of Australia and New Zealand, following the direction of the circumpolar gyre (Fig. 1).

Climatological wind stress in the atmosphere contributes to these rotational fields, resulting in stable high-pressure systems [2]. Ekman transport, the movement of water perpendicular to the direction of wind, creates those surface currents that transport floating debris toward the center [3].

The subtropical gyres are characterized by warm surface waters, contrasting the colder and more biologically productive waters of the subpolar and circumpolar gyres [4]. A subtropical convergence zone (STCZ) forms where the colder waters are driven below the warmer waters in the subtropical gyre [5]. This is a physical front, where low phytoplankton productivity in warmer waters, indicated by low chlorophyll-a



1. Melville Gyre
2. Beaufort Sea
3. Transarctic gyre
4. North Pacific Subtropical Gyre
5. South Pacific Subtropical Gyre
6. North Atlantic Subtropical Gyre
7. South Atlantic Subtropical Gyre
8. Indian Ocean Subtropical Gyre
9. North Pacific Subpolar Gyre
10. Antarctic Circumpolar Gyre
11. North Atlantic Subpolar Gyre

Fig. 1 Location of 11 gyre systems in the world's oceans (adapted from "Flotsametrics," [1]) values, meets higher values in the colder waters. Called the Transitional Zone Chlorophyll Front (TZCF), it is observed on satellite-derived color maps of ocean basins [6]. In the North Pacific, the TZCF and sea surface temperatures were correlated with densities of plastic marine pollution, in what is called the Debris Estimated Likelihood Index (DELI) [5]. The transitional zones between subtropical and subpolar (circumpolar) gyres are present in all five subtropical gyres, and observed plastic debris concentrations rapidly decline across these fronts [7].

The accumulation zones of plastic that form in the subtropical gyres are a result of the diminished winds and currents occurring at latitudes synonymous with continental deserts. These oceanic deserts, with low productivity, do not appear to be static regions that aggregate plastic indefinitely. There are chemical, mechanical, and biological processes at play that accelerate the fragmentation of plastic in the subtropical gyres.

1.2 Historical Observations

Plastic debris was first reported in the western North Atlantic in 1972 [8]. Two years later a substantial analysis of plankton tows in the same region reported widespread distribution of preproduction plastic pellets, foamed polystyrene spheres, and angular fragments floating near the eastern United States, Gulf of Mexico, and Caribbean Sea [9]. Explorations in the South Atlantic near Cape Town, South Africa, in 1980 reported preproduction plastic pellets and balls of tar, reportedly from the flushing of oil tankers into the sea [10]. Six years later, extensive studies in the North Atlantic sampled further offshore, coining the term “plasto-tarball” for the aggregations of plastic pellets, fragments, and tar, and this offers the first suggestion that plastic debris accumulates in the gyres. “Data from our oceanic survey suggests that plastic from both intra- and extra-gyral sources becomes concentrated in the center of the gyre, in much the same fashion that *Sargassum* does” [11].

Simultaneously, exploration of the North Pacific was under way [12, 13], and at the Second International Marine Debris conference in 1989, Day et al. reported results from 203 stations across the North Pacific, including the Sea of Japan, eastward to Hawaii, and northeast toward Alaska, and into the Bering Sea [14]. The authors observed a predictable boundary of debris concentrations in the waters surrounding the subarctic gyre below Alaska, where surface waters move away from the center. The highest observed abundance of 316,800 pieces of plastic km^{-2} was well inside the western accumulation zone of the North Pacific Subtropical Gyre [14]. Yet, this study had missed the waters between Hawaii and the west coast of the United States. For nearly a decade, the study of plastic debris fell silent. A 2001 study of the waters between California and Hawaii conducted 11 neuston tows with a mean of 334,271 pieces per km^2 [15] greater than the highest single abundance Robert Day and collaborators had reported in 1990. With wide media attention, the term “garbage patch” entered the public and scientific lexicon [16, 17], propelling public and research interest rapidly forward.

Accumulations of plastic debris have been observed regionally in the South Pacific [18, 19], South Atlantic [20], Bay of Bengal [21], circumnavigating Australia [22], Southern Ocean [23], Mediterranean Sea [24], North Pacific [25] and North Atlantic [26], and globally [7, 27]. Recent calls for standardization of methods [28] and citizen science [29] aim to broaden the utility and monitoring capability of future efforts.

2 Sources of Plastic to the Marine Environment

A generally accepted estimate indicates that up to 80 % of plastic debris originates from land-based sources [30] and 20 % originates from maritime activities. However, despite being widely cited, this figure is not well substantiated and fails in quantifying plastic waste inputs [31]. Thus, the following sections attempt to provide a more detailed analysis.

2.1 Land Inputs

The major land-based sources of plastic debris include wastes from dumpsites in coastal regions, watersheds and rivers, industrial outfalls, littering of beaches, tourism, and recreational use of the coasts [32]. Extreme events such as storms, tidal waves, and tsunamis are also a significant immediate source of land-based plastic debris. Particularly, the pulse of debris washed into the North Pacific by the 2011 Tohoku tsunami was well documented [33, 34]. Estimating the plastic input from land to ocean is a difficult task. Early estimates from the US National Academy of Science claim that a total of 6.4 million tons (5.8 million metric tons) of waste are released into the ocean every year and of this 0.7 % is plastic, roughly 41,000 metric tons [35]. A careful reading of this reference suggests that this number is based on an extrapolation of values from estimates of wastes produced by individual households and these inferences may not be entirely accurate.

2.1.1 Waste Generated by Coastal Populations

A study calculating the amount of mismanaged plastic waste generated by coastal populations worldwide estimated that 4.8–12.7 million tons (metric tons) can potentially enter the ocean as marine debris [31]. The framework integrates data on solid waste, population density, and economic status for 192 coastal countries. The annual amount of mismanaged plastic waste generated by populations living within 50 km of the coast was estimated at 31.9 million metric tons ranging from 1.1 to 8.8 million metric tons/year for individual countries with a conversion rate from mismanaged plastic waste to potential plastic debris ranging from 15 to 40 %.

This conversion rate range was assumed conservative and based on municipal water quality data from the San Francisco Bay watershed in California, estimating that 61 % of all materials littered in the watershed was not captured by street sweeping or catchments and thus was available to enter the waterways.

The study on global plastic waste inputs also predicts an order of magnitude increase in marine littering from coastal population pressure by 2025 if no improvements are made on waste management infrastructure [31]. The work also suggests that 83 % of the global mismanaged plastic waste in coastal regions for 2010 was generated by the top 20 countries largely dominated by Asian countries (11 countries in the top 20) with China ranking first (1.32–3.53 million metric tons of annual plastic debris input) and Indonesia second (0.48–1.29 million metric tons).

Overall, this study represents the most recent estimate of potential global plastic input, with an estimated 4.8–12 million metric tons of mismanaged waste leaving coastlines globally each year from the 192 countries analyzed. This study relied on World Bank data on waste management, which excluded local incineration, burial, and informal plastic collection, collectively labeling them as "mismanagement." Informal plastic collection, commonly called "waste picking," in China may account for 17–38% wt. of municipal solid waste diversion [36] and may represent 3.3–5.6 million people. Across Latin America and Asia, waste picking is the livelihood of an estimated 2 % of the population [37], representing a significant contribution to keeping plastic from entering the ocean. The quantity of waste managed informally by waste pickers, or that which is locally burned or buried, is difficult to quantify per capita or per country. Therefore, this quantity was omitted from the study, although the informal collection of mismanaged waste may consist of the other 60–85 % of the mismanaged plastic waste that was estimated *not* to make its way to the ocean in each country (J. Jambeck, personal communication). Future estimates of waste inputs must include these significant factors.

2.1.2 Waste Introduced by Rivers

Plastic debris originating from intentional or involuntary dumping on river banks [38], dumpsites, and surface runoff in urban environment can potentially be introduced into rivers [39]. The plastic may sink, be deposited on riverbanks downstream, or enter the marine environment. Manufactured micro- and nanoparticles of plastics used in consumer products can also potentially enter the marine environment via runoff [40]. These include micro-sized particles used as exfoliants by the cosmetic industry [41–43] and industrial abrasives [44]. Synthetic nanoparticles in the form of microfibers from the washing of synthetic textiles are abundant in rivers and coastal sediments [45]. Several studies using floating debris-retention booms or stationary driftnets estimated the amount of plastic waste carried by various rivers worldwide.

An estimated 4.2 metric tons/day (more than 1,500 metric tons/year) of plastic waste is introduced into the ocean by the Danube River [46]. The figure was calculated using data from a 2-year survey using drift nets. Particularly, the study emphasizes significant amounts of floating pellets and spherules originating from the plastic resin industry flowing in Europe's second largest river (see also [47]).

Using an extensive regional network of floating debris-retention booms, a study quantifying floating debris in the Seine River reported that 0.8–5.1 % of total debris collected by weight was plastic [39]. The regional network intercepts between 22 and 36 metric tons of plastics, annually. Most collected plastic debris was made of polypropylene and polyethylene. In 205 days, 390 kg of debris of which 73.6 % was plastic were collected in two watersheds on the island of Hilo in the Hawaii archipelago [48], which infers more than 0.5 metric tons of plastic debris per year.

In Southern California, samples of river water, taken with a variety of nets in the Los Angeles and San Gabriel Rivers were used for a research effort quantifying the contribution of the Los Angeles basin to the issue of plastic debris release into the marine environment [49]. The study reported an extrapolated 72-h average plastic debris weight of 30 metric tons using data from rainy and dry days.

Other quantities were reported for the Thames River [50] with nearly 8,500 submerged plastic items collected during a short sampling period and for the Tamar River [51] where 82 % of collected debris were plastic. A study on anthropogenic riverine litter along riverbanks and river mouths in Chile [52] also concluded that riverine transport has an important impact on litter abundances on coastal beaches.

2.2 *Maritime Inputs*

The dumping of waste from ships, though a common practice historically, has sufficiently been reduced since the 1990 international shipping regulation MARPOL Annex V, indicated by waste management procedures on commercial, private, and military vessels.

The current maritime sources of plastic debris include shipping, fishing, fish farming, offshore mining, illegal dumping at sea, and natural disasters [32]. Marine litter from shipping sources include merchant, public transport, pleasure, and naval and research vessels. Maritime activities were first assumed to represent 20 % of the total source of marine litter [30]. Commercial fishing gear alone was estimated to account for 5 % of the total debris found in the ocean [53]. Overall, the fishing industry is suspected to be accountable for 18 % of the marine plastic debris found in the ocean environment [44]. In areas with limited input from other anthropogenic sources, fishing gear may contribute significantly higher proportions of litter [54, 55, 118].

A study on fjords, gulfs, and channels of Southern Chile reported high quantities of expanded polystyrene [92] used as floatation device in local mussel farms and food sacks from salmon farms suggesting that aquaculture plays a significant role as input of floating plastic debris. The contribution of aquaculture in generating plastic debris with the introduction of expanded polystyrene was also suggested in the Gulf of Aqaba [56], South Korean beaches [75], and Hiroshima bay in Japan [84].

2.3 Catastrophic Events

While most litter is continuously supplied to the oceans, catastrophic events create pulses of debris. Flood events, cyclones, and tsunamis may flush large amounts of litter into the oceans [121]. This occurs infrequently and generally in local areas. Little attention has been paid to the identification and quantification of litter contributed by these catastrophic events. Several studies have shown that river floods flush large amounts of marine debris into coastal waters [48, 49, 52]. The recent 2011 tsunami in Japan is the first event that has spurred systematic research efforts in quantifying and tracking plastic (and other) litter introduced to the oceans [33, 64, 72].

Catastrophic events may introduce on a sporadic basis large amounts of plastic debris to areas that usually receive relatively small amounts of debris. They may also cause loss of large quantities of artificial structures (floats, buoys, ropes, boats, etc.) that have already been colonized by coastal organisms. In particular, this detachment of overgrown structures is cause of concern, because, if positively buoyant, these rafts may be transported over large distances. Therefore, the frequency, quantification, and impact of debris introduced to the oceans by these catastrophic events (flood events, cyclones, tsunamis) deserve more research attention in the future.

3 Fragmentation and Characterization

3.1 Mechanisms of Fragmentation

Fanciful notions of "plastic, like diamonds, last forever" parallel public misconceptions about degradation and fragmentation rates, including timescale lists of how long specific plastic products persist in the environment, and often one reads "all plastic ever produced still exists somewhere on the planet." Degradation is a chemical change that drastically reduces the average molecular weight of the polymer [44] and is completely environmentally dependent, ranging from plastic in a campfire to sequestration in benthic sediments. In addition to incineration, there are other mechanisms of degradation and fragmentation that reduce large plastic items to microplastics or break the long polymer chains. These mechanisms and rates of decay may include ultraviolet (UV) degradation, embrittlement and crushing by waves, thermooxidative degradation, hydrolysis, biodegradation, grazing and shredding by macrofauna, and abrasion along coastlines.

Plastic debris may be transported along coastlines with tidal movements, resulting in abrasion and UV degradation accelerated by thermal loading on exposed dry surfaces [59, 123]. Exposed plastics incur photooxidation where polymers are exposed to UV radiation and oxygen [130]. Evaluation of the surface characteristics of beached plastic items shows evidence of degradation from both sunlight and abrasion, each with different physical characteristics ([78]; Plastics Design [104]). Mechanical weathering from abrasion is evident by groves and gouges, fractures, adhered particles, and mechanical pits [129]. Wave mechanics drag plastics along hard- and soft-bottom shorelines and reef substrata, creating groves and gouges, whereas photooxidation results in roughened surface features, discoloration, and a flaking or dustlike decay when touched.

Floating debris exposed at the sea surface may incur these same degradation processes, though submerged debris, or even persistent wet debris, may have degradation rates delayed by biofouling, lower temperatures, or submersion beneath the photic zone.

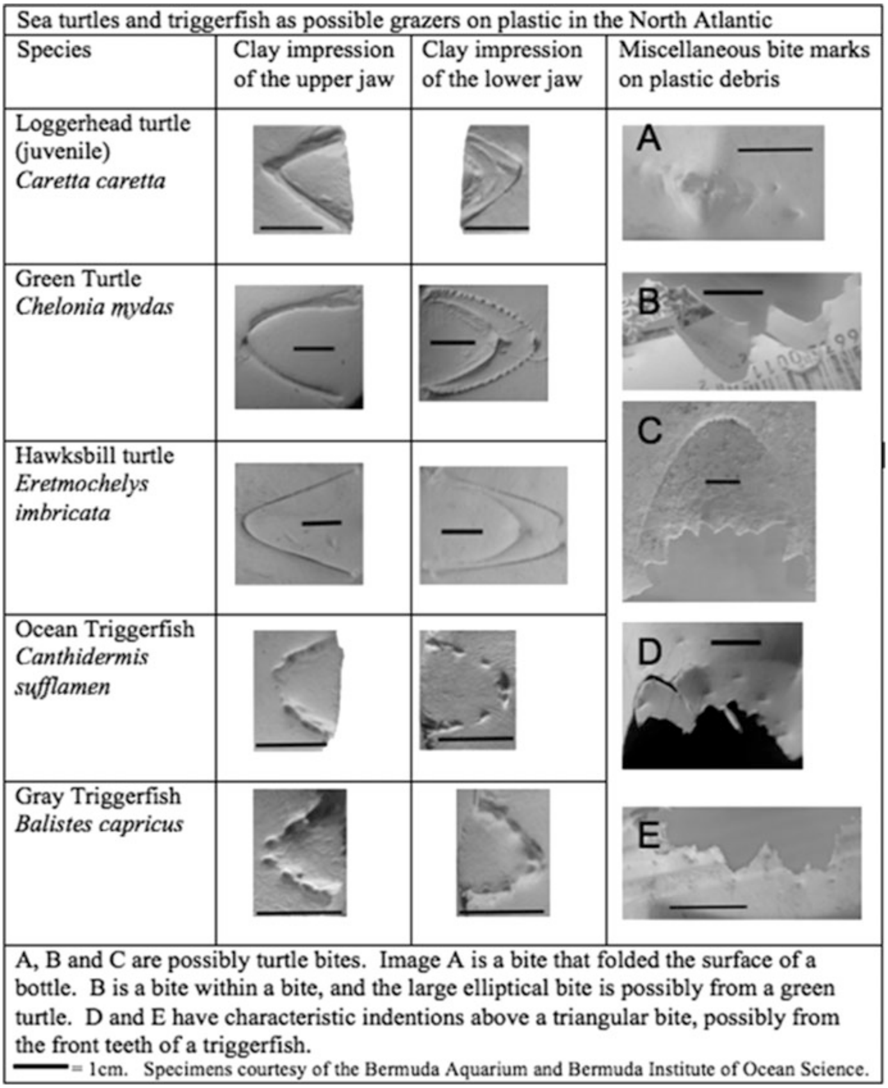
3.1.1 Biodegradation and Fragmentation by Grazing

Of the many interactions between plastic debris and marine organisms, microbial biodegradation and grazing by macrofauna facilitate fragmentation. Floating plastics are rapidly colonized by marine organisms, beginning with biofilms, algal mats, and then invertebrates [110]. Among these microbial films, there has been evidence of biodegradation on debris surfaces, primarily on polyethylenes and polypropylene [90, 117], but also on PVC and polycarbonates [62, 116], which float primarily with trapped air. Biodegradation is further accelerated with increased debris surface area, which can be facilitated by photodegradation and mechanical breakage [98]. The dustlike residue from handling photodegraded plastics may be degraded completely by bacterial decomposition [81]. While recent studies have indicated that plastics are colonized and degraded by microbes, little is known about the rates of biodegradation and the significance of factors, such as substratum type, seawater nutrient concentrations, UV radiation, temperature, salinity, and pH.

The ingestion of plastic debris by marine organisms has been well documented [88, 102], with increasing attention toward ingestion by fishes. In the North Pacific, mesopelagic fishes have been found with ingested microplastics [68, 79] and macroplastics [77]. In the North Atlantic, ingestion has been observed in the Sargasso Sea [94], English Channel [106], Mediterranean Sea [61], and North Sea [83]. It is unknown whether these fish are ingesting plastic directly or retain plastic from the gut of smaller fish they consume.

The significance of marine life grazing, or tearing fragments of small pieces of plastic from larger ones, is not well understood. It is not uncommon to find bite marks on floating or beached debris, from scratches and scrapes from copepods [113] to bites from sharks [102]. In a study of debris washed ashore at Kamilo Beach, Hawaii, 5,518 pieces of plastic were collected, of which 15.8 % showed evidence of having been bitten [73]. Predators may be pursuing attached organisms or testing the plastic itself for edibility.

In a recent survey of plastic debris washed ashore in Bermuda, we collected plastic bottles with distinct bite marks (Fig. 2). The skulls of five marine vertebrates associated with mats of *Sargassum* sp. in the North Atlantic Subtropical Gyre were used to make impressions of their lower and upper jaws in clay for comparison to the plastic with bite marks on plastic. Three turtle species (*Caretta caretta*,



Sea turtles and triggerfish as possible grazers on plastic in the North Atlantic

Species	Clay impression of the upper jaw	Clay impression of the lower jaw	Miscellaneous bite marks on plastic debris
Loggerhead turtle (juvenile) *Caretta caretta*			A
Green Turtle *Chelonia mydas*			B
Hawksbill turtle *Eretmochelys imbricata*			C
Ocean Triggerfish *Canthidermis sufflamen*			D
Gray Triggerfish *Balistes capricus*			E

A, B and C are possibly turtle bites. Image A is a bite that folded the surface of a bottle. B is a bite within a bite, and the large elliptical bite is possibly from a green turtle. D and E have characteristic indentions above a triangular bite, possibly from the front teeth of a triggerfish.

━━ = 1cm. Specimens courtesy of the Bermuda Aquarium and Bermuda Institute of Ocean Science.

Fig. 2 Sea turtles and triggerfish as possible grazers on plastic in the North Atlantic Subtropical Gyre

Chelonia mydas, Eretmochelys imbricata) and two triggerfish species (*Canthidermis sufflamen, Balistes capricus*) were used.

Impressions of the jaw of trigger fish (Fig. 2) show a triangular arrangement of both the upper and lower teeth, which appear similar to bite mark patterns on plastic bottles (D and E). It appears that the triggerfish bite mark is performed with the upper jaw grasping the plastic while the lower teeth shear off a triangular fragment, with the two front teeth leaving indentions above the apex of the bite.

Possible turtle bite marks on plastic in Fig. 2 (B and C) appear to match the jaw size and pattern of *Chelonia mydas* or *Eretmochelys imbricata*. Bite mark A appears to be made from a bite that folded the plastic, leaving upper and lower indentions on opposite sides of the bite mark.

3.2 Characterization of Debris in the Gyres

The characterization of plastic debris in the gyres varies regionally due to debris sources, polymer type, and object design, and the migration or accumulation of debris due to current dynamics. Nearly all human activities, regardless of proximity to the ocean, utilize plastic; yet loss of plastic from these activities to the ocean can be narrowed to three broad input categories: rivers, runoff from highly populated coastal cities, and maritime activities including fishing and shipping lanes [103]. These exclude airborne plastics from recreational balloons, weather balloons [112], or wind-driven micro- and nanoplastic particles and fibers. Though many types of plastic may come from these sources, the characterization of debris may vary widely in the gyres (Table 1).

Plastic abundance in the oceans has been estimated to be 269,000 tons from 5.25 trillion particles [7]. This is significantly less than the input estimate from Jambeck et al. [31] averaging 8.0 million metric tons annually, and illuminates both the difficulty in making such estimates and the wide range of mechanisms that remove plastic from the marine environment.

Table 1 Types of plastic marine pollution

Polymer	Specific Density (g/cm^3)	Common debris items
Polypropylene (PP)	0.89–0.91	Fishing line, ropes and floats, detergent bottles, toothbrushes, combs, preproduction pellets
Low-density polyethylene (LDPE)	0.89–0.94	Fishing floats, thin grocery bags, cups and containers, preproduction pellets
Cellulose acetate (CA)	1.3	Cigarette filters
High-density polyethylene (HDPE)	0.94–0.96	Bottles for milk and dishwashing liquids, fishing floats, buckets, and crates
Thermoplastic polyester–polybutylene terephthalate (PET and PBT)	(PET) 1.29–1.40 (PBT) 1.30–1.38	Water and carbonated drink bottles
Polyvinylchloride (PVC)	1.30–1.58	Soft vinyl toys, shampoo bottles
Polystyrene (PS)	1.04–1.08	Yoghurt cups, foam meat or fish trays, egg cartons, vending cups, plastic cutlery, packing material, fishing floats
Polycarbonate	1.2	CDs and DVDs, tail lights on cars, hard plastic canteens, cigarette lighters

Density of: Seawater 1.02–1.03 g/mL, freshwater <1.015 g/mL

Many types of plastic products and polymers enter the marine environment (Table 1) through wind and waves, rivers, and wastewater treatment facilities, and many of these may be deposited in estuarine or near-shore environments. The majority of plastics produced are near neutral buoyancy (within 0.1 g/mL of seawater) and may sink with only a minute fraction of sediment attached. Other plastic products with negatively buoyant polymers may trap air, either by foaming agents, compressed fuels, or simply caps remaining on bottles. The result in the gyres is a reflection of coastal waste characterization coupled with the accumulation, fragmentation, and redistribution processes that vary regionally and by polymer and product type.

3.2.1 Distribution by Type

In all subtropical gyres debris types of floating plastics can be generally classified into five categories: fragment, pellet, line, thin film, and foamed polystyrene. These items result from the fragmentation of debris emanating from coastlines or maritime activities, such as shipping, recreation, fishing, and aquaculture, and may contribute debris to the ocean, including nets, line, floats, fish packing crates, and a range of consumer products lost overboard [92]. The variability between subtropical gyres in the distribution of particle characterization is largely unknown, though two datasets from the North Pacific (Moore 2007, 2008 unpublished data) and the North Atlantic (Eriksen 2010 unpublished data) show similar distributions of these five types (Table 2). In both subtropical gyres, fragments dominate the total particle densities, but an analysis by size class shows that pieces of line, primarily from nets and ropes, dominate macroplastic count densities.

Table 2 Distribution of five plastic types based on count densities (items/km^2) in two northern hemisphere subtropical gyres

	Fragment	Pellet	Line	Thin film	Foam
North Pacific					
>4.75 mm	2,868.4	48.3	4,869.6	672.5	12.8
1.00–4.75 mm	61,159.6	1,473.7	3,673.1	3,745.6	418.8
0.35–0.99 mm	37,256.0	41.6	2,672.0	3,506.1	33.6
Percent of total	83.0	1.0	8.8	6.9	0.4
North Atlantic					
>4.75 mm	3,502.4	0	2,077.6	688.3	12.9
1.00–4.749 mm	28,127.8	800.5	1,298.3	743.4	40.4
0.355–0.999 mm	21,385.9	3.9	255.2	95.1	5.3
Percent of total	89.8	1.4	6.2	2.6	0.01

Unpublished data from the North Pacific (Moore C. 2007–2008) and North Atlantic (Eriksen M. 2010)

4 Estimating Abundance, Weight, and Distribution

4.1 Modeling the Global Distribution of Marine Debris

Extensive modeling work on marine debris concentration at global scale has been conducted [103, 108, 125]. The various numerical models confirmed the formation of five main areas of concentration located in the subtropics and detected by early observers on the field [8, 15, 18, 26]. The high-concentration zones are maintained by converging Ekman currents in the five oceanic basins.

The first attempt to numerically reproduce the likely pathways of marine debris used a global set of trajectories of satellite-tracked drifters [108]. A probabilistic model is developed to eliminate the bias in spatial distribution of drifter data due to heterogeneous deployments. The study considers an initial state with drifting particles uniformly spread over the global ocean. Particle quantities are advected using probabilistic forcing calculated from observed surface drifter data.

An alternative approach was proposed using a global ocean circulation model for Lagrangian particle forcing [103]. Dynamics of marine debris are calculated in two stages: first a hydrodynamic model describes oceanic circulation and second virtual particles are introduced into the flow field and allowed to move freely through modeled hydrodynamic forcing. The initial Lagrangian particles are no longer uniformly spread over the ocean but released from terrestrial and maritime inputs. The rate of particle release is calculated using proxy scenarios including urban development in watersheds, coastal population pressure, and shipping activities. Industrial and recreational fishing and aquaculture are not directly considered. The origin of the particle can be retraced allowing detailed analysis of the contribution of individual sources to the major accumulation zones.

A numerical model integrating a plastic debris source function scaling with coastal population as in Lebreton et al. [103] and advecting concentration quantities with observational data from the Global Drifter Program as in Maximenko et al. [108] was eventually proposed [125]. The advection of tracers from the probabilistic model is no longer constant in time but varies with seasonal cycles. The framework allows studying the fate of marine debris on interannual to centennial timescales. A detailed analysis of the debris dynamics at large timescale shows different evolution of the major aggregation zones. With the exception of the North Pacific, the high-concentration zones in other basins are much more dispersive than previously assumed. The great oceanic garbage patches are much better connected than previously thought.

4.2 Abundance and Weight Estimates

Model-predicted concentrations of advected Lagrangian particles are compared with field data from expeditions conducting net tows and/or visual transects of plastic debris. The numerical models can be calibrated against measured quantities of floating plastic particles, allowing the formulation of regional and global estimates.

A study on the global distribution of microplastic [27] using non-accumulation, outer accumulation, and inner accumulation zones from a global distribution model [108] and data from various expeditions and regional surveys suggests that the total floating microplastic load in the world's oceans ranges between 7,000 and 35,000 MT. The research assembles data from the Malaspina circumnavigation and other reported measurements included 3,070 total samples collected around the world. Plastic measurements are spatially averaged over 2° resolution grid cells and compared with 15 major zones characterized by their degree of convergence [108]. Two sets of measurements are considered, a wind-corrected dataset and a non-corrected dataset.

The global load of microplastic in the world oceans was confirmed by a more recent study [7] which estimated 35,500 MT of floating debris with a size below 4.75 mm representing 4,850 billion particles. The study compares numerical model predictions of particle concentration [103] with wind-corrected measurements collected by expeditions from 2007 to 2013, surveying all five subtropical convergence zones and other coastal regions or enclosed seas globally, including surface net tows (680 samples) and visual transects for large plastic debris (891 samples). Differentiating microplastics, mesoplastics, and macroplastics, the study estimates that in total at least 5,250 billion particles weighing nearly 270,000 MT are currently floating at sea.

For both studies, plastics of all sizes were found in all ocean regions converging in aggregation zones located in subtropical latitudes. Generally, the frequency of occurrence of plastic debris was reported significantly high in all regions of the world's oceans with 88 % of all samples containing plastic for Cozar et al. [27] and up to 93 % for Eriksen et al. [7].

In the Northern Hemisphere, the predicted loads of microplastic were in the same order of magnitude with previously reported regional estimates. A study using an 11-year data set in the North Pacific [25] estimates a weight of about 21,290 MT of floating microplastic while Cozar et al. [27] predicted up to 12,400 MT and Eriksen et al. [7] 12,100 MT. In the North Atlantic, an estimate for the western region of the subtropical gyre using a 22-year data set [26] reported 1,100 MT for 80 billion pieces, while for the whole North Atlantic Ocean, the total microplastic load was estimated between 1,000 and 6,700 MT by Cozar et al. [27] and around 5,250 MT for 856 billion pieces by Eriksen et al. [7].

The two Northern Hemisphere ocean regions contain more than half of the global floating plastic mass with reported masses between 49 and 54 % for microplastics [7, 27] and nearly 57 % when including macroplastics [7] for a combined mass of 152,870 MT (96,400 MT for the North Pacific and 56,470 MT for the South Pacific). This increase in proportion for the two Northern oceans when including macroplastics could be related to shipping and fishing activities, significantly more developed in the Northern Hemisphere [103]. Persistent plastic objects such as buoys or fishing gears are invariably lost or even discarded at sea by the global fishing and shipping industries. Buoys represented 58 % of the total weight of observed macroplastic debris reported by Eriksen et al. [7].

In the Southern Hemisphere coastal population density and shipping traffic are much lower than in the Northern Hemisphere; yet the reported plastic densities were very high, suggesting that plastic pollution is moved more easily between aggregation zones and between hemispheres than previously assumed [103]. Cozar et al. [27] predicted a relative homogeneity between microplastic loads in the three Southern Hemisphere oceans with an estimated mass of, respectively, 800–5,100 metric tons, 1,700–5,400 metric tons, and 800–5,600 metric tons for the Indian Ocean, South Atlantic Ocean, and South Pacific Ocean, whereas Eriksen et al. [7] concluded that the Indian Ocean appears to carry a greater particle weight than the South Atlantic and South Pacific oceans combined with 7,470 metric tons in the Indian Ocean, 1,540 metric tons in the South Atlantic Ocean, and 2,340 metric tons in the South Pacific Ocean. A similar distribution is observed when including macroplastics with, respectively, 59,130 metric tons, 12,780 metric tons, and 21,020 metric tons for the Indian, South Atlantic, and South Pacific oceans. These predicted quantities suggest that there might also be important sources of plastic debris in the Southern Hemisphere, such as currents from the Bay of Bengal that cross the equator south of Indonesia (e.g., [21]).

4.3 Discrepancy with Source Estimates

Estimates of plastic waste entering the ocean are one to three orders of magnitude greater than model-predicted mass of floating plastic debris from regional and global observation data set [31]. This large discrepancy can be attributed to both mechanisms of plastic debris removal at sea and methodological assumptions made to estimate plastic entering the ocean from land-based sources.

Both Cozar et al. [27] and Eriksen et al. [7] reported global estimates of floating debris, omitting estimates of plastic debris in the water column and on the seafloor and using crude estimates of the vertical distribution of microplastics, and making estimates based on limited data sets. These authors also observed a tremendous loss of microplastic from the ocean surface. Most small microplastics are fragments resulting from the breakdown of larger plastic items and are expected to be more abundant than larger microplastics. Eriksen et al. [7] observed the opposite in all regions except in the South Pacific where large and small microplastic counts were nearly equal. This discrepancy in abundance suggests that the ultimate fate of buoyant microplastics is not at the ocean surface.

There are mechanisms at sea that remove microplastics from the sea surface. UV light degradation, coupled with embrittlement and wave mechanics, reduces macro- to microplastic, as well as some microbial biodegradation and grazing by fishes, seabirds, and turtles. These microplastics may then be subject to biofouling and lose buoyancy, and ingested particles may sink as fecal pellets. Collectively, these poorly understood variables may explain the underestimation and discrepancy with coastal input estimates.

In Jambeck et al. [31], coastal inputs of plastic from the 192 coastal nations surveyed were derived from World Bank data on per capita consumption of plastic, waste management strategy, and populations living within 50 km from the ocean. The authors estimate that an average of 8 million metric tons of plastic enters the oceans. It is unknown what percentage of this total washes ashore soon after leaving land. The significance of local incineration, burial, and recovery by waste collectors is not accounted for in this study, and is difficult to quantify. Collectively, these variables contribute to a possible overestimation of actual debris loads entering the ocean.

Therefore, while Eriksen et al. [7] possibly underestimate plastic debris loads with a global estimate of 269,000 tons floating at the sea surface, Jambeck et al. [31] likely overestimate plastic entering the ocean, with an 8 million tons annual input estimate; if the variables identified above were quantified and contributed to these estimates, the disparity between them would likely close significantly.

5 Ecological Impacts

Interactions between plastic debris and marine organisms range from entanglement [69, 88, 102] to ingestion (Ryan, this volume; Browne, this volume), and settlement substratum (e.g., [63, 87]). Plastics, as any other clean substrata that enter the ocean, are immediately colonized by marine organisms. Colonization may occur before the plastic has become marine debris, as is the case for buoys and ropes used in fishing and aquaculture activities. Many floating structures anchored in coastal waters are colonized by a wide diversity of organisms. When these structures are detached and lost at sea, attached coastal organisms are transported via these floating plastics. They may travel along the coasts, spreading and connecting coastal populations. If these floating plastics are pulled into oceanic currents, the associated biological community can be transported over long distances, including across large ocean basins. The recent arrivals of large debris from the 2011 Japan tsunami on the NE Pacific coasts with extensive communities of coastal organisms bear testimony to this [72, 76, 93].

Large amounts of floating plastic debris also enter the oceans in a clean state. These plastics are then colonized by oceanic travelers. Some of the most common colonizers on floating substrata are gooseneck barnacles from the genus *Lepas*. These sessile organisms rapidly settle on any substratum floating at the sea surface, including macroalgae, wood, volcanic pumice, and plastic debris [87, 91, 126]. Small plastic pieces have also been found as foundation substratum for the gooseneck barnacle *Dosima fascicularis* [115]. Many other sessile organisms (algae, corals, oysters, bryozoans) have been reported from floating plastic litter [58, 65, 82, 119]. A wide diversity of mobile organisms also use plastic debris as rafts. These include mostly snails and crustaceans (e.g., [66, 71, 89]), but also polychaetes and others have been found on floating plastics [87, 99]. The larger a plastic item, the more species can grow on it (Fig. 3). Also, larger items can support larger organisms, but this relationship has not been examined specifically.

Floating plastic debris are not homogeneously distributed in the oceans. Currents and winds accumulate any floating objects in patches and frontal systems [57]. Here, plastic debris and floating objects of natural origin (algae, wood, pumice) are mingled in intricate patches (diameters of centimeters to several meters) or in drift rows (a few meters in width and kilometers in length). These

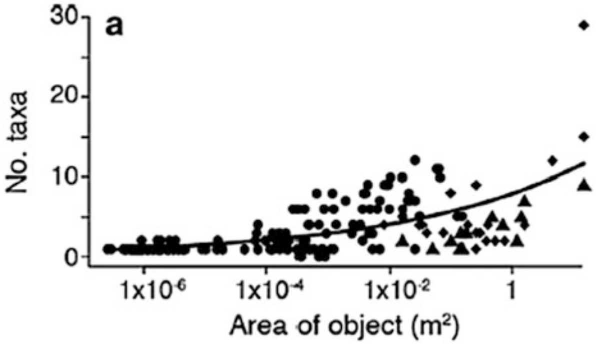


Fig. 3 Relationship between surface area of floating litter and the species richness of associated organisms (from [87])

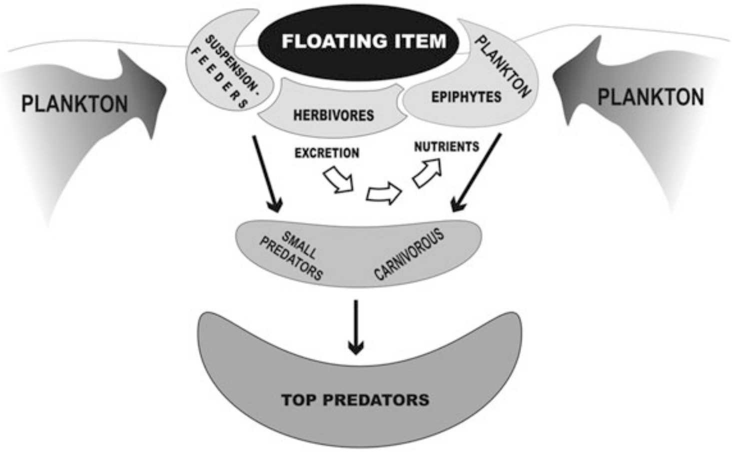


Fig. 4 Trophic interactions around floating objects (from [120])

heterogeneous and dense agglomerations of debris and natural floating objects represent concentrations of organic matter (dead or alive). In the nutrient-poor waters of the subtropical gyres, these agglomerations of floating material are true oases that provide habitat and food for many different organisms [57]. They attract many consumers such as turtles, fishes, or seabirds, which seek food and shelter around these floating patches (Fig. 4). The floating items serve as catalyst for multiple trophic interactions (Fig. 4).

Consumer interactions are important on and around these aggregations of floating materials (Fig. 4). Consumers also feed on the fouling communities on floating plastics. As on natural substrata, there is a relatively basic succession on floating debris, initiated by micro- and macroalgae, which attract grazers and are followed by suspension feeders (gooseneck barnacles, hydrozoans, bryozoans), which in turn attract numerous predators. These consumers continuously eliminate a large proportion of the fouling community. These interactions between growing fouling communities and consumptive removal of these result in continuous variation of buoyancy on these plastic items, which may be particularly important for smaller items where effects of the associated fouling community become more important for the overall buoyancy.

On these patches of larger floating plastic debris, the macroscopic organisms growing on this debris will also be exposed to high concentrations of microplastics. Consequently, they face the risk of ingestion of large quantities of small plastic particles. This has been shown for suspension-feeding gooseneck barnacles *Lepas* spp. collected from larger floating plastics: many of the larger individuals of *L. anatifera* and *L. pacifica* had consumed large amounts of microplastics [85]. Whether around these aggregations of floating plastic debris in the gyres contaminant concentrations also are enhanced is not known at present; however, the observation that all sorts of small materials from the sea surface (including tarballs and/or coal particles) are accumulated there suggests that this might be the case. Thus, transfer of contaminants to associated organisms might also be enhanced in these patches of floating plastics and organic matter.

The increasing amounts of plastic debris not only represent substratum for many sessile and mobile organisms, but they also serve as attachment sites for their eggs. Many fishes and invertebrates attach their eggs to floating objects [86, 95, 107, 127]. These egg attachment substrata may have been of limited supply in the past, as for example suggested for flying fishes [96] and ocean striders [86]. The ubiquitous presence of floating plastics may reduce this limitation for those species that require attachment substrata for successful reproduction.

The intricate nature of the patches of floating materials makes the separation of natural items and plastic debris difficult (Fig. 5). It also illustrates that removal of

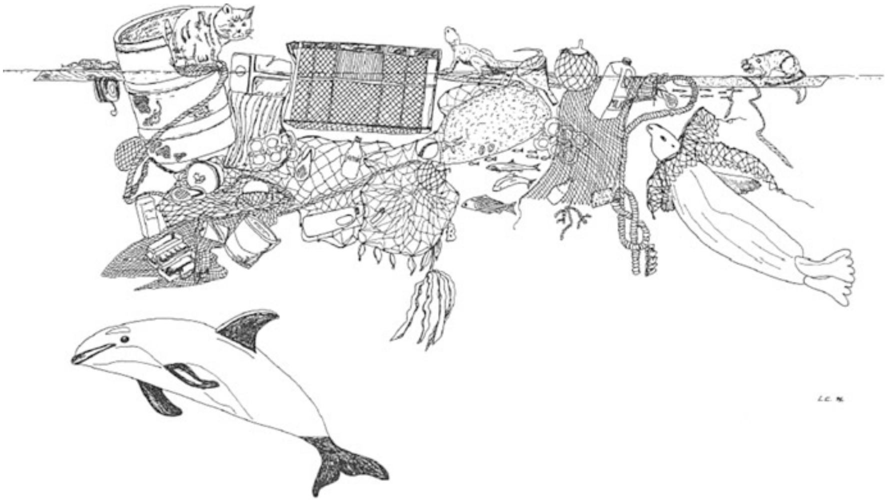


Fig. 5 Artist's representation of litter patch of multiple debris items accumulating in drift rows in the open ocean. From Winston et al. [127]

floating plastic debris from the open ocean will cause substantial ecological impacts, because many open ocean rafters and other organisms are inseparably associated with this litter [131].

6 Fate of Microplastics

The fate of microplastics in the subtropical gyres is a complex set of interactions that change as different variables come into play. Particle size impacts buoyancy, which impacts UV and chemical degradation, and subsequently impacts biofouling and biodegradation. In turn, sedimentation on island shores or the abyssal plains is a likely fate if ingestion by mesopelagic fishes does not occur. Collectively, these are responsible for the tremendous loss of microplastics from the subtropical gyres.

6.1 Loss of Microplastics from the Sea Surface

Two independent studies of the abundance and distribution of microplastics produced similar global estimates, with Cozar et al. [27] providing a range of 6,600–35,200 metric tons and Eriksen et al. [7] estimating 35,500 metric tons of particles <5 mm floating on the ocean surface. Both studies also reported substantial losses of microplastics, with Cozar et al. [27] estimating a 100-fold decrease in the abundance of microplastics compared to estimated total land inputs, and Eriksen et al. [7] showing a 40 % decrease in the global abundance of small microplastics (0.33–1.00 mm) compared to large microplastics (1.01–4.75 mm) based on very conservative fragmentation estimates. There are likely multiple mechanisms at play that remove microplastics from the ocean surface and cause a differentially increased rate of loss for particles less than 1 mm.

The deposition of microplastic particles in global environments logically follows the global distribution. Microplastics have been found in ice cores [111], on the seafloor [74, 128], and in coastal sediments worldwide [45, 67].

6.2 Vertical Movement

The mechanisms of fragmentation due to UV degradation and biodegradation are likely to accelerate as plastic particles decrease in size due to the increased ratio of surface area to volume, providing more sun exposure or more area for plastic-eating microbes to colonize a smaller mass of material. This increase in surface area for microplastics not only increases biofouling, but also increases the likelihood that neutral buoyancy or sinking will occur because the compensation for material buoyancy is less with relatively smaller volumes as microplastics fragment further.

Microplastics have been found suspended in the vertical column [80, 114] with an estimated 42 % of the total microplastic load beneath the surface [101], but rates of sinking and rising, and the influence of sea state, are poorly known. The buoyancy of biofouled particles is impacted by other factors beneath the surface. A substantial loss of colonization occurs when particles sink [60]. Changes in available sunlight, salinity, and temperature affect diversity and abundance of colonizing organisms, as well as fluctuations in the carbonate compensation depth (CCD) [124] dissolving heavy $CaCO_3$ and giving rise to particles with a lightened load.

This yo-yo effect, the vertical rise and fall of particles, increases the bioavailability of microplastics to a wide diversity of filter feeders and selective foragers living at different depths beneath the surface. Studies of mesopelagic fishes in the North Pacific Subtropical Gyre observed ingested microplastics, 35 % in one study [68] and 9 % in another [79]. As negatively buoyant particles sink deeper, they may be subjected to deeper currents. Wind-driven gyre currents dissipate beneath the surface, and neutrally buoyant particles may ride the ocean conveyor to regions far outside the subtropical gyres, only to rise there again. The oceans' eddy and wind fields play a significant role in establishing the variability of the oceans overturning, while the ocean conveyor transports deeper waters globally [105]. This variability in the lateral and vertical movement of warmer and more saline waters, as well as wind-driven convergence, is likely a significant transporter of microplastics out of the zones of accumulation and fragmentation in the subtropical gyres.

6.3 Trends

Increasing or decreasing trends in the abundance of microplastics are difficult to ascertain. In the example of floating tarballs, which were reported simultaneously with the occurrence of microplastics in the early 1970s [8, 9], a policy-driven reduction in the washing of oil tankers effectively reduced the number of tarballs found in surface tows in subsequent decades. A decreasing trend was informally established for tar, as reports of their occurrence diminished.

For microplastics, trends are more difficult to establish due to the varied input of plastic type, volume, and location [122]. Also, changes in waste management policies and the import of poorly designed plastic products affect the regional export of plastic to the ocean. "An analysis of 22 years of floating plastic debris in the western North Atlantic found no evidence for an increasing trend in plastic debris abundance in the region of the ocean where floating debris accumulates due to ocean surface currents, despite a strong increase in global plastic production and in plastic in the United States municipal waste stream during that period. However, because of large spatial and temporal variability in the data set (e.g., see Law et al. 2014), such a trend could be difficult to detect. A more sophisticated statistical analysis is underway on an updated North Atlantic data set to determine if there is evidence of an increase in floating plastic abundance between 1986 and 2012" (K. L. Law, personal communication).

These processes described here collectively create a life span for microplastics, though it is difficult to quantify on what timescales particles are removed. It is safe to say that the frequently used slogan "Plastics, like diamonds, are forever" is inaccurate for floating plastics in the subtropical gyres.

7 Conclusions

Our new understanding provides us with new language and focus to describe and mitigate the problem while offering a call to action to engage citizen science to monitor plastic marine pollution over time.

Early metaphorical descriptors of "patches" or "soup" of plastic in the gyres perpetuate public misconceptions about the resilience, residence, and characterization of floating debris. The nature of plastic debris in the subtropical gyres, reflecting the trends of increased input of plastic waste, rapid fragmentation, and global distribution out of the gyres is more akin to "smog" (Fig. 6), like the particulates of carbon in air pollution over urban centers distributed by atmospheric currents and slowly settling to the ground. Similarly, plastic smog is a particulate of hydrocarbon distributed by ocean currents and slowly settling to the seafloor.

This perspective supports that mitigation efforts are more successful when land based. When the issue of air pollution dominated the environmental movement in the 1970s the public and policymakers could look skyward and recognize that preventative measures were the only viable long-term solution. The issue of plastic debris drifting in the middle of the ocean lacks the benefit of visibility to quickly educate the public, leaving persistent misconceptions to drive mitigation efforts. The most common fallacy is recovery from the open ocean. Such proposals usually do not have an adequate understanding of ocean dynamics, marine ecology, and life

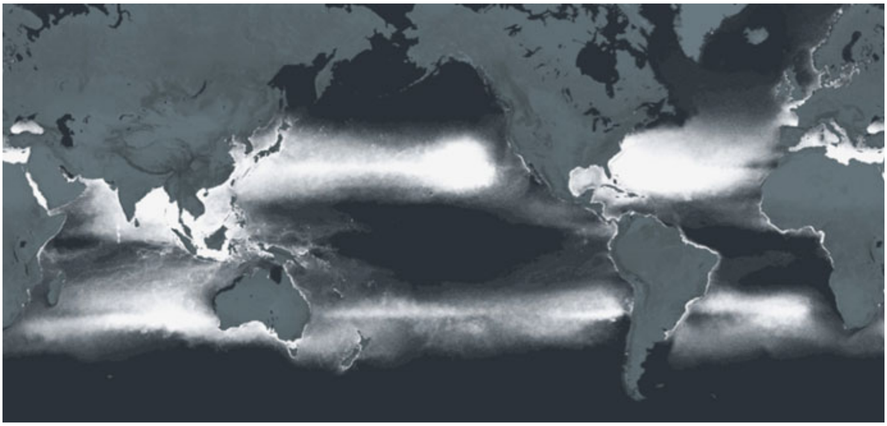


Fig. 6 5.25 trillion particles of plastic in the surface waters of the global ocean

cycles of plastics, aside from the fact that these projects are not engineered for the harsh conditions in the vast expanse of the world's oceans.

However, the abundance of plastic materials designed for durability at sea, primarily fishing gear, may justify recovery programs implemented by those engaged in maritime activities. In a recent global estimate of plastic marine pollution 269,000 tons of debris were estimated to be floating in the world's oceans, of which 58.3 % were fishing buoys and 12.1 % derelict fishing nets [7]. Fishing for Litter campaigns in Ireland, the UK, and Scotland report increasing success in the tonnage of debris recovered by incentivizing fishermen to recover anthropogenic waste from surface and bottom trawling operations [100].

These citizen-driven efforts, including coastal cleanup events, are applicable to contributing valuable information on plastic abundance and distribution. As a means of waste prevention, incentivized waste collection programs do not discourage littering and may perpetuate poor product usage and handling by not directly addressing sources of waste. Upstream strategies, such as leasing nets or accountability for returning the tonnage of nets purchased, could significantly decrease the loss of fishing equipment, thereby rectifying current anomalies in the fishing gear value chain [70].

To date, field data on plastics floating in the subtropical gyres has been limited to a few thousand stations worldwide. Although there is typically good correspondence between drifter models and surface abundance data [18], there is a disparity in the amount of data to calibrate these models. There is an ongoing need to expand data collection. Citizen science programs are now providing robust data sets on beach accumulation [28], sorption of toxicants on plastics [97], and microplastics in seawater [109]. These efforts generate regional or global datasets with an efficiency of time and funding that professional scientists cannot match alone.

The future of research in the subtropical gyres is largely to refine our understanding of fate and impacts of plastic debris, while mitigation efforts are being driven back to land by the realities of plastic life cycles in the oceans. With better communication of new science, and increased attention to improve waste management and smarter plastic product design, the problem of plastic debris drifting in the furthest reaches of the planet can be controlled.

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Hazardous Chemicals in Plastics in Marine Environments: International Pellet Watch

Rei Yamashita, Kosuke Tanaka, Bee Geok Yeo, Hideshige Takada, Jan A. van Franeker, Megan Dalton, and Eric Dale

Abstract Marine plastic debris, including microplastics <5 mm, contain additives as well as hydrophobic chemicals sorbed from surrounding seawater. A volunteer-based global monitoring programme entitled International Pellet Watch (IPW) is utilizing the sorptive nature of plastics, more specifically of beached polyethylene (PE) pellets, in order to measure persistent organic pollutants (POPs) throughout the world. Spatial patterns of polychlorinated biphenyls (PCBs) and organochlorine pesticides have been revealed. Original data of IPW show large piece-to-piece variability in PCB concentrations in pellets collected at each location. This is explained by the combination of slow sorption/desorption and large variabilities of speed and route of floating plastics. The sporadically high concentrations of POPs, both sorbed chemicals and hydrophobic additives, are frequently observed in pellets and the other microplastics in open ocean and remote islands. This poses a chemical threat to marine ecosystems in remote areas.

Keywords Additives, Equilibrium, Open ocean, Pellets, Sorption

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Contents

1 Types of Chemicals in Marine Plastic Debris

Plastics carry various hazardous chemicals in marine environments. Figure 1 shows concentrations of chemicals in mm-size plastic debris collected from open ocean and urban and remote beaches [1]. The chemicals include polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane and its metabolites (DDTs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), nonylphenols (NP), octylphenol (OP) and bisphenol A (BPA). Their concentrations ranged from 1 to 10,000 ng/g. They are derived from two origins [2]. One group of chemicals consists of additives such as BPA that were originally compounded into plastic products. Another group of chemicals consists of hydrophobic compounds such as PCBs and DDTs that were sorbed from surrounding seawater. Some

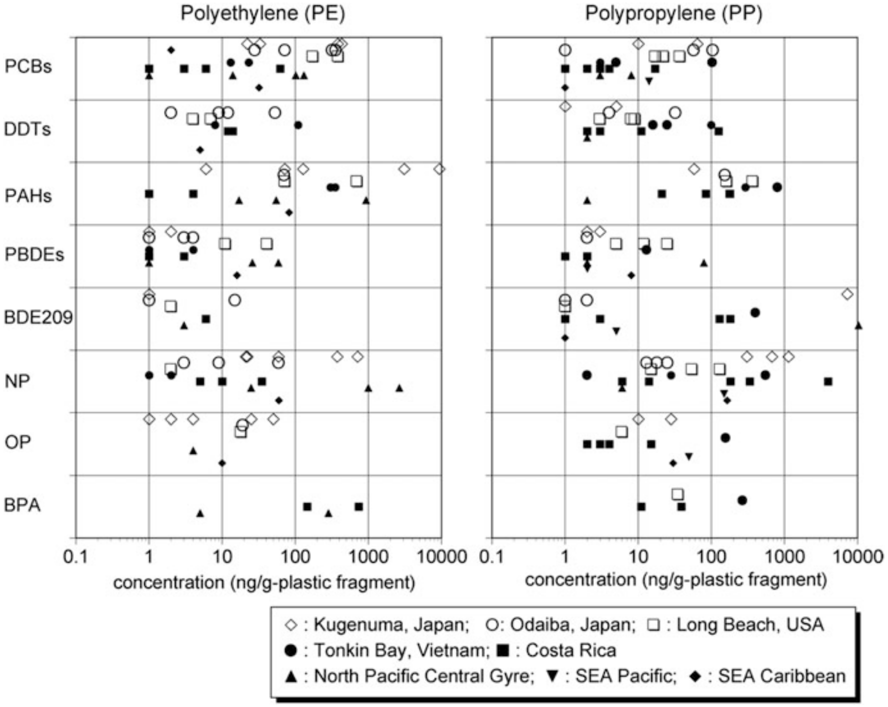


Fig. 1 Concentrations of organic micropollutants in plastic fragments from urban and remote beaches and open ocean. After Hirai et al. [1]

chemicals such as PBDEs and NP come from both origins. Details for the chemicals and their origins are described below.

2 Additives

Plastic products contain various additives to maintain their performances, as discussed in Andrady and Rajapakse [3]. Additives include plasticizers, UV absorbers, antioxidants, anti-static agents, flame retardants and so on. Although the presence of additives in the plastics and their release to surrounding media are discussed in Kwan and Takada [4] and Manoli and Voutsa [5], one more example is shown in Fig. 2 of the present chapter which illustrates concentrations of NP in caps of mineral water and beverage polyethylene terephthalate (PET) bottles. The bottle itself is made of PET which does not contain NP as additives. However, caps

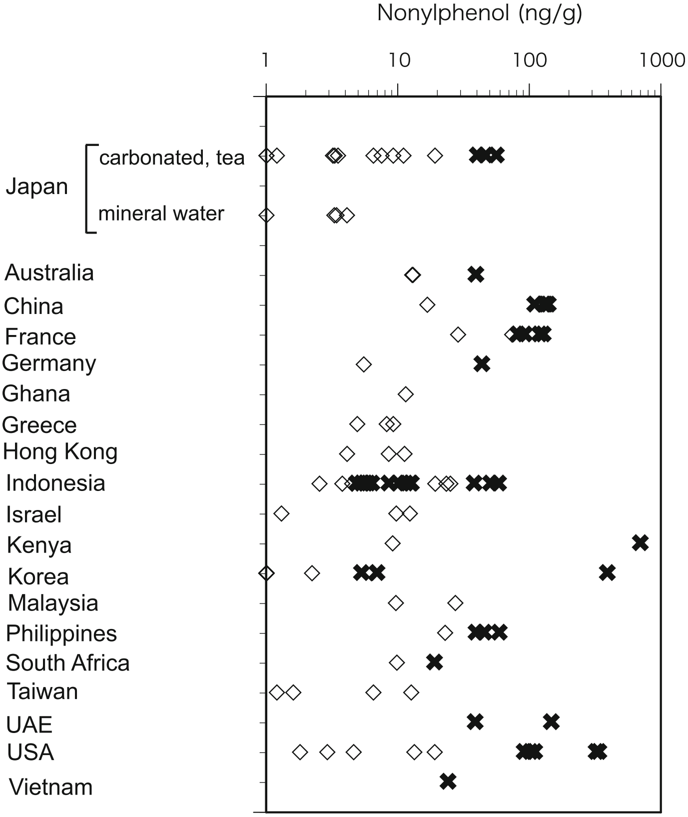


Fig. 2 Nonylphenol concentrations in caps of PET bottles for mineral waters. Only Japanese samples include bottles for carbonated and tea. All the caps were taken before disposal

are normally made of polyethylene (PE) and sometimes contain NP as additives. Approximately 100 caps of PET bottles from 19 countries including the USA, EU, Asian and African countries were purchased from the local markets of each country. The caps were extracted with n-heptane, and NP was determined by gas chromatograph-mass spectrometer (GC-MS). NP was significantly detected in 45 out of the 109 caps. NP concentrations were up to 600 ng/g. NP or its derivatives are thought to be compounded as antioxidants and/or anti-static agents. Detection was sporadic, i.e. NP was detected in some brands whereas not detected in the other brands for individual countries. This sporadic compounding is a characteristic of plastic additives.

Because plastic caps and their fragments are most frequently observed on beaches, plastic caps were collected from several beaches in Japan and analysed for NP that was sporadically detected in plastic caps from individual beaches. This sporadic detection is consistent with sporadic occurrence (compounding) in plastic caps among brands. By using characters imprinted on the plastic caps, caps on the beaches can be interconnected with caps on the market. Because large quantities of Chinese plastic debris, including plastic caps from PET bottles, strand on the beaches in the western islands of Japan, imprinted Chinese characters were used for identification. Figure 3 compares NP concentrations between commercial products on the market and beached plastic caps for the same brand of plastic caps. Though significant concentrations of NP were detected in all the beached plastic caps, their concentrations were two orders of magnitude lower than those in the commercial products purchased on the market. This can be explained by the mechanism that the NP was leached out into seawater during their journey across the East China Sea. In other words, plastic caps release NP to seawater while floating. Plastic caps act as mobile sources of endocrine-disrupting chemicals to marine environments.

In the above section, leaching of NP from plastic debris during drifting and transport in water was suggested. Leaching of chemicals from plastic depends on hydrophobicity with the more hydrophobic chemicals being slower to leach [6]. Therefore, additives such as polybrominated diphenyl ethers (PBDEs; log K_{ow}, 6.66–9.58 for tetra BDEs to deca BDEs [7]) that are more hydrophobic than NP (log K_{ow}, 4.48) may not efficiently be leached out and can be detected at higher concentrations in plastic debris in open ocean. Figure 4a shows occurrence of PBDEs in mm-size plastic fragments collected from urban and remote beaches and open ocean. PBDEs dominated by higher brominated congeners were detected even in remote beaches and open ocean. This pattern can be explained by the fact that PBDEs, especially higher brominated congeners, are originated from additives, i.e. flame retardants. In other words, PBDEs are retained in mm-size plastic fragments in open ocean because of their slow release (leaching) due to higher hydrophobicity. Nevertheless, the concentrations of PBDEs in open ocean were much lower (~3 orders of magnitude) than those in plastic products. This is probably due to photodegradation during drifting on sea surface and on beaches.

Ingestion of mm- and cm-size plastics by seabirds has been frequently reported [8]. This is probably due to their dietary behaviour and size of digestive tracts,

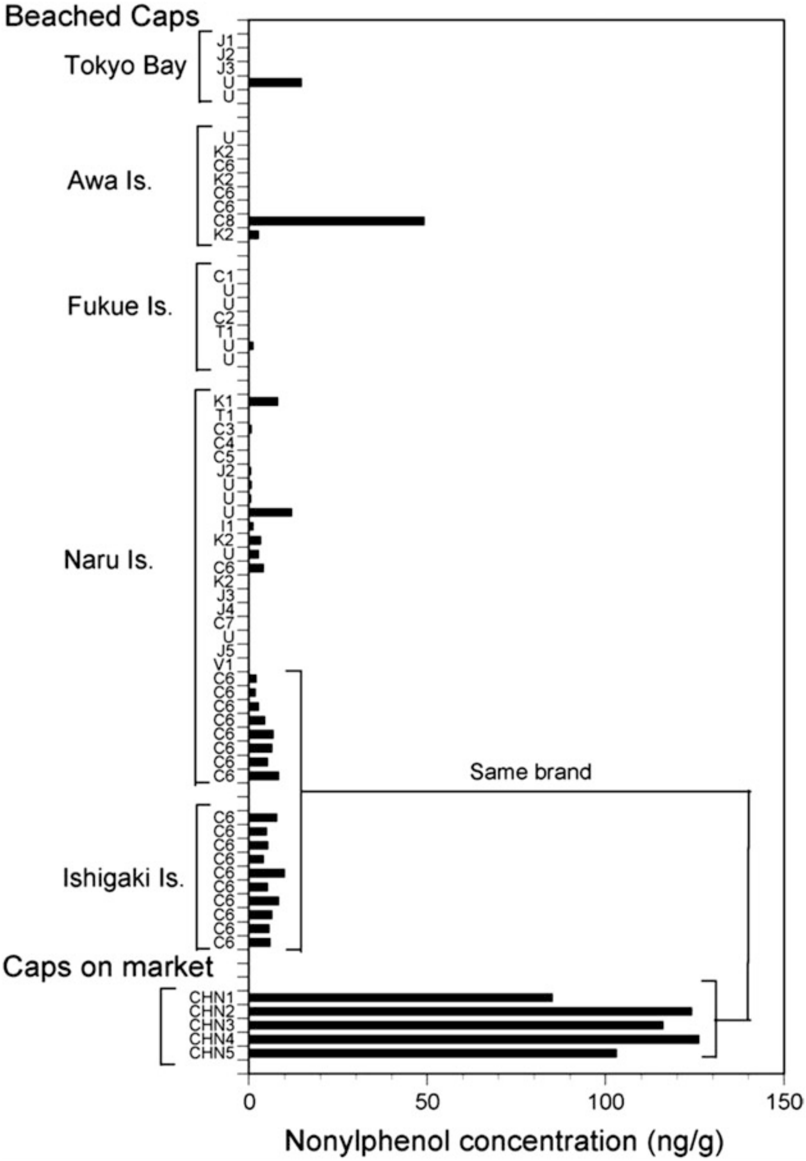


Fig. 3 Nonylphenol concentrations in beached caps of PET bottles

especially narrowness of exit of the intestine. Because hydrophobic additives, e.g. PBDEs, are still retained in mm-size plastics even in open ocean, plastic fragments ingested by seabirds act as internal exposure sources of hydrophobic additives. As examples, concentrations of hydrophobic chemicals in mm-size and cm-size plastic fragments ingested by two species of seabirds are shown in Fig. 5.

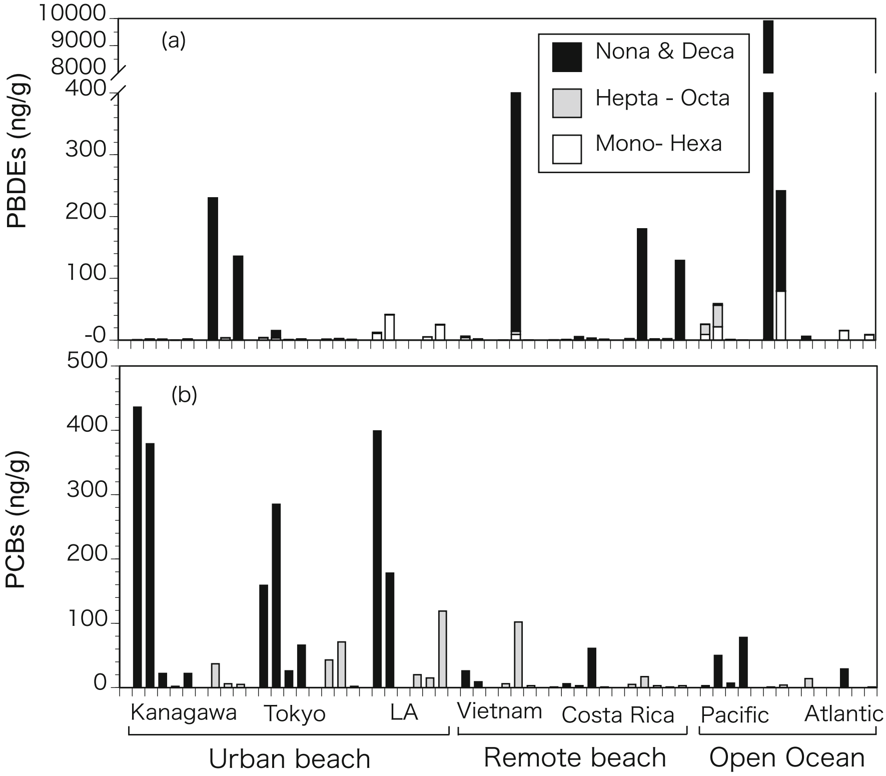


Fig. 4 Concentrations of PBDEs and PCBs in plastic fragments on urban and remote beaches and open ocean. Data from Hirai et al. [1]

Albatross plastic fragment samples were collected from Midway Atoll where the plastic fragments were associated with carcass of albatross, indicating that the plastics were retained in digestive tract of the albatross. They were identified as plastic [i.e. PE, PP and polystyrene (PS)] and sorted into two size groups, i.e. cm-size, large fragments, and mm-size, small fragments. For each group, all types of polymers (PE, PP and PS) were combined and analysed together. Fulmar plastic samples were collected from dead fulmar chicks caught at three sites (site #1, 62°25′N, 7°20′W; site #2, 62°25′N, 6°25′W; and site #3, 62°18′N, 5°30′W) around Faroe Islands. One hundred individuals were available at site #1 and #2 whereas only 34 individuals at site #3. For individuals for each site, plastics (pellets and fragments) from the stomachs were pooled and mixed. One hundred pieces of both pellets and fragments were randomly selected from the pooled plastic samples of site #1 and #2 whereas 51 fragments and 100 pellets for site #3. The pellets and fragments were identified as PE, PP and acrylonitrile butadiene styrene (ABS) and other plastics by FTIR. PE was predominant (60–70%), PP was minor (30–40%), and the others were trace. For pellets and fragments for each site, all types of the

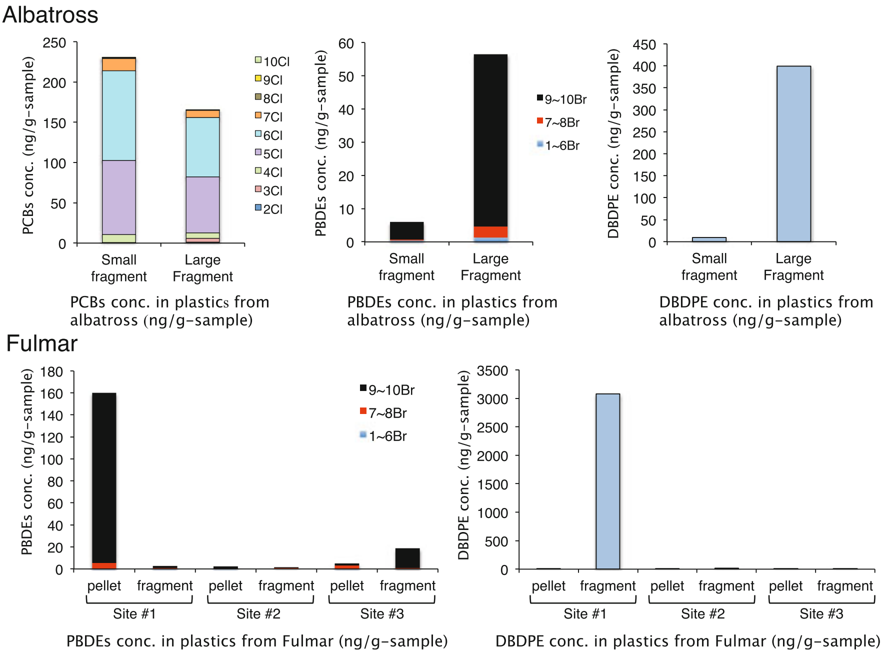


Fig. 5 Concentrations of PCBs, PBDEs and decabromo diphenyl ethane (DBDPE) in plastic fragments associated with carcass of albatross (upper) and plastic pellets and fragments in the stomach of fulmar chicks (lower). Small <1 cm, large >1 cm

polymers were combined and analysed together. In all the plastic fragments and pellet samples, significant concentrations of PBDEs were detected. Especially, in cm-size fragments from albatross and pellets from fulmar chicks, ~50 and ~150 ng/g of BDE209 were detected, respectively, implying that ingested plastics are exposure source of hydrophobic additives to the seabirds. Transfer (i.e. leaching of the additives to the digestive fluid, their absorption through intestine and accumulation in the seabird tissue) is discussed in Tanaka et al. [9]. In addition to PBDEs, decabromo diphenyl ethane (DBDPE) was detected in albatross (400 ng/g) and fulmar (3,000 ng/g) ingested plastic fragments. DBDPE was introduced more recently than PBDEs as brominated flame retardant, and its production has been increasing. Higher concentrations of DBDPE than PBDEs may be associated with the transition of the production of brominated flame retardants. NP was also detected in the fragments from albatross. However, their concentrations (113 ng/g for the large fragments and 165 ng/g for the small fragments) were not so high compared with the blank value of NP (10 ng/g).

3 Sorption of Hydrophobic Chemicals and International Pellet Watch (IPW)

Due to the hydrophobic nature of many persistent organic pollutants (POPs), this class of chemicals are well known to strongly associate with hydrophobic polymeric materials, including common plastics. In marine environment, Mato et al. [10] demonstrated the sorption of hydrophobic chemicals including PCBs and DDE to plastic (PP) resin pellets by using in situ sorption experiment. By using a similar in situ experiment, sorption of hydrophobic organic pollutants to plastic resin pellets was confirmed in the present study (Fig. 6). Virgin plastic resin pellets were deployed in the seawater of Tokyo Bay, and pellets were occasionally recovered for the analysis of PCBs, DDE, PAHs, NP and octylphenol. Concentrations of all the analysed compounds showed consistent increase up to 16 days. Higher sorption of PCBs to PE pellets than to PP pellets was indicated, as shown in Fig. 6. This was consistent with measurement of PCBs in plastic resin pellets collected from a beach in Tokyo Bay (Fig. 7; [11]). They made piece-by-piece analysis of 65 pellets and showed a trend that PCB concentrations in PE pellets were one order of magnitude higher than those of PP pellets, though large piece-to-piece variation was observed for both polymer types. Comparison of concentrations of congeners of PCBs in

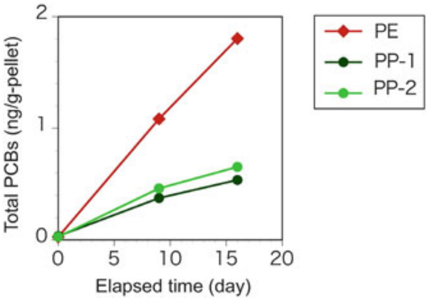


Fig. 6 Concentrations of PCBs in plastic resin pellets with time after deployment of the pellets in surface water of Tokyo Bay. PE, polyethylene; PP-1 and PP-2, polypropylene

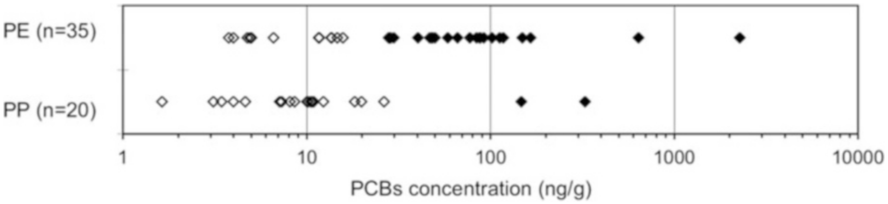


Fig. 7 Results of piece-to-piece analysis of PCBs in polyethylene (PE) and polypropylene (PP) pellets on a sandy beach of Tokyo Bay. Concentrations over the limit of detection (LOD) are plotted as solid diamonds, and those under the LOD as open diamonds. After Endo et al. [11]

Table 1 Concentration (C) factors of CB congeners to PE pellets

	C in seawater			C in pellet (ng/g)	Log (C factor[a])
	Dissolved (pg/L)	Particulate (pg/L)	Total (pg/L)		
Dec. 2011					
CB-66	61.5	47.8	109.3	17.2	5.20
CB-101	28.6	23.3	51.9	54.0	6.02
CB-110	24.8	25.8	50.6	92.0	6.26
CB-118	13.0	23.7	36.7	46.9	6.11
CB-105	3.1	8.9	12.0	21.8	6.26
CB-149	4.1	11.2	15.3	45.6	6.47
CB-153	4.3	15.3	19.6	79.2	6.61
CB-138	4.6	20.4	25.0	130.9	6.72
CB-128	0.1	2.8	2.9	18.1	6.79
CB-187	n.d.	1.4	1.4	8.7	6.78
CB-180	0.3	3.0	3.2	14.2	6.64
CB-170	n.d.	3.0	3.0	14.1	6.67
CB-206	n.d.	0.2	0.2	0.1	5.93
∑13PCBs	144	187	331	543	6.21
Aug. 2012					
CB-66	15.3	112.5	127.8	12.2	4.98
CB-101	4.0	39.9	43.9	18.9	5.63
CB-110	3.9	36.7	40.6	35.9	5.95
CB-118	1.7	30.4	32.1	15.4	5.68
CB-105	1.1	8.0	9.1	6.1	5.83
CB-149	0.8	12.1	12.9	54.8	6.63
CB-153	0.3	15.3	15.6	90.3	6.76
CB-138	0.4	20.2	20.6	112.8	6.74
CB-128	n.d.	2.2	2.2	19.5	6.95
CB-187	n.d.	1.2	1.2	20.6	7.24
CB-180	n.d.	2.1	2.1	39.4	7.27
CB-170	n.d.	0.3	0.3	28.6	7.93
CB-206	n.d.	0.04	0.04	0.5	7.09
∑13PCBs	27	281	308	455	6.17

[a] Concentration factor = C in pellets (ng/g)/C in seawater (total, pg/L) $\times 10^6$

beached pellets and those in seawater just off the beach (Table 1) provided concentration factors up to one million. Karapanagioti et al. indicated that sorption of PAHs to PE is controlled by migration into polymer matrix, whereas that to PP pellets is limited at the surface polymer layers [12]. Higher sorption capacity of PE may be due to migration into polymer matrix. On the other hand, Rochman et al. [13] did not observe consistent higher sorption for PE than PP, though they also demonstrated that PE and PP had higher sorption capacity than PET and PVC.

Based on the findings of sorption of POPs to plastic, International Pellet Watch (IPW) was initiated in 2005 [14]. In IPW, volunteers around the world collect plastic resin pellets on beaches and mail them to the Laboratory of Organic Geochemistry (LOG) of the Tokyo University of Agriculture and Technology, in Tokyo, Japan. Because PE has higher concentrations of POPs than PP, PE pellets were sorted and used for the analysis. Only a certain range of yellowing PE pellets (yellowness index 40–50) was analysed. To minimize the effect of piece-to-piece variation in POP concentrations in pellets, five pools (subsets; each pool consisted of five pellets) were analysed for each location, and median value among the five pools was taken to get representative pollution status at each site, as discussed later. The target POPs were determined by gas chromatography with mass spectrometer (GC-MS) or electron capture detector (GC-ECD) following solvent extraction and silica gel column chromatography. Details of the analytical procedure are described elsewhere [15]. Concentrations of POPs in the pellets from 193 locations were displayed by colour-coding in Takada and Yamashita [16] and given in Figs. 8, 9, and 10. They show that POPs are spread widely throughout the Earth. The target POPs were detected in all the samples including pellets from remote islands such as Saint Helena and Cocos Islands. The dispersion of POPs to remote areas is thought to be through atmospheric transport and lateral transport via plastic fragments. Their concentrations in pellets from these islands were trace and several orders of magnitude lower than those found in human-impacted coastal zones. Based on the analysis of plastic resin pellets collected from seven remote islands (the Canary Islands, Saint

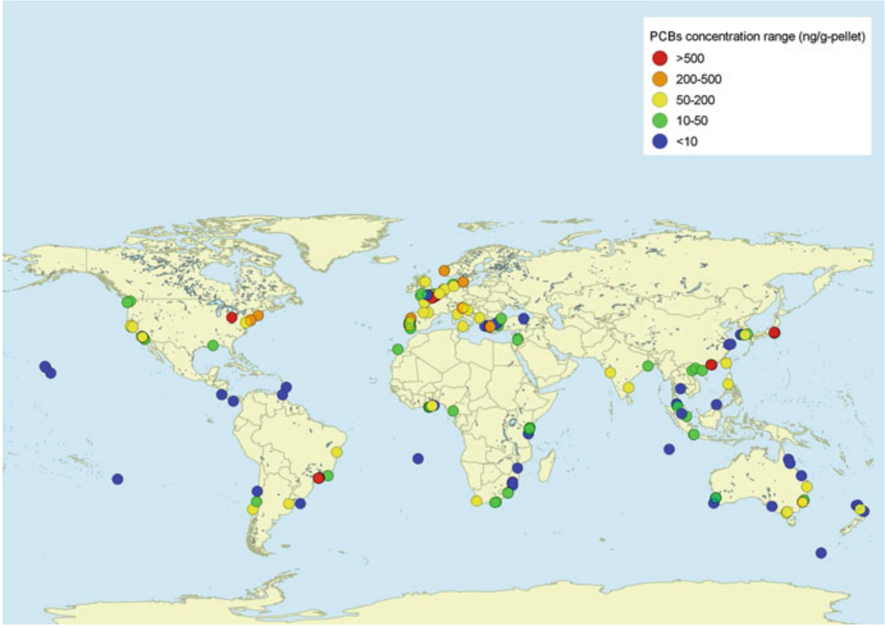


Fig. 8 Concentrations of ∑13 PCBs (ng/g) in beached plastic resin pellets. ∑13 PCBs: sum of concentrations of CB#66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170 and 206. After Takada and Yamashita [16]

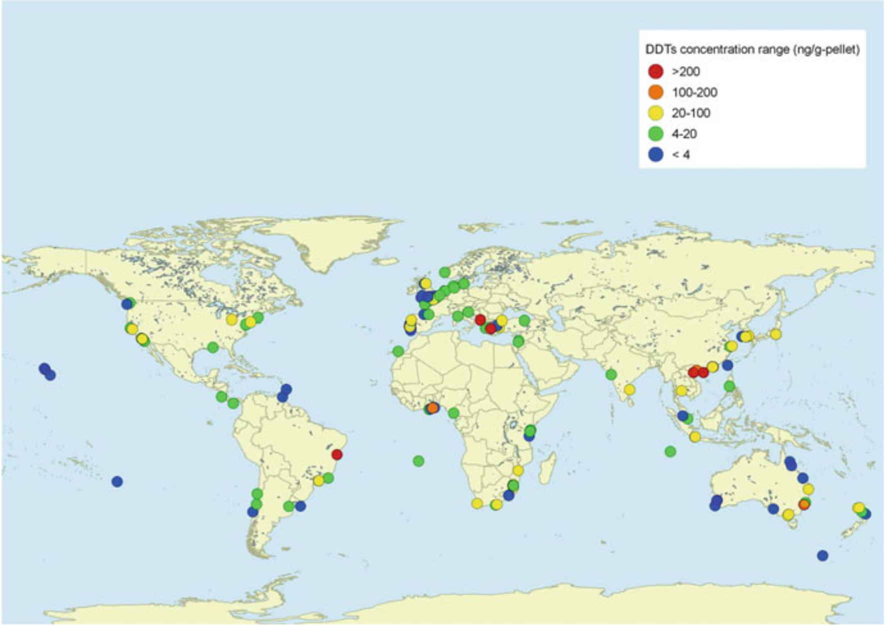


Fig. 9 Concentrations of DDTs (ng/g) in beached plastic resin pellets. DDTs: sum of concentrations of p,p′-DDT, p,p′-DDE and p,p′-DDD. After Takada and Yamashita [16]

Helena, Cocos Islands, Island of Hawaii, Island of Oahu and Barbados), background levels of POPs were established [17]. The background levels of PCBs, DDTs and HCHs were set at 10 ng/g-pellet, 4 ng/g-pellet, and 2 ng/g-pellet, respectively. POP concentrations higher than the background levels would thus suggest local inputs of POPs.

Hot spots of PCB pollution were identified in Western Europe and the US west and east coasts and Japan (Fig. 8). These regions experienced rapid economic growth in the 1950s–early 1970s when large amounts of PCBs were used and discharged to coastal zones where they remain accumulated in bottom sediments, which act as secondary source (legacy pollution source) of PCBs to the water column [15, 18, 19]. PCB hot spots were also observed in recently developing countries such as Australia (Sydney) [20], Brazil (São Paulo) [21] and South Africa (Durban) [22], probably due to current inputs. In some developing countries such as Ghana [23] and the Philippines [24], levels of PCBs that were significantly higher than global background levels were observed. Current emissions of PCBs are likely to occur in these areas. Discharge of PCBs from e-waste scrapyard was investigated by the combination of pellet watch with sediment analysis [23].

Moderate to high levels of DDTs are widely distributed. This diffuse pollution is probably due to wide application of DDT pesticides for agriculture worldwide before it was banned in the 1980s (Fig. 9). In addition to legacy DDT pollution, current inputs of DDTs are suggested by the results at some hot spots, such as northern

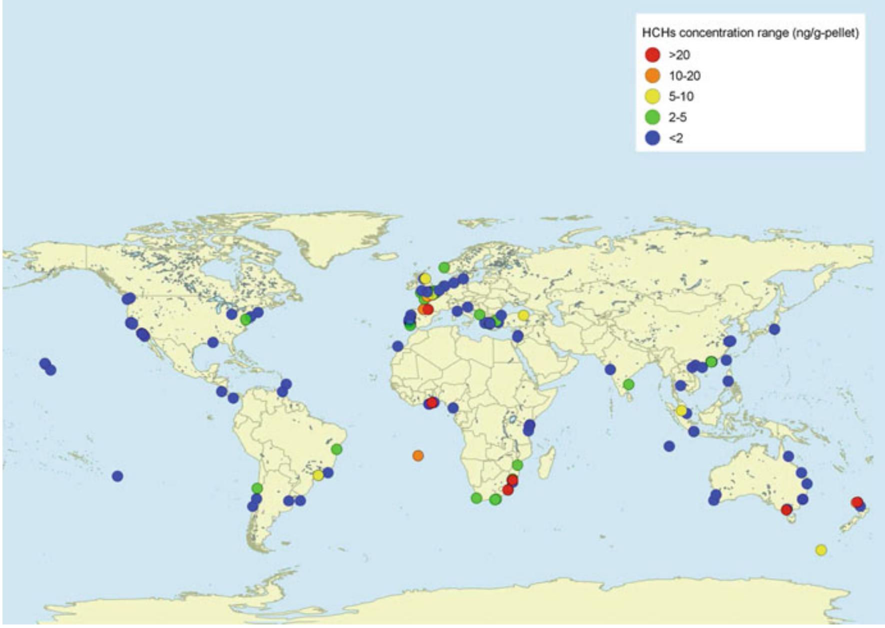


Fig. 10 Concentrations of HCHs (ng/g) in beached plastic resin pellets. HCHs: sum of concentrations of α-HCH, β-HCH, γ-HCH and δ-HCH. After Takada and Yamashita [16]

Vietnam [25], southern China and Ghana. These high concentrations in tropical and subtropical regions may be attributed to its continuing use for malaria control. Illegal application of DDT insecticides is another possibility. Application of antifouling agents containing DDT might be the cause of current pollution in some sites close to harbours, such as Sydney [20] and Athens.

In most of the sampling locations, HCH concentrations were relatively lower than DDTs (Fig. 10), probably due to their lower hydrophobicity (log K_{ow} ~3.8) than DDTs (log K_{ow} ~5.8) and also their smaller amounts of production and rapid evaporation because of their higher volatility. However, some HCH hot spots were observed including in Mozambique and South Africa, New Zealand and France. In Mozambique, South Africa (Durban) and Ghana, drastic decreases in HCH concentration were observed in the samples collected in 2005–2010 and 2012–2014. This could be attributed to the Stockholm Convention, which started to regulate HCHs in 2008, but continuous monitoring is necessary to confirm this.

The advantage of IPW is the extremely low cost of sampling and shipping as compared with conventional monitoring. Furthermore, as the sampling does not require any special instruments or technical training, it can be undertaken by members of the public and covers wide areas of coastal zones [26]. Despite these advantages, the mobile nature of plastic pellets may limit their utility as passive samplers. Some plastics can travel hundreds of kilometres or more. However, most of PE with sizes of 2–4 mm (i.e. target pellets of IPW) is retained for a long time within ~5 km from the coast due to nearshore trapping caused by stokes drift, as demonstrated by Isobe et al. [27]. However, some pellets can escape from nearshore trapping and can make a long travel, and, therefore, we see pellets on beaches even in remote islands without any industrial activities. Sorption of pollutants to the plastic pellets is a bidirectional reaction and moves toward equilibrium, though it takes time (~1 year or more as described in detailed below). This means that even pellets that arrive from some other areas can reflect local pollution as long as they stay for a long time in the stranding location. To analyse pellets with a certain range of residence time in the coastal waters, pellets with a certain degree of yellowing are used for the analysis for IPW. Yellowing occurs with exposure in the environments due to oxidation of phenolic additives to semiquinone or quinones which are orange in colour. Therefore, yellowing can be utilized as a practical index of residence time in the sea [11]. Our analysis of white, yellowing and brown pellets collected at the same time from Tokyo Bay revealed that median concentrations of PCBs in white, yellowing and brown pellets were 71 ng/g (range, 26–172 ng/g), 376 ng/g (range, 301–2,921 ng/g), and 2,052 ng/g (range, 1,239–53,350 ng/g), respectively (Fig. 11). Thus, yellowing pellets with yellowness index ranging from 40 to 50 were used for the IPW analysis. Lower PCB concentrations in yellowing pellets than in orange pellets (Fig. 11) also mean that the yellowing pellets that we utilize for monitoring are not at equilibrium but are still in the uptake phase.

As discussed above, kinetics of sorption is key to discuss POP concentrations in marine plastics. The rate of uptake and release of POPs from plastics largely depend on size of plastics. With increase in the size (thickness) of plastics, sorption and desorption become slower. To thin polyethylene film with thickness of 50 μm PCBs (CB52), sorption requires 50 days to reach equilibrium [28], whereas sorption of PCBs to PE pellets with diameter of 3 mm is slower and takes approximately 1 year to reach equilibrium [6, 13]. The slow sorption and desorption was explained by slow diffusion in aqueous boundary layer [6] and/or in intraparticle (matrix)

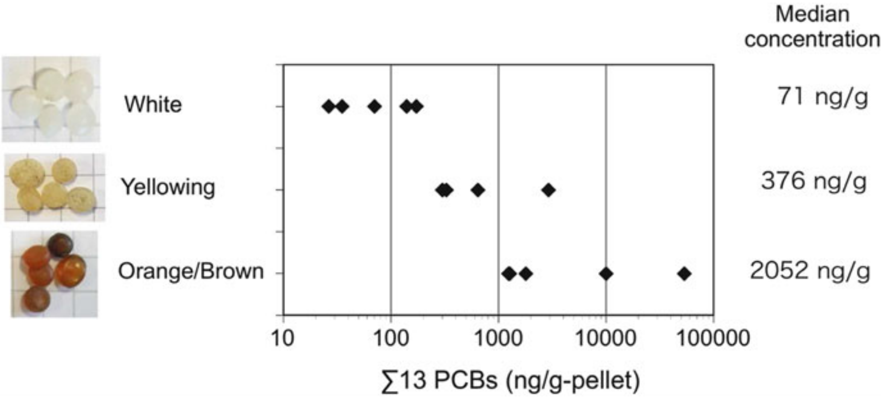
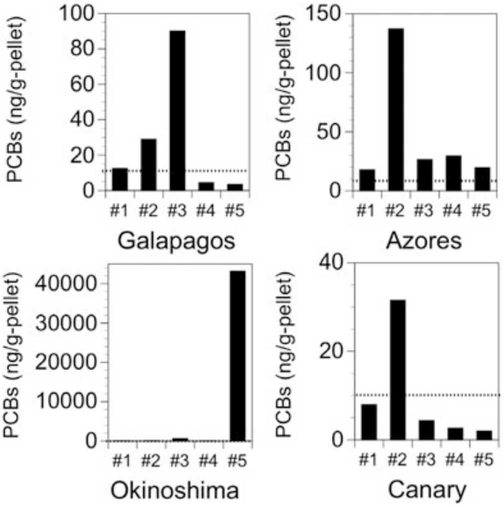


Fig. 11 PCB concentrations of white, yellowed and orange/brown pellets from Odaiba beach in Tokyo Bay. For each colour of pellets, five pools were analysed

diffusion [12]. Slow sorption rate provides a unique role to mm-size plastics; larger range of microplastics, including pellets as vectors of POPs; and especially as long-range transporters. Traditionally, it was thought that POPs are carried in aquatic environments by natural particles, including soil particles, soot, phytoplankton, faecal materials and the debris of terrestrial and marine organisms. These particles are heavier than water and, eventually, are deposited onto bottom sediments, and it was assumed that they do not laterally carry POPs over a long distance. However, plastics (lighter polymers such as PE and PP) float on sea surface and can be carried for a long distance over thousands of kilometres. Due to the slow sorption, long-range transported plastics can carry POPs for longer distances than traditional carriers.

For example, let's study a case that pellets are transported from a polluted area such as Los Angeles to a remote area such as Galapagos Island. PCBs in pellets are high at Los Angeles due to the exposure of high concentrations of PCBs in Los Angeles seawater. During long-range transport, PCB concentrations in pellets decrease due to desorption toward equilibrium with seawater in open ocean where PCB concentrations are much lower than in LA seawater. However, some pellets may be transported rapidly to the remote island, Galapagos Island due to oceanographic conditions, and may bring higher concentration of PCBs before they are completely leached out. Actually, among five pools of pellets from Galapagos Island, a pool with sporadically high concentration of PCBs (90 ng/g) was observed in a pool (sample #3), whereas the other four pools had much lower PCB concentrations of less than 30 ng/g (Fig. 12). IPW takes median concentration to exclude sporadic high concentrations and to get a representative pollution status for individual locations. Therefore, PCB concentration at this location in Galapagos was 12 ng/g which is close to global background level of PCBs in pellets (10 ng/g). This is reasonable because it is a remote area without nearby industrial activities. Pellets

Fig. 12 Concentrations of PCBs in five pools of pellets from remote islands



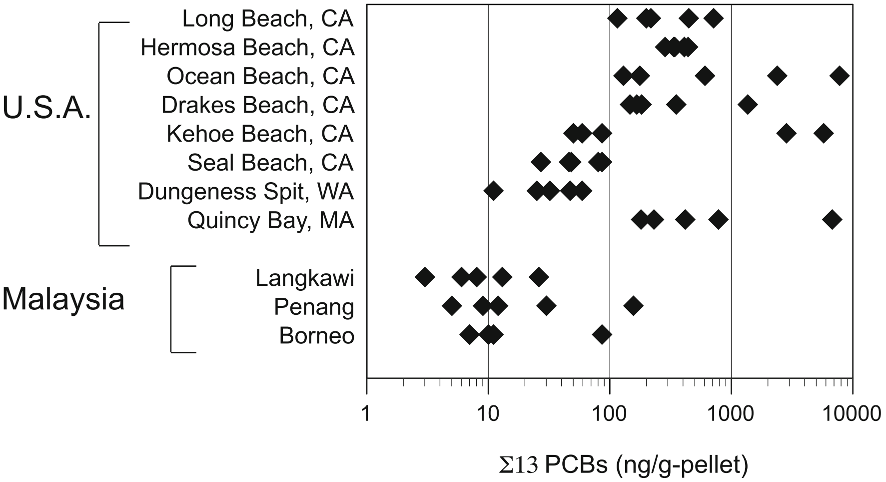


Fig. 13 Concentrations of PCBs in five pools of pellets from US coasts and Malaysia

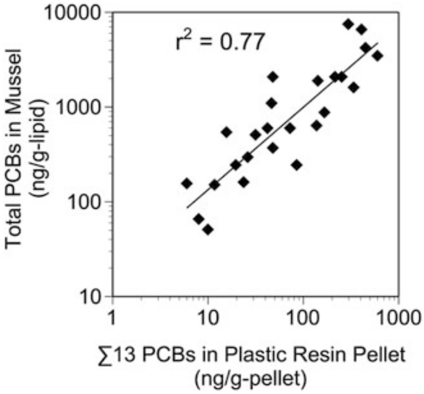


Fig. 14 Correlation of PCB concentrations between plastic resin pellets and mussels collected at the same costal zones. After Takada and Yamashita [16]

with sporadically higher or lower concentrations of POPs are often observed on IPW (Figs. 12 and 13). However, median concentrations of PCBs in pellets have good correlation with PCB concentrations in mussel, as shown in Fig. 14.

By taking median among the five pools, global monitoring of POPs is feasible as shown above. However, marine organisms cannot take median doses (i.e. 12 ng/g in the case of Galapagos), but they take everything, i.e. exposed to arithmetic average (i.e. 28 ng/g). Thus the plastic sample with sporadically high concentration of POPs poses more threat to marine organisms. In remote areas, wild animals are exposed to minimal amounts of POPs through natural media (water, air and the food web). These wild lives are also vulnerable to the threat of POPs through sporadic high

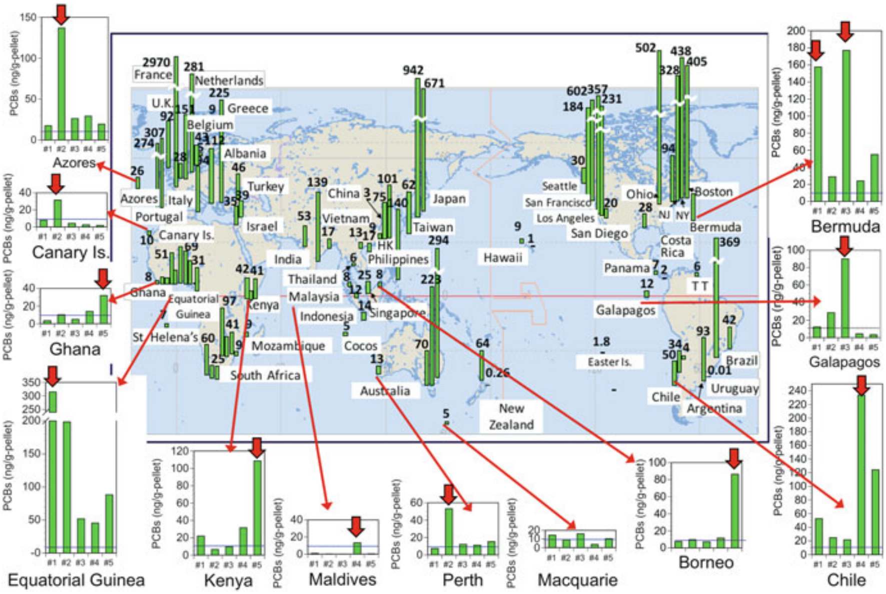


Fig. 15 Median concentrations of PCBs in plastic resin pellets (centre) and PCBs concentrations in five pools for remote locations

concentrations. This example at Galapagos is not extreme case, but IPW observe this type of sporadic high concentrations of POPs in one pool among five pools for many locations in remote areas such as Bermuda, Borneo and Equatorial Ghana (Figs. 12, 13, and 15). Furthermore, similar sporadic high concentrations of sorbed POPs were observed not only in pellets but also plastic fragments on beaches (Fig. 4b, [1]). In addition to adsorbed POPs, because of the slow leaching, additives are retained in microplastics in marine environments as discussed in previous section. Because more hydrophobic compounds have slower rate of sorption/desorption, highly hydrophobic additives such as higher brominated diphenyl ethers (e.g. BDE209) were detected in plastic fragments stranded on remote beaches and those floating on open ocean (Fig. 4 [1]). The existence of sporadic high concentrations of POPs is a unique but hazardous aspect of marine plastics. Sizes of the plastic fragments in the study [1] were mm to cm range. Studies for smaller sizes of plastics in seawater are introduced in the next section.

4 POPs in Microplastics in Seawater

As indicated by Andrady and Rajapakse [3] and Thompson [29], plastics are fragmented into smaller pieces by UV radiation, heat and physical impacts of wave, and large plastic debris are fragmented into smaller pieces to be less than 5 mm which are defined as microplastics (Fig. 16). Concern about the ecological

Fig. 16 Microplastics collected from Pacific Ocean. Small scale, 1 mm; large scale with number, 1 cm

impacts of microplastics has been increasing in recent years, because the small pieces can be ingested by fish [30, 31] and shellfish [32]. We have very limited data on POPs in microplastics collected from seawater. Data on POPs in microplastics from two extreme environments are shown as an example. One set was collected from canals in Tokyo Bay (urban waterways in the most inshore zone of Tokyo Bay). Another set was collected from Pacific. Microplastic samples from the canals were collected at two locations in Tokyo Bay (canal station 22, Cn.22, and canal station P, st. P) in July 2014 and September 2015 by using Neuston net with 0.315 mm mesh size. The contents in the net (i.e. mixture of zooplanktons and microplastics) were sieved by using meshes with different mesh sizes to be sorted into three fractions (>5 mm, 1–5 mm, 0.3–1 mm) where later two fractions are called as L-MP and S-MP, respectively. Materials on the meshes were freeze dried, and plastics were picked up by using stainless-steel tweezers and sorted in terms of polymer types by using FTIR. Microplastics were dominated by PE and PP. PE and PP in L-MP and S-MP at two locations in two seasons, totally 16 samples, were analysed for PCBs and PBDEs by GC-MS and GC-ECD following solvent extraction and thorough chromatographic purification. Pacific samples were collected by Japan Meteorological Agency in western Pacific (Fig. 17). The microplastic samples were collected by using Neuston net with 0.3 mm mesh size at 14 locations, and all were combined to be a composite sample due to smaller sample size at individual locations. Air-dried samples were sorted in terms of polymer type and size. PE and PP in L-MP and S-MP, totally four samples, were analysed for POPs. The analytical results are shown as an example (1) to understand concentration range of POPs in microplastics in seawater, (2) to examine the utility of IPW data to estimate POP concentrations in microplastics in seawater and (3) to examine the idea of slow sorption/desorption of POPs to/from microplastics.

PCB concentrations (∑13 PCBs) in microplastics in Tokyo Bay range from tens to hundreds ng/g, whereas those in open ocean were a few ng/g (Fig. 18). The concentration ranges and spatial pattern (i.e. urban coast vs. open ocean) were similar to those observed in IPW where PCB concentrations in PE pellets from Tokyo Bay were hundreds ng/g-pellet. On the other hand, background levels of

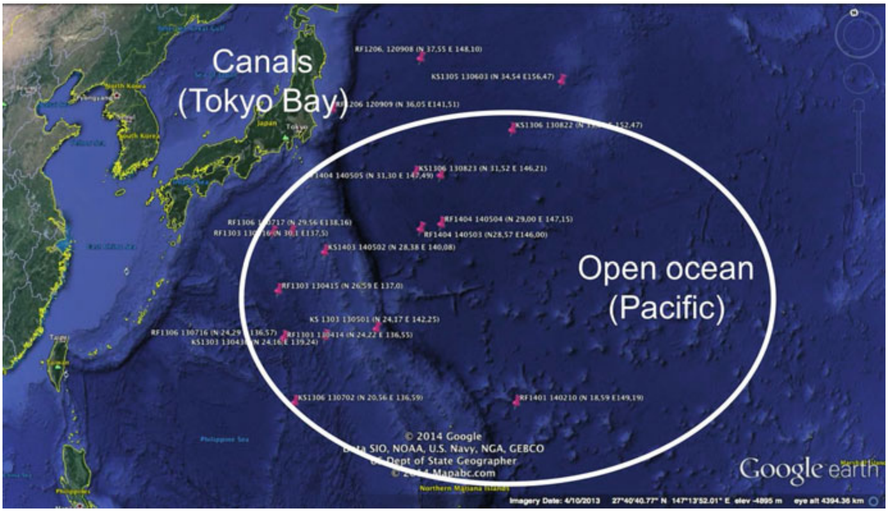


Fig. 17 Sampling locations of microplastics in surface water from Pacific Ocean and Tokyo Bay

PCBs were ~10 ng/g based on the analysis of pellets from remote islands (Fig. 8). This suggests that PCBs levels in microplastics in surface water can be estimated from the results of IPW. Between PE and PP, no consistent difference in PCB concentrations was observed. In terms of size of microplastics, a trend that S-MP has higher concentrations of PCBs than L-MP was observed. This is probably because sorption of PCBs in smaller plastics can reach equilibrium more quickly due to smaller diameter and larger specific surface area than larger plastics. Microplastics in canals in Tokyo Bay may have shorter residence time in seawater, and L-MP did not reach equilibrium. On the other hand, no consistent difference in PCB concentrations between S-MP and L-MP was observed in the open ocean (Fig. 18). This may be due to longer residence time of MP in seawater. More data on PCBs in MP from coastal zones and open ocean are necessary.

Hydrophobic additive, BDE-209, was detected in L-MP from open ocean as well as in those from Tokyo Bay (Fig. 19), suggesting that BDE-209 was not completely leached out of the L-MP during offshore transport. On the other hand, so far, no BDE-209 was detected in S-MP in open ocean, whereas BDE-209 was significantly detected in S-MP from canals of Tokyo Bay (Fig. 19). This can be explained by that fragmentation to smaller particles could increase the specific surface area and could facilitate the leaching of BDE-209 out of the S-MP. In remote ecosystems, additives in L-MP or larger plastics could pose risk to organisms, whereas S-MP may not pose risk to organisms in terms of additives when ingested in remote ecosystem. In coastal environments, both S-MP and L-MP have risk to the organisms. In any way, more data on POPs in microplastics (μm-size plastics) from coastal areas and open ocean are necessary.

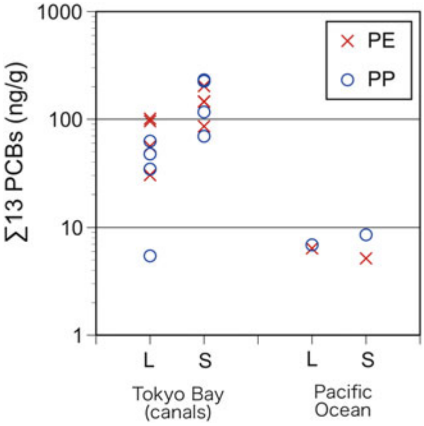


Fig. 18 Concentrations of PCBs in microplastics from surface water in canals of Tokyo Bay and Pacific Ocean. L, 1–5 mm; S, 0.3–1 mm. ∑13 PCBs: sum of concentrations of CB#66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170 and 206

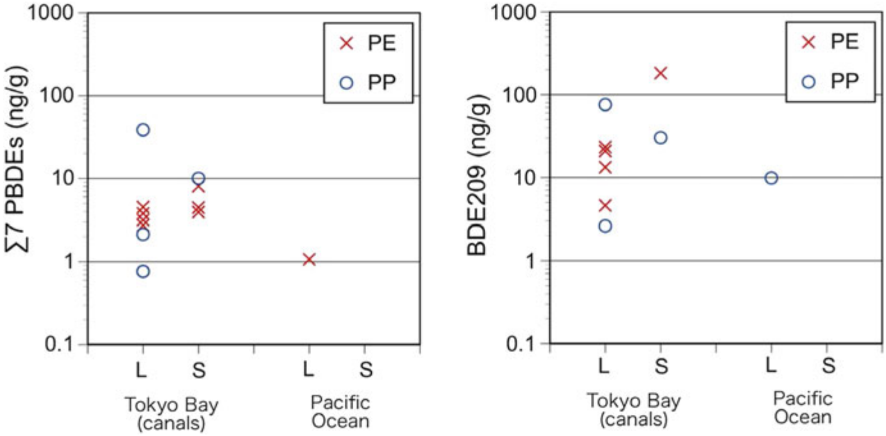


Fig. 19 Concentrations of PBDEs in microplastics from surface water in canals of Tokyo Bay and Pacific Ocean. L, 1–5 mm; S, 0.3–1 mm. ∑7 PBDEs: sum of concentrations of BDE28, 47, 99, 100, 153, 154, and 183; BDE28 may contain BDE33

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Sorption of Hydrophobic Organic Compounds to Plastics in the Marine Environment: Equilibrium

Satoshi Endo and Albert A. Koelmans

Abstract Marine plastics have shown to contain various environmental chemicals. For evaluating the potential of plastics to influence regional and global dynamics of these chemicals and to serve as a vector to marine biota, understanding of sorption and desorption of chemicals by plastics is important. In this chapter, the equilibrium sorption of neutral organic chemicals from water to plastics is discussed. First, the basic principles of equilibrium sorption are explained, and then, factors that influence the magnitude of the sorption coefficient, such as types of plastics and chemicals, temperature, coexisting organic and inorganic constituents in water, are overviewed. Successively, effects on the equilibrium sorption properties of field-relevant mechanisms such as degradation and biofouling as well as nano-sized plastics are discussed. It is evident that studies on sorption properties of aged plastics in field conditions are far less available than those of intact plastics in laboratory conditions.

Keywords Degradation, Intermolecular interaction, Marine plastic, Nanoplastic, Sorption coefficient

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Contents

1 Introduction

Plastic particles and fragments existing in marine environments have been found to contain various types of chemicals. Some chemicals are additives that are intentionally compounded into plastic during manufacturing processes, while others are environmental contaminants sorbed by plastic from external phases (e.g., seawater). The ability of plastic to sorb and concentrate hydrophobic organic contaminants (HOCs) from ambient seawater has been recognized since the early 1970s [1, 2] and has received growing interest afterwards [3–11]. Subsequent research has addressed the composition of the chemical mixtures that reside in the plastic particles (e.g., [3, 4, 8]), the global distribution of plastic-bound chemicals by using the plastic as continuous in situ passive samplers [6], the relative ability of various plastic types to sorb chemicals [9, 12, 13], and several more specific mechanistic issues such as the role of plastic as a transport medium [3, 14, 15]. Chemicals in marine plastics can desorb to seawater when the conditions allow them to do so. Moreover, if plastics are ingested by organisms such as birds, fish, and benthic organisms, chemicals could desorb from the plastics within the gastrointestinal tract and become available for successive uptake into the organism body [7, 16–18]. Clearly, understanding of the sorption and desorption behavior of chemicals to and from plastics is of utmost importance for the evaluation of plastic–chemical interactions in marine environments as well as a possible transfer of chemicals from plastics to organisms.

The aim of this chapter is to provide fundamental and practical knowledge regarding equilibrium sorption of organic chemicals from water to plastic. Kinetics of sorption (and desorption) of organic chemicals by plastics are out of scope within this chapter and will be dealt with in another chapter of this book. The first half of this chapter summarizes the principles of equilibrium sorption of organic chemicals to plastics. The concepts of equilibrium sorption and sorption coefficients are introduced, and the relation of sorption coefficients with the properties of plastics and chemicals is described. In the latter half of this chapter, we collate and synthesize the recent research in relation to sorption of organic chemicals by marine plastics. Influences of weathering and biofouling on sorption coefficients and field-based values are overviewed.

2 Principles of Sorption to Polymers

2.1 Sorption: Types and Definitions

Sorption is a process in which chemicals are transferred from a fluid phase (e.g., water and air) to a solid phase. The term "sorption" collectively refers to both absorption and adsorption. In absorption, molecules of the chemical penetrate and become associated within the matrix of the solid phase, while in adsorption, molecules become confined at the interface between fluid and solid phases. The term sorption is widely used, because it is often unknown whether absorption or adsorption is operative, and also because absorption and adsorption can simultaneously occur. The relative importance of absorption and adsorption depends on the properties of the solid and the chemical and on the surface-to-volume ratio of the solid. Plastics have a variety of properties and dimensions, and thus both absorption and adsorption can be relevant. A term that is closely related to sorption is "partitioning." "Partitioning" is more general, referring to a transfer of chemical between any types of phases, in contrast to "sorption," which usually involves a solid as one phase. This word usage is, however, not universal. In fact, "sorption" and "partitioning" are often used as synonyms, and in some scientific fields such as environmental chemistry, "partitioning" is used only to refer to a chemical transfer "into" liquid and solid phases (i.e., absorption) (e.g., [19, 20]).

Sorption processes can also be classified into chemical and physical sorption. Chemical sorption (also referred to as chemisorption) denotes the association of chemicals by solid through the formation of covalent bonds. Thus, for chemisorption to occur, there need to be structural domains in solid and chemical molecules that can mutually react. Chemisorption can be irreversible, i.e., the sorbed chemical will not desorb from the solid to the surrounding phase (unless the covalent bond that connects the chemical and the plastic breaks up). Physical sorption (or physisorption) takes place due to non-covalent intermolecular interactions such as van der Waals (vdW) interactions. Non-covalent interactions occur between any solid and any chemical (though the interaction forces strongly depend on their combinations) and physisorption is usually reversible. Usually, sorption of HOCs by typical marine plastics is physisorption. Therefore, in the following sections of this chapter, we only deal with physisorption.

2.2 Equilibrium Sorption and Sorption Coefficients

In a closed system consisting of a solid phase and a fluid phase (e.g., plastic and water), transfer of a chemical occurs from one phase to the other until the concentrations of the chemical in the two phases become "balanced." The final state, in which there is no net transfer of the chemical between the two phases, is referred to as sorption equilibrium. The concentration ratio at sorption equilibrium is referred to as the sorption coefficient and is typically denoted with K. For sorption by plastics,

$$K_{\mathrm{pw}} = {C_{\mathrm{p}}}^{*}/{C_{\mathrm{w}}}^{*} \tag{1}$$

where K_{pw} [$\mathrm{L_{water}/kg_{plastic}}$] is the sorption coefficient of the chemical from water to plastic and C_{p} [$\mathrm{mol/kg_{plastic}}$ or $\mathrm{mg/kg_{plastic}}$] and C_{w} [$\mathrm{mol/L_{water}}$ or $\mathrm{mg/L_{water}}$] are the concentrations of the chemical in plastic and water, respectively. The superscript * indicates that the two concentrations are in equilibrium. The unit of K_{pw} depends on the units of the two concentrations; thus, if C_{p} was defined with a unit of $\mathrm{mol/L_{plastic}}$ instead, then K_{pw} would be in $\mathrm{L_{water}/L_{plastic}}$. K_{pw} defines the balanced state of C_{p} and C_{w} and the value of K_{pw} depends strongly on the types of plastics and chemicals. For example, a measured value of K_{pw} for PCB 143 (a congener of polychlorinated biphenyls, PCBs) between polyethylene (PE) and water is 6.3×10^{6} $\mathrm{L_{water}/kg_{PE}}$ [21], whereas that of lindane is 4.2×10^{2} $\mathrm{L_{water}/kg_{PE}}$ [22]. This means that, at equilibrium, there is a factor of as much as 10,000 difference between PCB 143 and lindane in terms of the enrichment factor from water.

The sorption coefficient K_{pw} is of tremendous importance for understanding the sorption/desorption behavior of a chemical to plastics, as the spontaneous transfer of a chemical always occurs in such a direction that the actual concentration ratio ($C_{\mathrm{p}}/C_{\mathrm{w}}$) approaches the value of K_{pw}. If the actual $C_{\mathrm{p}}/C_{\mathrm{w}}$ ratio is $<K_{\mathrm{pw}}$, then sorption from water to the plastic occurs. If $C_{\mathrm{p}}/C_{\mathrm{w}} > K_{\mathrm{pw}}$, then desorption from the plastic to water takes place. When $C_{\mathrm{p}}/C_{\mathrm{w}}$ reaches K_{pw}, then neither sorption nor desorption occurs any more (i.e., sorption equilibrium). Equilibrium (or near-equilibrium) situations can occur not only in closed systems, but also in any system where the phase transfer occurs much quicker than other disturbing processes (e.g., degradation of the chemical). For example, sorption of legacy pollutants such as PCBs from seawater to floating plastic particles in the open ocean may proceed until equilibrium is reached, because the seawater concentration of such chemicals is relatively stable over long time. In contrast, sorption of wastewater contaminants to plastics in estuarine systems may not reach equilibrium, as concentrations in the water phase fluctuate steadily.

If K_{pw} is constant through the whole concentration range of the chemical, the sorption is called "linear sorption," because the plot of C_{p}^{*} against C_{w}^{*} is linear. Such a plot is called a linear isotherm, and the slope of the plot equals K_{pw}. Thus,

$$C_{\mathrm{p}}^{*} = K_{\mathrm{pw}} C_{\mathrm{w}}^{*} \tag{2}$$

In case K_{pw} depends on the concentration of the chemical, the isotherm (i.e., C_{p}^{*}–C_{w}^{*} plot) is nonlinear, and the sorption is called "nonlinear." Nonlinear isotherms of plastic sorption can sometimes be approximated by the following Freundlich equation:

$$C_{\mathrm{p}}^{*} = K_{\mathrm{Fr}} \left(C_{\mathrm{w}}^{*}\right)^{n} \tag{3}$$

where K_{Fr} and n are the Freundlich coefficient and exponent, respectively. If the isotherm follows the Freundlich equation, K_{pw} is equal to $K_{\mathrm{Fr}}\ (C_{\mathrm{w}})^{n-1}$, which shows how K_{pw} depends on the concentration and that K_{pw} is equal to K_{Fr} for C_{w} equal to unity. Many other models exist (e.g., Langmuir, Polanyi, dual-mode [23]) to describe nonlinear isotherms. Concentration-dependence of K_{pw} can be a relevant issue for marine plastics, because lab-experiments are often conducted with concentrations that are much higher than the environmentally relevant range.

Regarding equilibrium sorption, two additional notes may be worth mentioning. First, a high or low K_{pw} value by itself implies neither fast nor slow sorption. Moreover, K_{pw} itself does not infer at all whether or not the actual situation is in equilibrium or the sorption process of concern will ever reach equilibrium in the real world. What K_{pw} implies, in combination with the actual $C_{\mathrm{p}}/C_{\mathrm{w}}$ ratio, is the direction of the phase transfer (either sorption or desorption), as explained above. How sorption/desorption reaches equilibrium is an issue of sorption kinetics. Second, we only discuss neutral chemicals here with a focus on HOCs. Sorption and partitioning of ionic and ionizable chemicals need more considerations than presented in this chapter (see, for example, Chap. 8 of [24]). Many pharmaceuticals, surfactants, and biocides are ionic or ionizable chemicals, for example.

2.3 *What Determines the Sorption Coefficient from Water to Plastic?*

2.3.1 Intermolecular Interactions

K_{pw} strongly depends on the combinations of chemical and plastic. A major determining factor for K_{pw} is the intermolecular interactions that the chemical undergoes in (or on) the plastic phase and in the water phase. If the energy due to the chemical–plastic interactions is more favorable than that of the chemical–water phase interactions, then a higher concentration of the chemical will be found in plastic than in water at equilibrium, i.e., $K_{\mathrm{pw}} > 1$ (assuming absorption mechanisms and full accessibility in plastic). This means that the chemical will be enriched in the plastic phase in comparison to the water phase. HOCs generally show $K_{\mathrm{pw}} > 1$ in plastics, and often K_{pw} is many orders of magnitude higher than 1 because of the favorable interaction energies of HOCs residing in plastics in reference to those in water.

The most relevant types of interactions for sorption of neutral organic chemicals are vdW interactions, hydrogen (H)-bonding interactions, and cavity formation [25], and these types of molecular interactions additively contribute to the overall interaction energy of the chemical in a given phase. The former two types of interactions are attractive; thus, stronger interactions lead to a higher affinity of the chemical for the phase of concern. vdW interactions occur between any types of molecules, whereas H-bond interactions occur only between H-bond donor and acceptor molecules. For example, nonpolar polyethylene molecules exert only vdW interactions to any chemical, whereas the water molecule (an H-bond donor and acceptor molecule) undergoes H-bond interactions with many polar chemicals in addition to the universally present vdW interactions. The cavity formation is the (hypothetical) process to create a cavity in the phase to accommodate the molecule to be sorbed. Creation of a cavity needs disruption of mutual interactions between phase-constituting molecules and thus costs energy. Therefore, the larger the cavity formation energy, the smaller the affinity for the phase. The cavity formation energy in the water phase is large and much larger than that in the plastic phase, because of the strong cohesive energy between water molecules. In a given phase, the larger the molecule to be sorbed, the larger the cavity formation cost, because the size of the cavity depends on the size of the coming molecule.

Note that what is important for the sorption coefficient is the “difference” between the molecular interaction energies that occur in plastic and in water, and not the absolute interaction energy in either of the phases. In the literature, it is often incorrectly stated that a high log K_{pw} value is an indication of strong interactions between chemical and plastic. However, a high log K_{pw} value can occur with a relatively low chemical–plastic interaction energy as well, if the chemical–water interaction energy is even lower (e.g., due to a high cavity formation energy cost in water). Similarly, strong chemical–plastic interactions do not necessarily mean that log K_{pw} is high, because they can be compensated by similarly strong or even stronger interactions in the water phase (this is often the reason for relatively low K_{pw} of polar chemicals sorbing from water to nonpolar plastics). For molecular interactions and quantitative predictions of log K_{pw}, also see Sect. 3.5 below.

2.3.2 Phase Properties of Plastics

If we were dealing with the partitioning of chemicals from water into organic solvent, the molecular interactions discussed just above would be more or less the entire story for describing partition coefficients. However, in contrast to a liquid phase where the dissolved chemical can freely move, the matrix of plastics is not necessarily fully accessible for the sorbed chemicals. Marine plastics are synthetic

Table 1 Glass transition temperatures (T_g) of selected synthetic polymers

Plastics	T_g (°C)
Low density polyethylene (LDPE)	−125
Atactic-polypropylene (a-PP)	−20
Isotactic polypropylene (i-PP)	100
Polystyrene (PS)	100
Poly(vinyl chloride) (PVC)	81
Poly(vinyl acetate) (PVA)	28
Poly(dimethylsiloxane) (PDMS)	−123
Poly(ethylene terephthalate) (PET)	69
Polyoxymethylene	−93 to −8[a]

Data are from Carraher [26] unless otherwise noted
[a]Suzuki et al. [28]

organic polymers, and they usually contain crystalline and amorphous regions [26]. A crystalline region has an ordered structure where polymeric molecules are regularly arranged. The atoms consisting of polymer molecules are restricted in terms of the positions and motions. Disrupting tightly associated polymeric chains needs a high energy, and thus chemicals do not favorably absorb to crystalline regions. In an amorphous region, polymeric chains are more randomly oriented, molecular segments have a higher freedom to move, and a larger free volume is available for chemicals to be absorbed. Semi-crystalline polymers, which contain both crystalline and amorphous regions to an appreciable extent and include many commercial polymers such as PE and PP, can absorb the chemicals in their amorphous regions. Indeed, it was reported that the sorption coefficient from water to PE ($K_{PE/w}$) decreases with increasing crystallinity of PE [27]. The degree of crystallinity varies considerably even across polymers with the same repeating structure, as the chain branching and the processing during the polymer productions have strong influences on the formation of crystalline regions [26].

Another important factor is the glass transition. Amorphous regions of the polymer undergo a transition from a rubbery to a glassy state upon cooling below the glass transition temperature (T_g). Polymer molecules in a rubbery state are capable of segmental chain movements, whereas those in a glassy state are restricted to vibrational and short-range rotational motions. Polymers whose T_g is below ambient temperature are called rubbery polymers (e.g., PE; see Table 1), while those with T_g above ambient temperature are called glassy polymers (e.g., poly(vinylchloride) (PVC) and polystyrene (PS)). Various properties including sorption properties of a polymer differ dramatically when compared at temperature below and above T_g. Rubbery regions absorb chemicals as organic solvent dissolves them, because of the relatively high flexibility of the polymer segments. The sorption to a rubbery polymer is usually linear, non-competitive in multi-solute systems, and fully reversible. In contrast, chemicals are said to partition into characteristic nano-sized pores within glassy polymers, and this type of sorption is rather an adsorption-like or pore-filling process [29, 30]. As a result, the sorption of organic chemicals to glassy polymers shows nonlinear isotherms, competition with other coexisting chemicals, and hysteresis due to deformation of the pores [30–32].

2.4 Influences of External Conditions on the Sorption Coefficient

Temperature can have influences on plastic–water sorption coefficients in two ways. First, temperature can influence the bulk properties of the polymer such as crystallinity and glassiness and thereby change K_{pw}. A higher temperature generally leads to lower crystallinity and glassiness because the higher energy allows larger motions of polymer segments. Second, the intermolecular interaction energy also depends on the temperature. The data for low density polyethylene (LDPE)–water partition coefficients of PAHs and PCBs show a minor but significant temperature-dependence; an increase by 10°C causes a decrease of K_{pw} by a factor of 1.1–2 [21, 33]. This is comparable to typical solvent–water partition coefficients for HOCs which decrease by a factor of <2 (i.e., <0.3 log units) with an increase of 10°C [24].

Composition of the water phase can have an influence on apparent sorption coefficients. Particularly relevant for hydrophobic chemicals are particulate (POM) and dissolved organic matter (DOM) present in seawater. POM and DOM can significantly sorb chemicals and thereby decrease the sorption of chemicals to plastics. Here, we consider POM and DOM as additional sorbing phases in water and do not consider their potential influences on the sorption properties of plastic and water themselves (see Sects. 3.2 and 3.3 for the latter mechanism). The apparent sorption coefficient from the water phase (including POM and DOM) to plastic (K_{app}) can be expressed as [24],

$$K_{\mathrm{app}} = K_{\mathrm{pw}} / \left(1 + C_{\mathrm{POM}} K_{\mathrm{POM/water}} + C_{\mathrm{DOM}} K_{\mathrm{DOM/water}}\right) \tag{4}$$

where C_{POM} and C_{DOM} are the concentrations of POM and DOM, respectively, in water [$\mathrm{kg_{OM}/L_{water}}$], and $K_{\mathrm{POM/water}}$ and $K_{\mathrm{DOM/water}}$ are the respective sorption coefficients of the chemical [$\mathrm{L_{water}/kg_{OM}}$]. For highly hydrophobic chemicals, $K_{\mathrm{POM/water}}$ and $K_{\mathrm{DOM/water}}$ are large, and thus the denominator of Eq. (4) can be significantly >1, causing K_{app} to be smaller than K_{pw}.

Inorganic salts in water can cause a difference in sorption coefficients from pure water. Salts in water can induce a salting-out effect, which shifts the sorption equilibrium toward organic phases. The salting-out effect on the sorption coefficient can be described by using the Setschenow relationship [34],

$$\log\left(K_{\mathrm{plastic/salt\ water}} / K_{\mathrm{pw}}\right) = K^{\mathrm{s}} C_{\mathrm{salt}} \tag{5}$$

where $K_{\text{plastic/salt water}}$ is the sorption coefficient from salt-containing water to plastic, K^{s} [M^{-1}] is the Setschenow coefficient, and C_{salt} is the concentration of the salt in M (e.g., ~0.5 M NaCl for seawater). K^{s} depends on the type of salt and the organic chemical of concern. Thus, the extent of salting-out effect (i.e., $K_{\text{plastic/salt water}}/K_{\text{pw}}$) depends on the type and the concentration of salt and the type of chemicals. In seawater, NaCl is largely responsible for the salting-out effect [35], and in NaCl solution, the salting-out effect increases with the molecular size and decreases with the polarity of the chemical [34]. The available data and models indicate that the sorption coefficients for HOCs in seawater can be higher by up to a factor of 2 in comparison to their K_{pw} in pure water [34, 36]. Thus, the effect of salt in seawater is rather minor.

2.5 Quantitative Models for Estimation of Sorption Coefficients

Experimental data for K_{pw} are available for only limited combinations of polymer and compound (see Sect. 3.5 below for some examples). Therefore, K_{pw} values often have to be estimated using a model. It must be noted that these models have been developed for unweathered, pure polymers and that their applicability to plastics that are weathered under marine conditions has to be explored.

The most common approach to estimate K_{pw} is a simple log–log correlation with K_{ow}, the octanol–water partition coefficient,

$$\log K_{\text{pw}} = \alpha \log K_{\text{ow}} + \beta \tag{6}$$

Coefficients α and β are empirically calibrated using experimental data for K_{pw} and K_{ow}. Coefficients have been reported for several (pure) polymer types typical for marine litter [37, 38]. Such simple regression models are useful to estimate K_{pw} of chemicals that are structurally similar to the chemicals used to derive the regression coefficients. For example, a regression equation calibrated with data for PCBs is expected to provide sufficiently accurate predictions for other PCB congeners. However, predictions can be substantially less accurate for other chemicals because log K_{pw}–log K_{ow} correlations are not general for all chemicals.

A more general approach is to use a multiparameter model that explicitly considers the contributions of various intermolecular interactions to log K_{pw}. Such models are referred to as polyparameter linear free energy relationships (PP-LFERs). Among others, Abraham's linear solvation energy relationships (LSERs) are used most frequently [39]. LSERs for plastic–water sorption coefficients appear

$$\text{Log} K_{\text{pw}} = c + e\,E + s\,S + a\,A + b\,B + v\,V \tag{7}$$

E, *S*, *A*, *B*, and *V* are the solute descriptors, describing the chemical ability to undergo molecular interactions. *E* is the excess molar refraction, *S* is the solute dipolarity/polarizability, *A* is the solute H-bond donor property, *B* is the solute H-bond acceptor property, and *V* is the molar volume. The lowercase letters in Eq. (7) are regression coefficients, indicating the differences in the complementary interaction properties between plastic and water. In comparison to single parameter models, PP-LFERs are more general in that they can be applied to practically any neutral chemical irrespective of its chemical class. Prediction errors are typically $<$0.3 log units [40, 41]. The descriptors are available for several thousands of compounds [42]. The current limitation of PP-LFERs to be used for plastic sorption is that the regression coefficients are unavailable for plastic types occurring frequently in the environment, which signifies an important future research topic.

While the models shown above always require empirical descriptors and fitting coefficients, there are also estimation models that only require the molecular structures of polymer and chemical as input. The COSMO*therm* program, based on the COSMO-RS theory, uses a quantum-mechanically calculated surface electron density of the molecule to describe the intermolecular interaction forces and derives partition coefficients via thermodynamic calculations [43]. The application of COSMO*therm* for polymer sorption has been reported before [44]. Another predictive approach is SPARC, which calculates partition coefficients using molecular descriptors that are derived solely from the molecular structure [45]. SPARC's calculations of molecular descriptors are based on group contribution methods with a diverse calibration data set. Both COSMO*therm* and SPARC are commercial software. The strong advantage of COSMO*therm* and SPARC is that predictions are possible for virtually any neutral chemical and any phase, provided that the chemical and the phases have defined molecular structure. The prediction accuracy is within 1 log unit on average [46] and often poorer than empirical fit models if the empirical models are used within their domain of applicability.

3 Sorption to Marine Plastics

3.1 Marine Plastics

The partitioning of hydrophobic chemicals to pristine, unaltered plastics has been studied extensively in the framework of developing passive samplers (e.g., [37]). However, in the marine environment, sorption could become dependent on the state of the plastic, which changes over time and place. For example, the role of polymer degradation (weathering) [5, 47], fouling, i.e., biofilm formation or organic matter fouling [11, 48] and competition [13] in the plastic sorption have been discussed in the literature. This implies that "marine plastic" constitutes a mixture of polymer types, with a range of sizes and ages, causing a distribution of sorption affinities even at small spatial scales. This also implies that making inferences on equilibrium sorption from field observations is challenging, due to long equilibration times [4, 5, 9] and a high variability in age and characteristics of microplastics found on the same location (e.g., [4, 9, 49]). Furthermore, this may limit the applicability of the model approaches mentioned in the previous section, which is limited to well-defined pure polymers with properties staying constant over space and time. In the following sections, effects of degradation and fouling will be discussed, and a comparison of in situ sorption coefficients with those for passive samplers will be provided.

3.2 Effects of Biotic and Abiotic Degradation on Equilibrium Sorption to Marine Plastics

In the marine environment, fragmentation of microplastic leads to smaller sized particles that eventually may reach the nano-scale [50, 51]. Polymers consist of a mixture of polymer chains with varying length. The chains are linked by weak secondary bonds like H-bond or vdW interactions or by physical interactions through entanglement of chains, leaving void space in between the chains. Polymer breakdown is mainly initiated by chemical reactions (oxidation) that makes the plastic brittle and the weak interactions are susceptible to breakage at a low energy level. In combination with other forces like friction, this causes formation of smaller polymer particles at the millimeter, micrometer, and nanometer size range [51]. Especially at beaches, the combination of photo-oxidation by UV exposure, a high temperature and high humidity probably enhances fragmentation rates and reduces the size of the plastic particles [47]. The changes occurring in the particles may lead to changing equilibrium partition coefficients through different mechanisms. Mato et al. [3] and Endo et al. [4] discussed three mechanisms for changing sorption characteristics upon degradation of plastic pellets. Here, we extend their discussions on the three mechanisms with additional information from recent studies.

1. The aforementioned weathering of plastic leads to smaller particles, thus increasing the specific surface area of the particles. Moreover, small cracks developing on the surface will increase the microscopic surface area. Fotopoulou and Karapanagioti [47] observed slightly increased surface areas for beach eroded PP and PE. Increasing the surface area increases the adsorption capacity of the plastic, whereas it does not influence the bulk absorption. Velzeboer et al. [11] indeed observed higher sorption to nano-sized PS particles than to micrometer-sized PE, whereas this would be reversed if the particles had equal size.
2. UV-B photo-oxidation or microbial degradation increases the abundance of oxygen containing groups like carbonyl groups and therefore the polarity of the plastic, which will lead to a change of the sorption coefficients. The effect of overall polarity on partition coefficients has been well-established for natural

organic matter in the aquatic environment [52–54]. Fotopoulou and Karapanagioti [47] observed an increase in functional groups on the surface of beach eroded PE, leading to negative surface charge at seawater pH. Beached eroded PP, however, did not show an increase in functional groups on its surface, which illustrates the polymer specificity of the surface alterations.

3. Differences in crystallinity have been shown to explain the differences in partition coefficients among different types of polymers [27, 55], as well as differences in partition coefficients for the same polymer at different states of weathering. A rearrangement of the amorphous rubbery regions inside the polymer and an increase in crystallinity would cause a decrease in the equilibrium partition coefficient if sorption to the amorphous regions is stronger than to the crystalline regions. However, an increased crystallinity might also enhance overall sorption if the crystalline domain has a higher sorption coefficient. For instance, Karapanagioti and Klontza [5] observed higher distribution coefficients for eroded plastic pellets, which they attributed to increased crystallinity of the pellets due to weathering.

It follows from these mechanisms that they could have both positive and negative influences on K_{pw} and may partly compensate for each other. Endo et al. [4] assessed the relationship between the carbonyl index of beached PE pellets as a measure of weathering and PCB concentrations in the field-sampled plastic pellets, yet they did not find any relationship.

3.3 Effects of Biofouling on Equilibrium Sorption to Marine Plastics

Like any surface in the marine environment, plastic will be colonized with micro- and macroorganisms, a process referred to as biofouling (e.g., [56, 57]). Lobelle and Cunliffe [57] describe how biofilm formation, leading to biofouling, develops in four phases: adsorption of DOC, attachment of bacteria, attachment of unicellular eukaryotes, and attachment of larvae and spores. For the formation of biofilms, rather elaborate quantitative models are available, often focusing on marine snow (e.g., [58]). Biofilms may subsequently cause the attachment of invertebrates and algae, which further increases the degree of biofouling.

We are not aware of literature specifically addressing the effect of biofouling on sorption. However, the main effects may be inferred from sorption phenomena known to occur for similar natural particles or particle assemblages. Biofouling turns the polymer particle into a dual domain sorbent, i.e., a microplastic core with an outer shell of organic material. This is similar to mineral particles with an organic matter coating or to mineral particle aggregates held by organic matter, like suspended solids, marine snow, or sediment. Because the organic matter shields the polymer surface from the direct ambient water layer, sorption to the microplastic implies that this organic matter layer has to be passed. The overall kinetics of the process then may become dependent on the resistances to transfer in the polymer, in the biofilm, and in the aqueous boundary layer surrounding the biofilm coated microplastic particle, where the slowest transfer process will determine the overall sorption rate [48].

These sorption kinetics can be modeled using the concepts of intra-organic matter diffusion (see [24]), which however is beyond the scope of the present chapter.

Sorption equilibrium also can be expected to exhibit dual domain behavior, with total sorption being the sum of the sorption to the microplastic (i.e., Eq. 1) and the sorption to the organic matter. Note that the organic matter may be located on the outer surface of the polymer particle, as well as inside the macropores. The overall sorption coefficient for the fouled plastic particle, $K_{\text{fouled plastic/water}}$ [$\text{L}_{\text{water}}/\text{kg}_{\text{fouled plastic}}$], would be

$$K_{\text{fouled plastic/water}} = f_{\text{PL}} K_{\text{pw}} + f_{\text{OM}} K_{\text{OM}} \tag{8}$$

where f_{PL} and f_{OM} (−) are the mass fractions of plastic and organic matter (OM) in the fouled particle, respectively, and K_{OM} [$\text{L}_{\text{water}}/\text{kg}_{\text{OM}}$] are the sorption coefficient for the attached organic matter (including biofilm, attached algae, and invertebrates). As explained in Sect. 2.2, for glassy polymers or for polymers with a high crystallinity, sorption would not be linear and the first term in Eq. (8) may be replaced by a term accounting for Freundlich, Langmuir, or Polanyi–Manes sorption (e.g., [19]). Here, we provide the equation with nonlinear sorption to the plastic accounted for by a Freundlich isotherm:

$$K_{\text{fouled plastic/water}} = f_{\text{PL}} K_{\text{Fr}} C_{\text{w}}^{\text{n}-1} + f_{\text{OM}} K_{\text{OM}} \tag{9}$$

in which the notations are the same as for Eq. (3). K_{Fr} and n depend on the types and conditions of plastic as well as on the chemicals.

3.4 Sorption Competition

The sorption equilibrium to the plastic phase most probably is influenced by the presence of the organic matter, in case "adsorption" is the predominant mechanism of sorption. Attenuation of HOC sorption by organic matter fouling is well known for many geosorbents (e.g., black carbon, activated carbon) for which surface adsorption is the dominating mechanism (e.g., [59–61]). Velzeboer et al. [11] studied the effect of DOC on the simultaneous sorption of polychlorobiphenyls (PCBs) to microplastic and nano-sized plastic and observed no difference for micrometer-sized PE. This was explained from a partitioning (i.e., absorption) mechanism dominating sorption to the bulk of the plastic, which supports the additivity of sorption to plastic and OM as in Eq. (8). For 70 nm nano-PS, however, sorption generally was slightly lower in the presence of DOC, which suggests an adsorption mechanism and a sorption competition effect between DOC and PCBs. This also implies that the parameters in the first terms in Eqs. (8) and (9) depend on the concentrations of DOC and other competitors in the water. Apparent competition was also observed for sorption of phenanthrene and DDT to PVC and PE microplastic, i.e., phenanthrene sorption was lower at higher DDT concentrations in the study by Bakir et al. [13]. The studies are difficult to compare, however, because Velzeboer et al. [11] used 10–1,000 times lower aqueous phase concentrations and 6 weeks of equilibration instead of the 72 h used by Bakir et al. [13]. Several studies have shown long equilibration times for HOCs sorption to microplastics [3, 9, 62], suggesting that the data for 72 h may not fully relate to sorption equilibrium.

3.5 "In-Situ" Values of Sorption Coefficients

Data on sorption of HOCs to marine plastics under in situ conditions is important in order to assess the role of microplastics in transport and bioaccumulation of HOCs [17, 18]. As mentioned above, field-monitoring data of concentrations in marine plastics are not useful to obtain sorption coefficients, because of a tremendously large variability of plastic types, age, weathering state, fouling, and the extent of equilibration that occurs in the field. Field-exposure tests would provide insightful results, yet such data is very limited. In situ values for sorption coefficients can be calculated from chemical concentrations in plastic and ambient seawater, under equilibrium conditions (Eq. 1). Measurement of in situ sorption coefficients thus requires long exposure times [3, 9, 62]. Long exposure times also allow the weathering and fouling of the plastic, which further maximizes the relevance of the in situ values. To our knowledge, only one study measured chemical concentrations in plastic and ambient seawater after field tests [3]. They observed rapid uptake of various HOCs by plastic pellets in 6 days but concluded that this time was insufficient to reach equilibrium. Estimates of in situ PCB and PAH partition coefficients for LDPE, HDPE, PP, PET, and PVC can be inferred from long term sorption data provided by Rochman et al. [9], who measured the uptake of PCB and PAH by these polymers under controlled conditions in San Diego Bay. Uptake was measured up to 12 months and equilibrium concentrations were inferred from the uptake curves using a one-compartment two-parameter kinetic model. While Rochman et al. [9] did not directly measure HOC concentrations in seawater, we argue that the LDPE microplastic deployed for 1 year by Rochman et al. [9] can be considered as a regular passive sampler. The apparent aqueous phase concentrations in San Diego Bay can be calculated using previously published LDPE–water partition coefficients for passive samplers. Subsequently, the partition coefficients for HDPE, PP, PET, and PVC can be calculated using the calculated aqueous phase concentrations and the polymer phase concentrations reported by Rochman et al. [9] (Fig. 1). The validity of this approach is supported by the following. Previous studies using passive samplers used similarly long deployment times of, for instance, 60 days (LDPE [63]) up to 365 days (LDPE [64]). Furthermore,

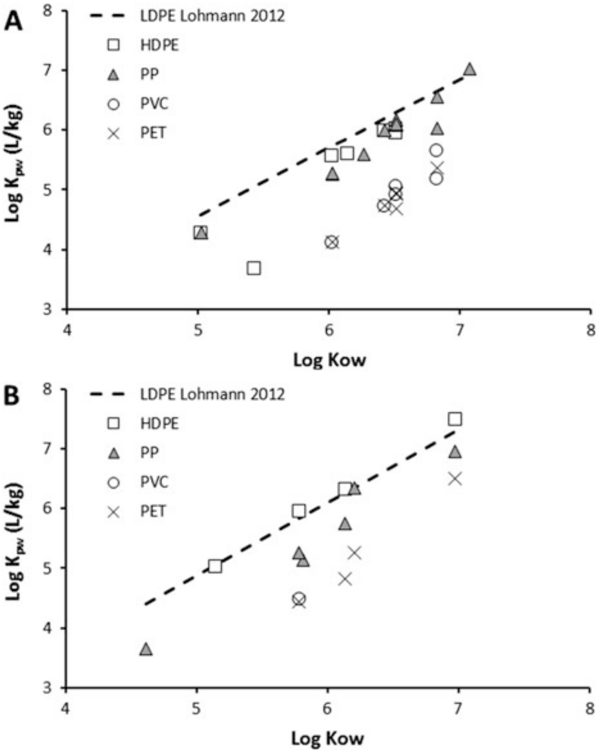

Fig. 1 In situ log K_{pw} as a function of log K_{ow} for five polymers, for PCBs (panel **a**) and PAHs (panel **b**), based on data by Rochman et al. [9], observed uniformity of partitioning to LDPE among passive samplers [37] and between LDPE passive samplers and PE microplastics in the laboratory [11, 62]

sorption kinetic behavior could be described with the same parameters for up to 128 days (environmental PE pellets [62]), which would not be the case if discernable weathering would occur within these time frames. Lohmann [37] reviewed the literature on HOC partitioning to LDPE and concluded that values for the various LDPE materials were very close, and that the thickness of the LDPE had no influence on the equilibrium partition coefficients. This can be explained from the fact that LDPE has a relatively low crystallinity and therefore linear sorption to the amorphous, rubbery polymer fraction dominates. This also explains that Velzeboer et al. [11] measured Log K_{pw}–Log K_{ow} regression parameters for HDPE microplastic particles in seawater that agreed very well to the regression provided by Lohmann [37], an agreement also observed by Lee et al. [38]. The observed similarity among LDPE passive sampler materials and the similarity observed between LDPE microplastic and sampler materials mean that variation across PE materials apparently has a limited effect on K_{pw}, which also implies that the LDPE employed by Rochman et al. [9] can be assumed to have the same equilibrium sorption behavior.

It appears that the five polymers LDPE, HDPE, PP, PVC, and PET show different in situ partition coefficients (Fig. 1), and that the patterns are identical for PCBs (Fig. 1a) and PAHs (Fig. 1b). Taking LDPE as a reference with the highest values, it appears that HDPE has very similar K_{pw} values, whereas the other polymers have log K_{pw} values that are ~0.3–0.5 log units (PP) and ~1–1.5 log units (PVC and PET) lower than the values for LDPE. Regressions of log K_{pw} against log K_{ow} (not shown) were all linear and highly significant.

A couple of studies that measured relative differences in either HOC concentrations sampled from the same locations or K_{pw} between polymer types can be compared with the data from field-exposure tests in Fig. 1. Endo et al. [4] as well as Hirai et al. [8] measured PCB concentrations in marine plastic pellets and found concentrations that tended to be higher in PE pellets than in PP pellets sampled from the same location, which is consistent with the difference shown in Fig. 1. Karapanagioti and Klontza [5] performed laboratory phenanthrene sorption studies with equilibration up to 164 days and observed K_{pw} values for virgin PE being an order of magnitude higher than for PP. Two visually identically plastic eroded pellets however showed different K_{pw} values, illustrating the indeterminate nature of randomly sampled pellets. In short term (only 72 h) sorption experiments, Bakir et al. [13] found apparent phenanthrene sorption coefficients to virgin PVC being 1.5 orders of magnitude lower than those for PE, which also agrees to the difference between PE and PVC in Fig. 1. Lee et al. [38] measured K_{pw} values for PAHs, chlorobenzenes (CBs), and hexachlorocyclohexanes (HCHs) to "pure" HDPE, PP, and PS, in the laboratory. They found consistent correlations with log K_{ow} for PAHs and CBs, whereas for the HCHs relatively low K_{pw}'s were observed due to the polarity of the HCHs. LDPE again showed higher K_{pw} values than PP, whereas PS-K_{pw} values were even higher for low-molecular-weight PAHs and CBs and only for high-molecular-weight PAHs, PE showed the highest K_{pw} values.

In summary, our re-interpretation of the data from Rochman et al. [9] shows that the relative partition coefficients of various plastic types after 1-year in situ exposure experiments are consistent with the available literature data based on the laboratory experiments. Thus, LDPE and HDPE show the highest affinity for sorption of HOCs like PCBs and PAHs, followed by PP and then PET and PVC, a conclusion drawn earlier by Rochman et al. [9]. Therefore, we tentatively conclude that influences of weathering and fouling on sorption coefficients are insignificant within a 1-year exposure time. Further research is needed to address the effects of even longer time exposure on sorption properties and also in varying environmental conditions.

3.6 Nanoplastic

Nanoplastic is probably the least known area of marine litter but potentially also is the most hazardous [51]. For nano-sized plastics, some specific features may affect sorption, such as its extremely high specific surface area, and aggregation. We are aware of one study of HOC sorption to nanoplastics. Velzeboer et al. [11] investigated the simultaneous sorption of 17 PCBs to 70 nm polystyrene particles, which was compared with sorption to PE microplastic, sediment, fullerenes, and multiwalled carbon nanotubes. K_{pw} values for the nano-PS reached values up to 10^9 L/kg, which was much higher than values observed for micrometer-sized PE or bulk PS. PS is an aromatic polymer made from the monomer styrene. The strong sorption therefore was explained by hydrophobic interactions and π−π-interactions between PCBs and the aromatic PS, as well as by the very high surface area of the nano-PS, compared to micrometer-sized plastic. Isotherms were concave or S-shaped, which might have been caused by changes in aggregation state with increasing aqueous PCB concentration.

4 Conclusions and Outlook

Experimental K_{pw} data are rarely available for marine-plastic relevant polymers other than PE. Accordingly, well-calibrated empirical models to predict K_{pw} are available for PE only. Further sorption studies for other types of polymers are warranted. Particularly, glassy polymers such as PS and PVC need more attention because of their more complicated sorption behavior than rubbery polymers. The first results for nano-PS demonstrated strong sorption for PCBs and may have implications for its hazard. Uptake of micro- or nano-sized particles across cell membranes may cause particle toxicity as well as chemical toxicity (e.g., [65]). Thorough studies on the relationship between the size and the sorption properties should shed more light on possible mechanisms of enhanced sorption. While most studies have used PCBs or PAHs as test chemicals, other HOCs such as polybrominated diphenyl ethers, phosphate esters, and phthalate esters are also relevant because of their use for plastic additives. Extending the diversity of test chemicals will enlarge the applicability domain of K_{pw}-prediction models toward more chemical types and will also contribute to improved understanding of chemical–plastic molecular interactions. Influences of plastic degradation and fouling on K_{pw} have been conceptualized, although they still remain to be validated and quantified by experiments.

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Sorption of Hydrophobic Organic Compounds to Plastics in the Marine Environment: Sorption and Desorption Kinetics

Hrissi K. Karapanagioti and David Werner

Abstract The interaction of plastics with hydrophobic organic compounds (HOCs) is well established. Several HOCs are known carcinogens and/or endocrine disruptors. To determine how chemicals in plastic affect the marine environment, it is necessary to understand the kinetics of HOC sorption/desorption. This includes the understanding of sorption kinetics and mechanisms along with simple modeling concepts such as the first order rate kinetic model that can often adequately describe the overall phenomenon. However, to more mechanistically understand the chemical uptake and desorption process, the diffusion of chemicals in plastic is also discussed as well as the direct observation of this process in sectioned plastic particles. Moreover, modeling is required to understand the diffusion of chemicals in microplastic particles. In addition, case studies from the literature are presented which seek to understand how compounds move in and out of the plastics found in the marine environment or when in contact with other fluids besides seawater such as stomach fluids or fish oil.

Keywords Diffusion coefficient, First order rate constant, Modeling, Sorption mechanisms

Contents

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1 Introduction

The interaction of plastics with hydrophobic organic compounds (HOCs) of concern such as carcinogens and/or endocrine disruptors is well documented [1]. Knowing HOC sorption/desorption rates is important to understand the impact of plastic-associated chemicals along with the increasing occurrence of plastics in the marine environment [2]. Sorption of HOCs into plastics has long been studied by polymer scientists interested in packaging or permeable membranes [3] and marine pollution scientists monitoring marine pollution using plastics as passive samplers (e.g., [4, 5]) or studying the bioaccumulation of HOCs by marine organisms through different exposure routes including ingestion of plastics (e.g., [6–8]).

The objectives of the present chapter are as follows: (a) to summarize sorption kinetic rates of HOCs from the aqueous solution into the plastic, (b) to present models of HOC diffusion inside polymers, and (c) to review studies that evaluate the impact of this phenomenon in the marine environment.

2 Principles of Sorption

2.1 Sorption Equilibrium

Some reactions either of chemical or physical nature reach an equilibrium. This means that the reaction starts with an initial change, but after a certain time, both reactants and products are present in concentrations which have no further tendency to change with time. When sorption of a chemical A occurs in a solution, the aqueous concentration of A decreases with time until it reaches equilibrium. Then, the concentration of A does no longer change with time.

Depending on the sorption mechanism, equilibrium can be achieved fast (e.g., adsorption on the external surface of a particle) or slow (e.g., absorption into a polymer phase).

2.2 Sorption Kinetics

The first process that affects the sorption kinetics is the diffusion of a chemical in the aqueous solution. This affects the rate with which chemicals move inside the water phase and how likely they meet with the solid phase. Once the chemical meets with the solid phase, then it will interact with it. If the chemical is adsorbed on the solid surface, then the sorption mechanism can be physical, and it will be fast and reversible, or it can be chemical bonding which is also fast but might not be reversible under the same conditions. For example, chemical bonds between a solid and a chemical can break in the presence of a mild acid solution. After being adsorbed on the solid surface, some chemicals may also be absorbed into the solid interior. This is another kinetic process.

There are two possibilities related to the interior of the solid. The solid can be rigid or porous. Even if the solid is rigid, there is still a possibility for the chemical to be absorbed in the interior of the solid phase and diffuse in it. The diffusion of the chemical in the solid phase is the rate-limiting step since diffusion of a chemical in a solid phase is typically slower than diffusion in the aqueous solution, and it is a kinetic process which is also reversible usually with the same rate. If the solid is porous, then the chemical diffuses through the porous network of the solid and is either adsorbed on the solid wall of the pores or it fills the micropores through a condensation mechanism. The micropores are filled first, but there is a kinetic mechanism for the diffusion of the chemical inside the pore network to reach micropores. Molecular sieving occurs when passages within the pore network are smaller than the molecular size.

For polymers, the relevant sorption mechanisms are adsorption on the polymer surface and diffusion within the polymer phase. Adsorption on the polymer surface is fast, whereas diffusion within the polymer phase is slow.

Nevertheless, some researchers describe the overall kinetics of sorption on microplastic particles as being a first order rate "reaction" [9, 10]. This is commonly described by the following equation:

$$q_t = q_e\left(1 - \mathrm{e}^{-kt}\right) \tag{1}$$

where q_t is the solid chemical concentration at time (t), q_e is the solid chemical concentration at equilibrium, and k is the first order rate constant.

Table 1 summarizes k values from different studies using various polymers and chemicals. The value from Zhan et al. [10] originates from laboratory results, whereas Rochman et al. [9] results come from a long-term study of the marine environment. The values from Bakir et al. [11] and Teuten et al. [8] are describing desorption kinetics. Long-term studies from Rochman et al. [9] demonstrate slow rate constants compared to other studies possibly due to the larger particle sizes, which can affect sorption kinetics as discussed in the following sections.

Other researchers use pseudo-first and pseudo-second order kinetic models to describe the removal of chemicals from the aqueous phase using polymers. This is,

Table 1 First order rate constant for chemical sorption by different polymers

Chemical	Polymer, diameter (mm)	First order rate constant (k) (1/d)	Reference
PCB77	PP fragments, 0.425–0.85	5.8	Zhan et al. [10]
	PP, 3	0.010	Rochman et al. [9]
PCBs	HDPE, 3	0.003	
	LDPE, 3	0.007	
	PP, 3	0.007	
	PET, 2	0.02	
	PVC, 3	0.02	
Total PAHs	HDPE, 3	0.04	
	LDPE, 3	0.03	
	PP, 3	0.02	
	PET, 2	0.05	
	PVC, 3	0.05	
Fluoranthene	HDPE, 3	0.05	
	LDPE, 3	0.02	
	PVC, 3	0.06	
Phenanthrene	PP, 3	0.05	
	PE, 0.2–0.25	1.4	Bakir et al. [11] desorption study
	PVC, 0.2–0.25	0.9	
	PE, 0.2–0.25	0.6	Teuten et al. [8] desorption study
	PP, 0.2–0.25	0.5	
	PVC, 0.2–0.25	1.0	
	PVC, 0.127	0.9	
Anthracene	LDPE, 3	0.07	Rochman et al. [9]
	PP, 3	0.03	
	PET, 2	0.02	
	PVC, 3	0.05	
Pyrene	HDPE, 3	0.02	
	LDPE, 3	0.01	
	PP, 3	0.02	
	PET, 2	0.07	
	PVC, 3	0.06	
Benzo[a]pyrene	HDPE, 3	0.007	
	LDPE, 3	0.003	
	PP, 3	0.01	
	PET, 2	0.02	
Dibenz[a,h]anthracene	HDPE, 3	0.007	
DDT	PE, 0.2–0.25	0.2	Bakir et al. [11] desorption study
	PVC, 0.2–0.25	0.3	

PE polyethylene, *HDPE* high-density PE, *LDPE* low-density PE, *PP* polypropylene, *PET* polyethylene terephthalate, *PVC* polyvinyl chloride for example, used to describe surface adsorption of oil on plastic for oil spill cleaning [12].

3 Diffusion Within the Polymer

Diffusion within the polymer is an important process that has long been studied by polymer scientists [3]. It is a significant topic for various polymer applications such as protective coatings, membranes, and packaging of foods and beverages. The transport of molecules through a polymer is due to random molecular motion. The driving force for this transport that includes sorption and diffusion is the concentration difference of the specific chemical between different regions of the polymer, for example, near surface versus interior. The nature of the polymer plays a crucial role for the diffusion due to the free volume within the polymer and the segmental mobility of the polymer chains that is affected by the extent of unsaturation, the degree of crosslinking, the degree of crystallinity, and the nature of substituents. For polymers having the same density of crosslinking, the nature of crosslinks becomes important. The presence of plasticizers facilitates the diffusion in the polymer, whereas fillers can play a dual role depending on their nature. When the filler is incompatible with the polymer, the permeability of the polymer increases and vice versa. The nature of the chemical that diffuses through the polymer is also important. Hydrophobicity, small size, and compact shape are properties that will accelerate diffusion.

For infinite exposure times and for spherical particles, the first order rate constant k can be theoretically estimated if the diffusion coefficient within the polymer D is known as well as the average radius α of the polymer piece as follows [13]:

$$k = \pi^2 D/\alpha^2 \tag{2}$$

Note that the appropriate units should be used. Thus, if values in Table 1 are used, values in Table 2 can be predicted. For example, for phenanthrene and PE results from Teuten et al. [8] with $k = 0.6$ (1/d) and $\alpha = 0.1$ mm, D based on Eq. (2) equals 7×10^{-11} cm^2/s. This predicted value for D is in the same order of magnitude as the value (2–3 × 10^{-11} cm^2/s) reported by Karapanagioti and Klontza [17] for phenanthrene and PE plastic pellets.

Lohmann [18] in a critical review paper presents a correlation between polymer diffusion coefficient and molecular volume or molecular weight. This works well with PAHs and PE. There is also a discussion included on the effect of aqueous boundary layer on the diffusion values reported in the literature. For thicker sheets or particles (>100 μm), the aqueous boundary layer resistance is less important than for the thinner ones.

Grathwohl [13] reported diffusion coefficients in different polymers for trichloroethene (TCE) ranging from 2.2×10^{-5} to 5.1×10^{-10} cm^2/s (Table 2). Note that TCE diffusion coefficient in water (D_{aq}) is 8.4×10^{-6} cm^2/s. Silicone demonstrated

Table 2 Polymer diffusion coefficients

Chemical (aqueous diffusion coefficient, D_{aq} cm^2/s)[a]	Polymer	Diffusion coefficient (cm^2/s)	Reference
Trichloroethene, TCE (9.1×10^{-6})	Silicone	2.2×10^{-5}	Grathwohl [13]
	HDPE	3.4×10^{-8}, 4.9×10^{-8}	
	Acrylic glass (Plexi)	1.5×10^{-7}	
	PTFE (Teflon)	5.1×10^{-10}	
Naphthalene (7.5×10^{-6})	LDPE	2×10^{-8}	Rusina et al. [14]
	POM	$<10^{-10}$	
	PE (beached plastic pellets)	4×10^{-10}	Karapanagioti et al. [15]
	PP (beached plastic pellets)	3×10^{-10}	
Fluoranthene (6.4×10^{-6})	LDPE	3×10^{-9}	Rusina et al. [14]
	POM	$<10^{-11}$	
Phenanthrene (7.5×10^{-6})	POM (plastic pellets)	$1–2 \times 10^{-10}$	Ahn et al. [16]
		$1–2 \times 10^{-11}$	Karapanagioti and Klontza [17]
	PE (plastic pellet)	$2–3 \times 10^{-11}$	
	PE (26-μm-thick sheets cut from plastic bags)	8×10^{-10}	Hale et al. [5]
	PP	$9 \times 10^{-11}–3 \times 10^{-10}$	Karapanagioti and Klontza [17]
	Degraded plastic pellets	$3–9 \times 10^{-12}$	
	PE (beached plastic pellets)	1×10^{-11}	Karapanagioti et al. [15]
	PP (beached plastic pellets)	6×10^{-11}	
Anthracene (7.7×10^{-6})	PE (26-μm-thick sheets cut from plastic bags)	8×10^{-10}	Hale et al. [5]
Pyrene (7.2×10^{-6})	POM	$2 \times 10^{-10}–2 \times 10^{-11}$	Ahn et al. [16]
	PE (26-μm-thick sheets cut from plastic bags)	2×10^{-10}	Hale et al. [5]
	PE (beached plastic pellets)	2×10^{-11}	Karapanagioti et al. [15]
	PP (beached plastic pellets)	6×10^{-11}	

Benzo[a]pyrene (9.0×10^{-6})	LDPE	7×10^{-12}	Rusina et al. [14]
	POM	$<10^{-12}$	
Dibenz[a,h]anthracene (5.2×10^{-6})	LDPE	3×10^{-12}	
	POM	$<10^{-12}$	
α-δ HCH ($6.2–7.3 \times 10^{-6}$)	PE (26-μm-thick sheets cut from plastic bags)	$3–7 \times 10^{-10}$	Hale et al. [5]
Aldrin (4.9×10^{-6})	PE (26-μm-thick sheets cut from plastic bags)	3×10^{-11}	
Dieldrin (4.7×10^{-6})	PE (26-μm-thick sheets cut from plastic bags)	6×10^{-11}	
Endrin (4.7×10^{-6})	PE (custom-made 51 μm thick sheets)	1×10^{-10}	
Heptachlor (5.7×10^{-6})	PE (26-μm-thick sheets cut from plastic bags)	6×10^{-11}	
Methoxychlor (4.5×10^{-6})	PE (custom-made 51 μm thick sheets)	3×10^{-10}	

PE polyethylene, *HDPE* high-density PE, *LDPE* low-density PE, *PP* polypropylene, *POM* polyoxymethylene

[a] Aqueous diffusion coefficient values from http://www.gsi-net.com/en/publications/gsi-chemical-database.html

the highest diffusivity, even higher than water. The rest of the polymers such as polyethylene, acrylic glass, and Teflon showed lower diffusion coefficients than water. Actually, Teflon showed the lowest diffusivity. High-density polyethylene (HDPE) which is the polymer mostly found in the environment showed about two orders of magnitude lower TCE diffusion coefficient than water.

There are several papers that studied the sorption kinetics of organic pollutants into polymers, and they include studies that focus on plastic marine litter and try to determine their interaction with organic pollutants (e.g., [9, 17]), studies that use polymers as passive samplers for organic pollutants in aqueous systems (e.g., [4, 5, 18]), and studies related to packaging (e.g., [19]). All these studies are interested in both the sorption kinetics and the desorption step in some cases from the monitoring point of view [5] and in others from the bioaccumulation point of view [8].

For example, Karapanagioti and Klontza [17] used virgin pellets and plastic-degraded pellets to elucidate their distribution characteristics through distribution kinetic studies. They found that distribution occurs through diffusion into the pellet for all materials (polyethylene (PE), polyoxymethylene (POM), and PE degraded pellets) except polypropylene (PP). Although diffusion into the polymer happens with similar rates for both freshwater and saltwater external solutions, apparent diffusion is becoming slower in seawater because salinity results in higher equilibrium distribution coefficients. Distribution coefficient into the degraded pellets is higher and diffusion is slower than into the virgin materials. This is attributed to increased crystallinity of the degraded pellets due to degradation. PP demonstrates diffusion rates that are increased by salinity and is apparently faster than into the other polymers suggesting a surface diffusion process. Considering food packaging, Valderrama et al. [19] estimated diffusion coefficients of polybrominated diphenyl ethers (PBDEs) in low-density polyethylene (LDPE) and silicone rubber when spiked in the polymer with solvents such as methanol/water or hexane. It seems that hexane results in polymer swelling and the chemicals are more homogeneously distributed. When the chemicals are more homogeneously distributed, the diffusion values are consistently slightly lower. Hexane enables the chemicals to travel faster and deeper into the polymer.

4 Direct Observations of Polymer Penetration by Chemicals

PAHs concentration profiles can also be measured directly within sectioned polymers [16]. In batch uptake experiments, individual POM plastic pellets were exposed in continuously rotated batches to an initially nearly saturated aqueous solution of phenanthrene or phenanthrene and pyrene. At sampling times, plastic pellets were removed from the vials with forceps and dried externally on a paper towel. To prepare samples for microprobe two-step laser desorption/laser ionization mass spectrometry (μL2MS) analysis, plastic pellets were fixed with forceps and sectioned across the center with a razor blade on double-stick tape.

μL2MS was used to directly observe the intraparticle concentration profiles resulting from the diffusion of PAHs in the interior of plastic pellets. For PAH-exposed and PAH-sectioned plastic pellets, laser shots were initiated first off the edge of the plastic pellet to quantify the background chamber signal intensity, and then shots were moved in 40 μm steps toward the particle center and continued in the same direction until the opposite edge of the plastic pellet was reached. Cross-sections were measured close to the shortest diameter of a sectioned plastic pellet. In addition, average signal intensities were measured on the outer surface of each plastic pellet from 50 shots at different locations.

POM particles were harvested after 10 weeks and sectioned across the center for μL2MS analysis. The signal intensity resembled the concentration profiles anticipated by spherical diffusion models in which a concentration wave is migrating to the particle center from each edge. After 10 weeks, the diffusion front had not yet reached the center of the POM particle, providing evidence for slow sorption kinetics. This agreed with the results of a parallel batch experiment where the apparent sorption coefficient of coarser POM was still increasing after 70 days indicating continued uptake of phenanthrene into the POM.

In a time-series of similar experiments, POM pellets were exposed in 40 mL vials to an initially near saturated aqueous solution of both phenanthrene and pyrene. The particles were razor-cut across the particle center after exposure without embedment. μL2MS-signal intensities were measured on the exterior surface of the particles and

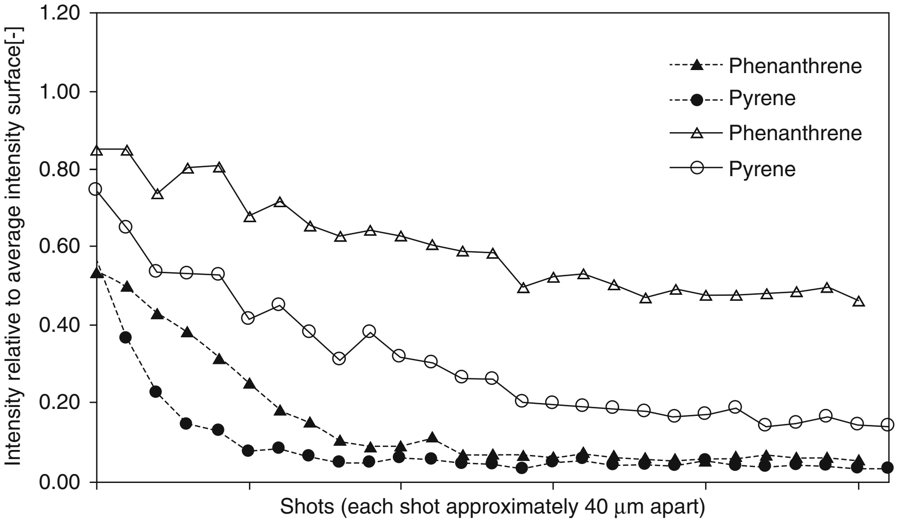

Fig. 1 μL2MS measurements for POM showing the phenanthrene (triangles) and pyrene (circles) molecular mass signals inside sectioned particles as a function of the distance from the outer surface at 8 (solid symbols) and 34 (open symbols) weeks [16]. The average values for shots equidistant from the outer surface of the particle, calculated from three profiles measured across the center of the same particle are shown. Each particle was enclosed in a 40 mL vial with water initially nearly saturated with phenanthrene and pyrene. Signal intensity was normalized by the average intensity measured as a 50-shot average on the exterior surface of the same particle

in three lines on the sectioned particle across the particle center as described above. Signal intensities on the sections were calculated as an average from shots taken at an equal radial distance from the particle edge and were normalized by the signal intensity measured on the exterior surface of the same particle. Figure 1 illustrates the average signal intensity in the radial direction from the particle edge to the particle center relative to the signal intensity measured on the exterior surface. For POM, an advancement of the diffusion front was observed with increasing time (from 8 to 34 weeks), and phenanthrene diffused faster than pyrene. Phenanthrene showed a nearly homogeneous signal intensity throughout the particle with 2–3 mm diameter after 34 weeks, whereas pyrene clearly had not yet reached the sorption equilibrium in this polymer pellet. This was in good agreement with the prior observations in the batch experiments. The concentration dependency of the radial diffusion in POM was also investigated with μL2MS. For POM particles, the intraparticle diffusion appeared to be independent of the PAH concentration.

5 Modeling Sorption Kinetics Based on Chemical Diffusion into a Polymer

The sorption kinetic results for spherical particles can be explained using Fick's second law in spherical coordinates [13]:

$$\frac{\partial C}{\partial t} = D_a \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] \tag{3}$$

where C is the solute concentration in the polymer, t is the time, r is the distance from the center of the sphere, and D_a is the apparent diffusion coefficient.

If the sorption isotherm is linear and the initial and boundary conditions are known, analytical solutions to the Fick's second law exist. Sorption experiments in batch reactors (bath of limited volume) can be described with the following conditions:

$C = 0$ at the beginning of the experiment $(t = 0)$ inside the particle $(0 < r < \alpha)$
$C = C_{\mathrm{eq}}$ at the end of the experiment $(t = \infty)$ at the surface and inside of the particle
$\partial C / \partial r = 0$ after the beginning of the experiment and in the particle center $(r = 0)$

where C_{eq} is the chemical concentration in the polymer at equilibrium with the aqueous phase and α is the particle radius.

The analytical solution given by Crank [13] describes the mass of aqueous chemical in the particle (M_s) after time t relative to the same mass at equilibrium ($M_{s,\mathrm{eq}}$) as follows:

$$\frac{M_s}{M_{s,\mathrm{eq}}} = 1 - \sum_{n=1}^{\infty} \frac{6\beta(\beta + 1)}{9 + 9\beta + q_n^2 \beta^2} \exp\left[-q_n^2 \frac{D_a t}{\alpha^2} \right] \tag{4}$$

where β is the ratio of the chemical mass in solution to the chemical mass in the polymer at equilibrium

$$\beta = \frac{M_{w,\mathrm{eq}}}{M_{s,\mathrm{eq}}} \tag{5}$$

It is calculated from the experimental results at equilibrium, e.g., mass of chemical in solution is calculated through the chemical aqueous concentration at equilibrium and the volume of the solution. The $q_n s$ are analytical coefficients defined as the nonzero roots of Eq. (6):

$$\tan q_n = \frac{3q_n}{3 + \beta q_n^2} \tag{6}$$

$D_a t/\alpha^2$ is the dimensionless time also known as Fourier number.

If the system is far from equilibrium resulting in ($D_a t/\alpha^2$) values lower than 0.01, a short-term approximation can be used (Eq. 7) [13]:

$$\frac{M_s}{M_{s,\mathrm{eq}}} = 6\left(\frac{1}{\beta} + 1\right)\sqrt{\frac{D_a t}{\pi\alpha^2}} \tag{7}$$

At nonequilibrium conditions, chemical sorptive uptake by the polymer particle can be described with the ratio of the apparent sorption distribution coefficient (K_{da}) to the sorption distribution coefficient at equilibrium (K_d) as follows [13]:

$$\frac{K_{\mathrm{da}}}{K_d} = \frac{\beta}{\left(\frac{1+\beta}{M_s} s / M_{s,\mathrm{eq}}\right) - 1} \tag{8}$$

The advantage of Eq. (8) compared to the previous Eq. (7) describing the short-term approximation is that the solution is less sensitive for different values of β and allows comparison of the sorptive uptake at different solid-to-solution ratios in batch experiments [13].

The fitting parameter in the analytical short-term solution for spherical particles is D_a. K_{da}/K_d ratios are calculated in the model that combines Eqs. (7) and (8) into Eq. (9) as follows:

$$\frac{K_{\mathrm{da}}}{K_d} = \frac{\beta}{\frac{1+\beta}{6\left(\frac{1}{\beta}+1\right)\sqrt{\frac{D_a t}{\pi\alpha^2}}} - 1} \Rightarrow \frac{K_{\mathrm{da}}}{K_d} = \frac{1}{\frac{1}{6\sqrt{\frac{D_a t}{\pi\alpha^2}}} - \frac{1}{\beta}} \tag{9}$$

These ratios are compared to experimental K_{da}/K_d ratios for the experimental measurement times. The D_a value chosen is the one that minimizes the error that is the $\sum$[(mean of K_{da}/K_d ratios measured – K_{da}/K_d ratios predicted by the model)/(K_{da}/K_d ratios predicted by the model)]^2 of all measurements.

The solute diffusion in polymer particles can also be modeled numerically. In Ahn et al. [16], the results of sorption kinetic experiments with PAHs were readily explained by the classic polymer diffusion model for spherical geometries, solved with a numerical model. For polymer diffusion, the governing equation of contaminant diffusion in a homogeneous spherical particle can be written in the form

$$\frac{\partial q_{\mathrm{poly}}}{\partial t} = \frac{D_{\mathrm{poly}}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}q_{\mathrm{poly}}\right) \tag{10}$$

where t denotes the time (s), r (cm) is the radial distance from the particle or aggregate center, q_{poly} (g/g) is the concentration of the chemical in the polymer, and D_{poly} (cm^2/s) is the diffusion coefficient of the chemical in the polymer. External mass transfer resistance is neglected, and it is assumed that the chemical concentration q_{poly}(R) on the external surface of the polymer particle is at all times in a linear partitioning equilibrium with the surrounding water phase.

$$q_{\mathrm{poly}}(R) = K_{\mathrm{poly}}C_w \tag{11}$$

R (cm) denotes the particle radius, C_w (g/cm^3) the chemical concentration in the water, and K_{poly} (cm^3/g) the linear partitioning coefficient between the polymer and the aqueous phase. Ahn et al. [16] described the POM sorption kinetic data from the batch experiments with a numerical model based on the polymer diffusion model, using the steady-state value of $K_{\mathrm{POM,app}}$. Polymer diffusion coefficients D_{poly} were obtained as the fitting parameter from the data figures and by minimizing the squared residuals between model prediction and data. For phenanthrene, the fitted D_{poly} of the two size fractions agreed well. The fitted D_{poly} of the finer sieve fraction was approximately a factor two larger than the fitted D_{poly} of the original pellets, which could be explained by a larger external surface to volume ratio of the cut particles. Razor-cut particles were not as well-rounded as the original-size resin and had a rough surface because of the internal, bubble-like cavities of the POM, which could facilitate the uptake initially. For pyrene, the difference between the fitted D_{poly} values was a factor of ten for the two size fractions. The value for the finer POM fraction seemed unusually high, especially when compared to the respective D_{poly} of phenanthrene. No explanation was found for this observation.

The numerical model was used to predict the radial PAH concentration profile within the coarse POM particles based on the batch experiments. The predicted concentrations were normalized by the predicted concentration on the external surface for the comparisons, and the distance between data points from the laser shots was set equal to 40 μm. The agreement between the predicted PAH concentration profiles and the measured μL2MS data was excellent, from which it was concluded that the spherical polymer diffusion model provides an accurate description for the sorption kinetics of PAHs in relatively homogeneous and approximately spherical pellets of a rubbery polymer such as POM.

6 Studies Performed in the Marine Environment or with Marine Microplastics

Zhan et al. [10] published a baseline paper studying sorption of PCB77 to PP particles (0.18–5.0 mm). The results showed that equilibrium was reached at 8 h and followed first order rate kinetics. However, when different size particles were tested for their sorption capacity after 24 h exposure time, a decreasing sorption capacity was observed with increasing diameter. The authors attributed this behavior to lower external surface area with increasing diameter; however, sorption kinetics for the higher particle size was not tested. The authors present a table summarizing kinetic studies that present varying exposure periods for different polymers and chemicals. The authors attributed the variations for the same polymer among studies due to hydrodynamics of the chemicals, but as discussed above, the size of the polymer is rather significant for the interpretation of the kinetic results.

Rochman et al. [9] conducted a long-term field experiment, studying the sorption rates and concentrations of PCBs and PAHs in various plastic types (2–3 mm) and for different marine locations. For PAHs and PCBs, PET and PVC reached equilibrium in the marine environment much faster and at much lower solid concentrations than HDPE, LDPE, and PP. This is significant considering that global production of PE is much higher than all the other polymers.

Koelmans et al. [20] performed an extensive critical review on desorption kinetic constants. They presented a table similar to Table 1 summarizing HOC desorption rate constants k from plastic in the gut of marine biota, obtained from (a) bioaccumulation studies, (b) desorption studies, and (c) theoretical calculations. The magnitude of the rate constant k for desorption of HOCs from microplastics in the gut across different microplastic types and sizes, organisms, and chemicals, obtained with different methods, has a range of about two orders of magnitude with a median of 2.1 (1/d).

Endo et al. [4] investigated the desorption behavior of polychlorinated biphenyls (PCBs) from marine PE plastic pellets. The desorption kinetics highly depended on the hydrophobicity of PCB congeners. After 128 d, the smallest congener (PCB8) had desorbed nearly completely (98%), whereas major fractions (90–99%) of bigger congeners remained in the pellets. An intraparticle diffusion model failed to reproduce desorption kinetics, whereas an aqueous boundary layer (ABL) diffusion model approximated the data. The desorption half-lives were estimated to range from 14 d to 210 years for PCB8 to PCB209 in an actively stirred solution (ABL thickness: 30 μm). Addition of methanol to water enhanced desorption to a large extent, and then polymer diffusion became significant.

Bakir et al. [11] investigated the potential for PVC and PE to sorb and desorb different chemicals in the laboratory. Desorption rates of organic chemicals were quantified in seawater (Table 1) and under simulated gut conditions using seawater surfactants. Also, the influence of pH and temperature was examined to simulate the conditions inside the body of cold- and warm-blooded organisms. Desorption rates were faster up to 30 times when gut surfactant was present in the solution and under conditions simulating warm-blooded organisms rather than in seawater alone. For example, phenanthrene with PE demonstrated a first order desorption rate equal to

1.4 (1/d) in seawater and 12 (1/d) in the surfactant solution at 38°C and, thus, demonstrated a high potential for transport from plastic to the organisms.

Teuten et al. [8] also observed enhancement of desorption rates for phenanthrene from different chemicals in the presence of a surfactant in the solution. The first order reaction rates presented in Table 1 for desorption in seawater were enhanced by the surfactant by a factor of about 7, 19, and 2 for 0.2–0.25 mm PE, PP, and PVC, respectively.

More recently, Tanaka et al. [21] also observed increasing desorption when plastic was in contact with fish or stomach oil. More specifically, pieces of plastic around 3 mm in diameter containing deca-brominated diphenyl ether were soaked in several leaching solutions, and measurements were taken at 5 and 15 days (and at 0.5 and 2 days for fish oil). Trace amounts were leached into distilled water, seawater, and acidic pepsin solution. In contrast, over 20 times as much material was leached into stomach oil by day 15 and over 50 times as much into fish oil (a major component of stomach oil) by day 2.

7 Conclusions

Studying sorption/desorption rates of HOCs can be accomplished with routine research procedures with repeatable results among researchers. However, when one considers the variety of HOCs found in the environment, the various types and sizes of plastics found in the stomach of some organisms along with the biodiversity that exist in the marine environment, there remains considerable uncertainty. It is well known that HOCs sorb/desorb to all plastic materials but with different rates and different diffusion ability within the polymer. At this point within the context of this chapter, the main recent finding is that desorption rates of HOCs from plastics can be slow but are increased in the presence of higher animal body fluids, and small plastic particles will uptake or release pollutants much faster than larger pellets.

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Biofilms on Plastic Debris and Their Influence on Marine Nutrient Cycling, Productivity, and Hazardous Chemical Mobility

Tracy J. Mincer, Erik R. Zettler, and Linda A. Amaral-Zettler

Abstract Plastic debris is entering our oceans at an alarming rate and almost instantaneously colonized by a microbial biofilm that is unique from the microbial flora in surrounding waters. Microbial inhabitants on plastic marine debris (PMD) are now known to fluctuate depending upon season, geographic location, substrate, and age. Cursory calculations estimate a range of 1,000–15,000 metric tons of microbial biomass harbored on PMD. Here, we consider the significance and implications of this large amount of microbial metabolic potential that PMD carries and pose future research questions involving the implications of this relatively recent anthropogenic substrate and its diverse microbial inhabitants.

Keywords Biofilm, Marine, Microbial interactions, Microplastics

Contents

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1 Introduction

Microbes are the hidden majority of life dominating our planet, comprising over 90% of the biomass in the world's oceans, exceeding 10^{29} cells in the open ocean alone [1]. Responsible for establishing the biogeochemical equilibria of the biosphere, microbes account for 95% of the respiration in the ocean [2], and represent the most metabolically diverse forms of life exploiting nearly every energetically favorable niche available, including hot springs and hydrothermal vents where water temperatures exceed 140°C, thriving in sediments contaminated with toxic anthropogenic heavy metals and hydrocarbons, and highly acidic geological seeps [3, 4]. Given this, it is understandable that the film of microbial life adhering to the surface of plastic marine debris (PMD), that we recently termed the "Plastisphere," is unique from the surrounding seawater and possibly hydrolyzing plastic resin substrates in the open ocean environment [5].

Plastic materials have become commonplace in our lives and are in ever increasing demand due to low-cost, durability, and ease in single-use applications, driving production higher each year with an estimated 299 million metric tons in 2013 [6]. Plastic materials were quickly recognized for their high utility and were widely adopted for many uses in the 1970s, which in combination with little to no plans for proper disposal readily accounts for increasing plastic pollution in the marine environment first documented by workers in the early 1970s [7]. The effects of PMD and its possible implications were posited as a serious threat to marine biota from the earliest reports where interactions with microbes, fish, and zooplankton were observed [7]. This pulse of clearly visible plastic pollution spurred the scientific community to propose a plan of action for policymakers [8], including development of hydrophilic photodegradable biopolymers, efficient plastic incinerators, and reclamation and recycling plans; however, even today the policies of the most progressive countries fall short of these prescient recommendations. Plastic has permeated the most distant regions including remote mangroves [9], benthic Arctic habitats [10], Polar sea ice layers [11], deep sea canyons [12], remote tropical islands [13, 14], and areas of Antarctica [13]. Plastic debris can even dominate certain habitats, for example, a survey of the Danube River in Germany found plastic particles outnumbered fish larvae [15] with input into the Black Sea estimated at an astounding 4.2 metric tons per day. Much of this PMD is carried on major ocean currents and transported to central gyres in the open ocean where it resides on decadal scales. The interior of each of the five major oceanic gyres have now been documented as having PMD amounts exceeding 2 kg/km^2 [16]. Recent calculations have found the major input of plastic debris to the marine environment to be land-based and as high as 12.7 million metric tons annually, or nearly 5% of world plastic production in 2010 [17].

With every new survey of plastic debris in the world's oceans, higher estimates of abundance are provided with the most recent pan ocean survey estimating of 5.25 trillion particles weighing 268,940 tons harbored in the world's open ocean habitats [18], although this amount takes into account large debris (anything greater than 200 mm in size) that were estimated visually while at sea and not actually quantified. Nevertheless, it is interesting that even the most recent ocean surveys do not account for the amount of debris estimated to be entering the ocean, differing by orders of magnitude, begging the question: "Where is all the plastic?" Notoriously refractory, PMD is known to persist for decades in the open ocean; however, a size fraction in the millimeter to sub-millimeter scale that should abound, given what is known about abiotic weathering of PMD, is curiously scarce in the most recent survey data and it has been hypothesized that this size fraction of polymer resin is interacting with marine organisms, breaking into particles small enough to pass through nets, or sinking into the water column in a previously unexpected fashion [16].

The microbial biomass harbored on PMD can be significant, upwards of 6% of the total mass of a piece of microplastic [19] and the influence that the Plastisphere can wield on large scales is unclear. We are now in the midst of a "great experiment" where massive amounts of a refractory surface substrate are being introduced into habitats where it previously never existed. Perturbing delicate low-nutrient (oligotrophic) open ocean habitats with large amounts of surface area can have unintended consequences. Refractory surfaces are known to stimulate microbial respiration due to a long-known "bottle-effect" where trace nutrients are concentrated onto the surface making them more bioavailable, a phenomenon initially described by Claude ZoBell [20]. Nutrient acquisition, however, is not the only driver as PMD can harbor entirely self-contained microhabitats including phototrophs, heterotrophs, predators, and symbionts [5]. In this chapter, we explore the idea that PMD is more than merely a pollutant and, rather, view PMD as a new marine niche habitat with a distinct biological community and physico-chemical characteristics with largely unknown impacts on existing coastal and open ocean marine systems.

2 Oceanographic Habitats Relevant to PMD

Drifter buoys and physical oceanographic models have shown that plastic can migrate over 1,000 km, from the nutrient rich coastal waters of the Eastern Seaboard of the USA to the oligotrophic interior of the North Atlantic Subtropical Gyre (NASG), in less than 60 days [21]. Plastic debris in the NASG [21] and North Pacific Subtropical Gyre (NPSG) is well documented [22, 23] and mathematical models and sampling confirm that accumulations of PMD have formed in all five of the world's subtropical gyres [14, 16]. Bordered by currents, PMD has few avenues

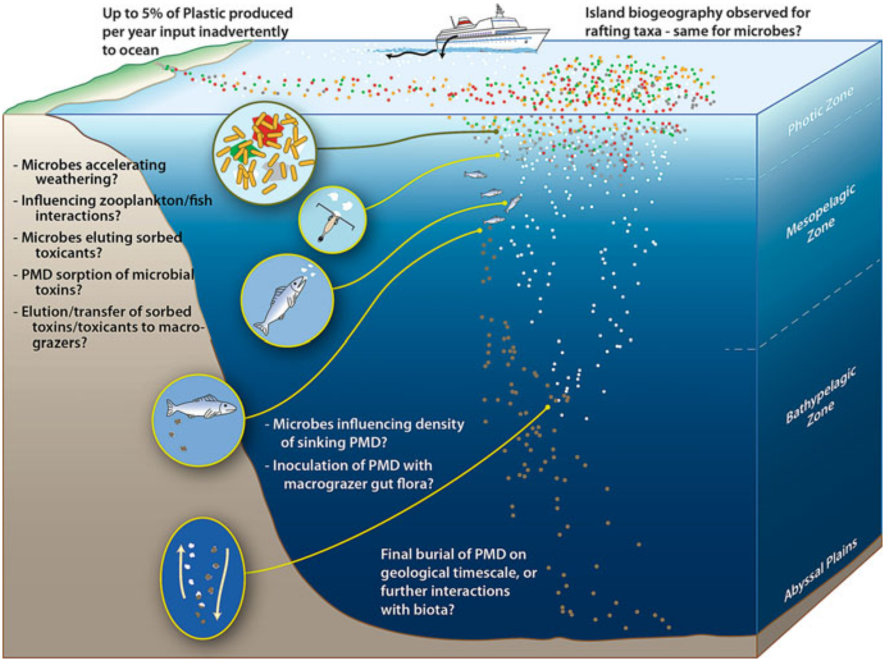

Fig. 1 Plastic resin and its multiple fates in the marine environment: significant plastic debris inputs from land can be transported directly out to open ocean gyres where they could persist for decades. Microbial biofilms rapidly attach to plastic debris and possibly influence weathering of PMD, sorptive properties, and its interactions with indigenous biota

for export and could reside in these open ocean gyre features for decades with the most recent study estimating that 4.8–12.7 million metric tons of mismanaged plastic waste enter the oceans per year [17] (Fig. 1).

Plastic debris provides a substrate for marine life that lasts much longer than most natural floating substrates and has been implicated as a vector for transportation of harmful algal species [24] and persistent organic pollutants (POPs) such as polychlorinated biphenyls and polyaromatic hydrocarbons which sorb onto plastic [25]. Thus, Plastisphere community members are in direct contact with sorbed POPs and have the potential to influence interactions of these compounds with PMD. It is currently unclear if Plastisphere microbes directly degrade plastic resins or sorbed POPs; however, it is clear that heterotrophic bacteria and fungi and autotrophic microalgae in the marine environment have the ability to generate highly reactive oxygen species known to oxidize refractive carbon compounds [26, 27]. Heterotrophic bacteria in particular have been hypothesized to deliberately produce high amounts of reactive superoxide in order to degrade refractive carbon to aid in the acquisition of nutrients in natural environments [26] and this oxidative mechanism has the potential to significantly accelerate the weathering of PMD. Conversely, Plastisphere members could be protecting PMD from UV degradation inadvertently via microbially produced mycosporine proteins and scytonemin-like pigments, known to protect microbes from UV and oxidative pressure that would otherwise be harmful to genomic DNA [28]. Whether Plastisphere flora have a net oxidative or protective quality is still debatable; however, presumptive signs of polymer hydrolysis and degradation have been noted in our scanning electron microscopy (SEM) analyses [5].

It is well documented that many marine fauna ingest microplastics [29]. Some open questions surrounding the fate of the Plastisphere community in the gut are: "What are the effects of pH on the release or transformation of POPs and other toxicants? Are Plastisphere communities automatically 'reset' after ingestion? Do some members survive the journey? Are new colonizers picked up along the way?" (Fig. 1). Other studies have provided evidence that POPs could be transferred to fish and thus represent a potential step in the biomagnification pathway of certain toxicants [30]. There is also evidence that some toxicants could be preferentially desorbed under simulated gut tract conditions [31] and in the sediment dwelling lugworm *Arenicola marina* [32]. Certain Plastisphere members could be potentially harmful, or possible pathogens [5, 24] and it is conceivable that these microbes if in a high enough titer could pose a burden to certain standing stocks of macrograzers and provide a vector for gene transfer and selection of specific pathovars.

3 Biofilm Formation and Biomass

PMD has a yo-yo type of movement through the water column due to biofouling, first shown by workers in Biscayne Bay, Florida [33]. Biofilm formation varies with season, substrate, and location, as workers reported from 6-week incubations of polyethylene terephthalate (PET) samples in the Baltic region [34]. Microbial biofilms also have the potential to influence invertebrate settlement [35] which would have an additional impact on the buoyancy of PMD, and could influence the transport of invasive invertebrate species.

Biomass of the total Plastisphere has previously been approximated by using nitrogen content as a proxy, determined by elemental analysis, assuming a 1% nitrogen content from PMD corresponds to 6.7% biomass using standard Redfield carbon to nitrogen ratios (typical floating plastic resins such as polypropylene and polyethylene are devoid of nitrogen at the time of manufacture) [19]. Extrapolating this estimation of biomass per mass of PMD to some of the most current abundances of PMD in the open oceans and estimating a 6% biomass coverage and a range of 14,400 metric tons [16] to 268,000 metric tons [18] of floating PMD in the oceans corresponds to roughly 860–16,000 tons of biomass carrying capacity within the Plastisphere. It has been estimated that the upper 200 m of oceans harbor about 3.6×10^{28} microbial cells [1], which can be grossly extrapolated to 3.6×10^{26} microbial cells in the upper 2 m of the ocean. If we assume that the average amount of carbon per microbial cell is 20 femtograms and an average of 5×10^{8} microbial cells per liter of open ocean seawater, this correlates to a range of 0.01–0.2% microbial biomass harbored on PMD per open ocean microbial biomass. To illustrate this another way, consider that a piece of PMD weighing one gram, possessing 6% microbial biomass harbors nearly an order of magnitude more microbial biomass (in terms of carbon content) than 1,000 L of open ocean seawater! This relatively large introduction of Plastisphere community members represents a potentially significant and "foreign" perturbation to these nutrient limited open ocean regimes likely creating "closed loops" of nutrient cycling and disrupting microbial processes pre-dating the introduction of PMD.

4 Time-Course Colonization and Succession on Plastics

Microbial biofilms were described in the very first published reports of plastic in the open ocean, when Carpenter and Smith [36] noted "Most plastics had populations of hydroids and diatoms attached to their surfaces." In a subsequent paper [7] bacteria were also noted on the surface of plastic from coastal waters. Despite 4 decades since the report of microbes on PMD, we know little about how these microbial communities form, how they change over time, and whether they vary seasonally and regionally. Because we cannot determine the age of most PMD collected in the field and do not know the history of where it has travelled, we know little about the time course of assembly and succession or biogeography of these attached microbial communities. Presumably, substrate physical and chemical characteristics, order of species arrival, species interactions, and disturbances play important roles determining the Plastisphere community.

There have been a number of field experiments that provide hints of how colonization of plastic in the ocean proceeds and varies regionally and seasonally. One of the earlier studies [33] immersed a variety of floating plastic types in Biscayne Bay, Florida, to study fouling communities and their effect on buoyancy. The researchers did not identify specific microbial colonizers but noted that fouling by invertebrates was preceded by a slimy biofilm that formed on the surface within days. Green algae and hydroid colonies were among the first multicellular and animal colonists in the weeks that followed. Diatoms seem to be the earliest and most abundant eukaryotic colonizers, often dominating fresh surfaces in the first couple weeks, and hydroids are commonly among the first animals [37]. In preliminary time-course incubations we have also noticed that diatoms appear to be the early and dominant eukaryotic colonizers (Fig. 2a, b).

A study incorporating various anthropogenic materials found that bacterial colonization occurred within 24 h in a salt marsh tidal creek [38]. These authors used substrates carefully prepared to exhibit different surface hydrophobicity and found that the *Roseobacter* subgroup was a ubiquitous surface colonizer and also posited that surface characteristics influenced the microbial community. In this study, some of the first bacteria to arrive disappeared by 72 h, and bacterial community succession was observed on all six substrates tested. In a follow-up study, these authors found that Rhodobacterales were also the dominant early colonizers of poly methyl-methacrylate (acrylic or Plexiglass$^{®}$) and poly vinyl

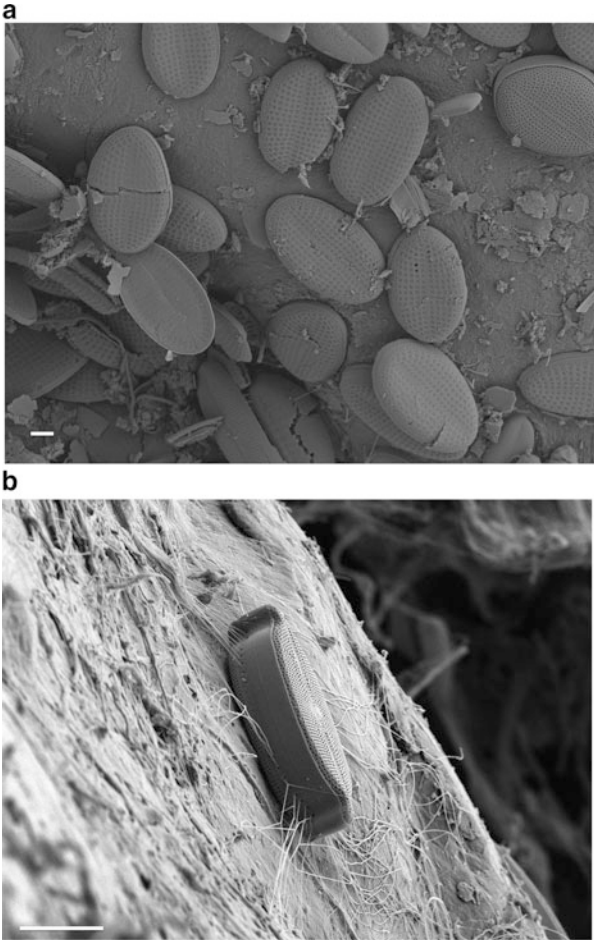

Fig. 2 (**a**) Pennate diatoms dominating the surface of expanded polystyrene after just 1 week of immersion in seawater off Woods Hole, MA, USA, scale bar corresponds to 2 μm; (**b**) Pennate diatom attached to PMD fragment from N. Atlantic Ocean, scale bar corresponds to 10 μm

chloride in the western Pacific Ocean [39]. Another study also noted Rhodobacterales as dominant colonizers of polycarbonate surfaces in temperate waters, and that the community changed as biofilms modified the surface characteristics [40]. A recent study in the North Sea used a combination of SEM imaging, denaturing gradient gel electrophoresis (DGGE), and sequencing of DGGE bands to characterize the microbial community that developed on PET drinking water bottles over 6 weeks in each of three seasons: Spring, Summer, and Fall [34]. This research recovered a diverse community of bacteria and eukaryotes. Despite considerable overlap, there were significant variations in the microbial community diversity with season and location. Diatoms were an important component of their communities, but in contrast to the Rhodobacterales reported as dominant plastic colonizers in other studies, communities in the North Sea were dominated by Bacteroidetes and Cyanobacteria [34].

In addition to stimulating respiration by concentrating nutrients, plastic surfaces can also enhance viability of bacteria in oligotrophic environments. Sealed flasks of water containing PET fragments maintained viable counts of bacteria for 6 months, while control samples of the same water without plastic substrate did not [42]. These authors also noted changes in the surface topography of the PET after bacterial colonization. Microbial biodegradation of fossil-fuel-based plastic in the ocean over reasonable timescales (weeks to months) is unlikely but some microbes do appear to modify plastic surfaces, contributing to fragmentation [5]. Lobelle and Cunliffe [43] also showed a correlation between biofilm development and hydrophilicity of polyethylene food bags over a 3 week immersion in Plymouth, UK. Colonization resulted in a decrease in buoyancy and the authors reasoned that biofilm formation could result in sinking of floating plastic.

Fewer biofilm colonization studies have been performed in tropical environments, but starch/bioplastic blends placed at various distances offshore in Puerto Rico showed samples farther from shore had lower bacterial counts and slower degradation rates [44]. A study in tropical waters of southern India measured the biofilm that developed on polycarbonate sheets over 6 months and sampled monthly [45, 46]. Total viable counts from Zobell marine agar remained fairly constant during the study, but biofilm dry weight and chlorophyll content varied, with higher values in early spring (March) and summer, suggesting the community changed seasonally. There were substantial differences between the enclosed fishing harbor and the offshore site, possibly tied to lower oxygen levels in the harbor. These authors also reported earlier work with high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene, and polycarbonate that showed colonization was positively correlated with substrate hydrophobicity.

A recent study of bacterial colonization of LDPE in coastal sediment microcosms showed that just as in the water column, plastic surfaces in sediment were colonized quickly (within 6 h) and populations increased over time. Despite differences in microbial communities in the surrounding sediments, the Plastisphere communities converged quickly and were dominated by *Arcobacter* and *Colwellia* spp. [47].

Certain remarkable differences between marine and terrestrial environments exist with respect to degradative capacity and should be taken into account as to how microbes in marine and fresh water might respond to biodegradable or compostable plastics. Evidence from previous research suggests that certain substances that are readily compostable in terrestrial reactors display very different decomposition profiles, as measured by respiration, in the marine environment [48]. For example, in a 700 day experiment, soy stalks, corn leaves and stalks, and alder wood chips incubated in a benthic marine habitat showed the terrestrial derived detritus to be remineralized at a rate at least an order of magnitude lower than planktonic marine detritus in a separate incubation under the same conditions [48]. Microbial activity has also been found to be highly variable on anthropogenic litter. For example, one group reported that biofilms in a freshwater ecosystem colonizing organic substrates such as cardboard and leaves displayed a significantly decreased gross primary productivity compared to biofilms on hard substrates such as glass, plastic, and aluminum [49].

Studies so far have just scratched the surface addressing important questions about microbial community assembly on PMD. In particular, what organisms colonize the plastic surface in the first minutes, hours, and days is poorly understood. Once these pioneering organisms attach to the plastic surface, how do they modify it, and how does that influence successive colonizers? Do different resins select for distinct microbial communities, and how do communities change over time and space as PMD drifts through different environments (e.g., river, estuary, coastal water, and oligotrophic open ocean)? Future experiments targeting some of these questions will help us understand how the Plastisphere community develops, changes, and impacts the plastic substrate and the surrounding marine environment.

5 Biogeography and Its Role in Dictating Microflora of PMD

Of extraordinary interest in the study of PMD is the impact it has based on the ability to transport microbiota on its surfaces. A critical question is whether the microbiota living on PMD are reflective of their surrounding environments – in essence whether or not PMD exhibits a biogeography. Do coastal species survive the journey on PMD and adapt to the nutrient-barren desert of the open ocean, or are PMD communities more characteristic of the environments where they ultimately reside? While there have been reports of rafting of organisms on PMD, proof of invasive species being introduced into a given environment via PMD is difficult to demonstrate conclusively for macroorganisms let alone microbiota inhabiting their surfaces. Furthermore, the “life cycle” of a PMD community can be highly variable depending on whether it originated from terrestrial versus marine sources, how long it has been suspended in the water column, how much UV and mechanical degradation it has experienced, whether it has journeyed through the gut of an unsuspecting predator, and so on (see Fig. 1). This variability has been demonstrated by comparing the microbial community structure of the Plastisphere to the surrounding seawater [5]. Plastisphere communities are distinct from seawater but they are also highly variable in composition between themselves as compared to much more predictable seawater communities.

Another dimension to PMD biogeography is the dynamic interactions between organisms on the PMD itself, for example, the impact of consumption by larval or protistan predation and lysis by viruses on the Plastisphere community. The latter presents an interesting scenario since viruses tend to be very host specific and thus, may be “lost” when their hosts are transported long distances. In fact, it may be interesting to study the “natural history” of PMD by examining the mobile DNA that is being transported along with it. For example, antibiotic-resistance genes, metal-tolerance or sequestration genes, and virulence factors are among the genes that may be enriched in Plastisphere microbiomes. Colonization of PMD over time and space and its relationship to communities in the surrounding seawater provides insights into the biogeography of the Plastisphere.

Harrison et al. [47] conducted a 14-day laboratory-based microcosm experiment employing different coastal sediments to explore bacterial interactions with LDPE. These authors used a combination of CARD-FISH and DNA fingerprinting to demonstrate that initial colonizers differed from the surrounding sediment. This is the first report of an incubation experiment that used molecular methods to uncover the microbial communities associated with LDPE. LDPE is also known to float in ocean gyres, but it is unclear how the sediment results relate to the pelagic environment. Nevertheless, the study shows some important trends: (1) LDPE-associated bacterial assemblages differed significantly from those occurring in the surrounding sediments, and (2) over time, the bacterial communities on plastic in different sediments converged. Surprisingly, members of the Epsilon-proteobacteria *Arcobacteria* and Gamma-proteobacteria *Colwellia* dominated these microbial communities. This study also found differential numbers of bacteria colonizing the LDPE depending on the type of sediment employed which may have important ecological implications for deposition of plastic in the marine environment.

In a follow-up, conducting a longer duration study employing PET bottle incubations in the water column, Oberbeckmann et al. employed DGGE followed by DNA sequencing analysis to show that PET Plastisphere communities differed both with season and location [34]. This is the first study to examine PET-associated microbial communities in situ, but again it is unclear how their results are reflective of the benthos, where PET, because it is denser than seawater, tends to accumulate. However, this study addresses the fraction of PET bottles that would float if the bottles were capped prior to entering the marine environment as marine debris. The major bacterial phyla detected in this study included Bacteroidetes, Proteobacteria, and Cyanobacteria. Eukaryotes in this study included Bacillariophyceae and Phaeophyceae.

The Oberbeckmann study showed that spatial and seasonal (temporal) variation exists in Plastisphere communities on suspended PET incubations. For community composition, seasonal variation was most pronounced in the winter [34]. Curiously, this study did not report Alpha-proteobacteria in the PET bottle communities but this may have been the result of their sequencing approach more than a reflection of what was present, as fingerprinting methods are known to capture predominantly the most abundant members of the community.

In a study comparing microbial communities colonizing polyethylene, polystyrene, and polypropylene particles in the North Pacific using SEM, the highest microbial abundances were on foamed polystyrene [41]. This study emphasizes yet another dimension to keep in mind with respect to the biogeography of the Plastisphere: polymer type may influence both the number and composition of the resulting biofilm community structure.

A final point to consider regarding the biogeography of the Plastisphere is the "unseen." We are not yet in a position to completely rule out the possibility that bacteria and fungi living on PMD are utilizing it as a carbon source [50–52] and that

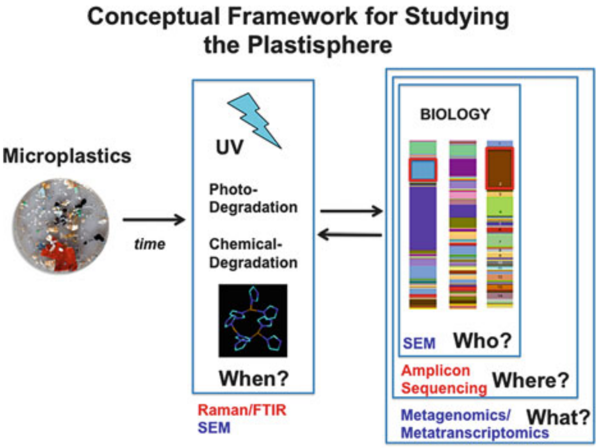

Fig. 3 Conceptual framework for studying the Plastisphere. Understanding this new habitat and its impact on marine ecosystems will rely on a combination of physical, chemical, and biological investigations at a variety of temporal and spatial scales

this portion of PMD escapes our sampling abilities. An important aspect of this possible fate is the time frames over which this occurs. Given that PMD is colonized on very short timescales, it has the potential to impact all marine life, even the smallest of creatures that call the ocean home.

6 Conclusions

Understanding the Plastisphere and the metabolic influence it has on higher ecological levels is at its infancy but requires an interdisciplinary approach (Fig. 3). First order questions such as “Who is there?” and “How big is this community?” are just beginning to be addressed and we still have very little information about what the inhabitants of the Plastisphere are doing or the scale of their contribution to marine biogeochemistry. Thus, the response of microbial communities to plastic debris in the oceans may have subtle but additive effects with the potential to shift major biological and climatological processes on Earth.

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Ingestion of Plastics by Marine Organisms

Peter G. Ryan

Abstract Many marine organisms ingest plastic items, providing a potential mechanism for the transfer and accumulation of hazardous chemicals associated with plastics. This chapter summarises the range of organisms known to ingest plastic items and the factors influencing the amount of plastic in their digestive tracts. Ingestion can be direct (primary ingestion) or indirect (secondary ingestion via contaminated prey), with direct ingestion being either deliberate (plastic items mistaken for prey items) or accidental (plastics consumed passively by, e.g. filter feeding). Ingestion rates can be summarised as the proportion of individuals to contain ingested plastic (frequency of occurrence = incidence) as well as the average plastic load per individual (expressed by number, mass or volume of items). The amount of plastic in the digestive tract of an organism is a balance between its intake rate and removal via excretion and/or regurgitation. Individual-level variation in plastic loads typically is large and strongly right skewed. Numerous factors probably account for this variation, including age-specific and individual differences in the likelihood of plastic ingestion and retention times, as well as temporal and spatial differences in plastic exposure. Retention times are poorly known for many groups of marine animals, and may be influenced by particle size, shape and type of plastic, as well as phylogenetic and age-related differences in how animals handle indigestible prey remains. Three categories of organisms can be recognised: species that regurgitate most plastic (e.g. gulls, terns and skuas), those that excrete most plastic shortly after ingestion (e.g. fur seals) and those that store plastic in their digestive tract for protracted periods before eroding them to the point where they can be excreted (e.g. petrels, phalaropes and some auks). Turtles probably lie between the last two groups, excreting most plastic, but retaining it far longer than prey items. Further information is needed on the importance of the

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retention time in the digestive tract of an animal for transfer of hazardous chemicals, but it is likely that long retention times enhance chemical uptake, at least for compounds included in plastics during manufacture. Species with broad, generalist diets that retain indigestible prey items in their digestive tracts for extended periods, such as petrels, storm petrels, phalaropes and turtles, probably are most likely to obtain large body burdens of hazardous chemicals from ingesting plastic items.

Keywords Accumulation, Intergenerational transfer, Mechanical wear, Phylogeny, Primary ingestion, Regurgitation, Retention rate, Secondary ingestion

Contents

1 Introduction: The Impacts of Plastic Ingestion

Of all the biological impacts of plastic pollution, ingestion by marine organisms probably is the most serious [1, 2]. Ingestion might lack some of the emotional power engendered by images of entangled animals being slowly constricted or drowned, but for at least some species, it affects virtually all individuals. Ingestion has the potential to have far-reaching implications at the population level, posing a threat to the conservation of individual species (e.g. [3]) and to the functioning of marine ecosystems.

Fig. 1 Ingested plastic removed from a post-hatchling loggerhead turtle (*top right*) that died after 18 days in captivity. The cloaca was blocked, forcing some plastic fragments into the bladder (from [8]; photo Georgina Cole)

Plastic ingestion has several possible impacts on marine animals. Until recently, impacts have been confined to relatively large plastic particles that remain in the digestive tract. The most obvious impact of these items is physical damage or blockage of the digestive tract (e.g. [4–7]). In extreme cases it can even force plastic into the urinary tract of turtles, rupturing the bladder (Fig. 1; [8]). Like entanglement, such blockages can have dramatic consequences at the individual level, but with the possible exception of some marine turtles, it is unlikely to occur frequently enough to have adverse demographic impacts. Large amounts of ingested plastic might also affect an animal's buoyancy, either directly through its low density [9] or, more likely, by impairing digestive function leading to gas build-up. This is a potentially serious consideration for turtles, sometimes preventing them from diving and, thus, leading to starvation. If the obstruction is removed, the appetite of the animal recovers, along with full diving and digestive functionality (e.g. [10]).

The second major physical impact occurs when species accumulate large volumes of plastics in their stomachs, creating a false sense of satiation, which reduces their appetite and hence food intake [11–15]. Ingested plastic may also slow the rate of digestion [16], but this probably depends on the amount and type of plastic (cf. [1, 17]). These problems tend to result in sublethal impacts on all but the most heavily polluted individuals. Such impacts have been inferred from lower body condition among individuals containing ingested plastic (e.g. [18–20]), although other studies have found no effect of plastic load on the condition (e.g. [21]). However, care is needed in interpreting correlations between plastic ingestion and body condition, because individuals may ingest more plastic because they are in poor body condition, rather than vice versa [22, 23]. Despite this issue, experiments have shown that ingested plastic reduces food intake among birds [15] and turtles [13, 24]. However, given the strong right skew in plastic loads among individuals within species (see Sect. 4), and the correlation between the incidence of plastic ingestion and plastic loads [25], only species with extremely high plastic ingestion rates are likely to suffer demographic consequences from false satiation or reduced food intake.

In the last few years, there has been increasing concern about the impacts of ever-smaller plastic particles on marine animals, especially small filter-feeding species such as mussels and zooplankton [26, 27]. Nanoparticles can migrate out of the digestive tract [28], or enter animals across respiratory surfaces [29], causing mortality in planktonic copepods [30] and disrupting cellular metabolic pathways at the submicron scale [31]. Ingestion of nanoplastic particles (<10 μm diameter) apparently can alter the activity levels and foraging behaviour of fish in experimental trials [32], but the mechanism underpinning these changes is unclear. Finally, coming to the topic of this volume, ingested plastics might carry other pollutants (e.g. persistent organic pollutants (POPs) and even heavy metals) that are either native to the plastics or adsorb to them at sea into marine organisms (e.g. [33–42]). More information is needed on the importance of plastic dose and exposure period on this effect, but at least in principle, this could be the most serious impact of plastic ingestion at a population level.

In this chapter, I explore how and why marine animals ingest plastic items, consider the challenges to assessing plastic ingestion and discuss the factors influencing the amount of plastic found in the digestive tracts of marine animals. I, then, briefly summarise the range of marine organisms recorded to have ingested plastic items.

2 Why Do Animals Eat Plastic?

Animals ingest plastic in three main ways: deliberate ingestion because they perceive plastic items to be potential prey, incidental ingestion while feeding or secondary ingestion through contaminated prey. Teasing apart these three mechanisms is not a simple problem. For some species, notably marine turtles, experimental trials with captive animals have elucidated some of the behaviours involved (e.g. [24]), but for most species we can only infer the processes from the types of plastic ingested and the incidence of ingestion in the taxa with different foraging behaviours and mechanisms for handling ingested plastic (see Sect. 4). Animals may also derive plastic in several different ways, e.g. lobsters (*Nephrops norvegicus*) may ingest plastic in their prey or accidentally while foraging or burrowing, with accidental intake enhanced by feeding on epibionts attached to plastic items [43].

2.1 Primary Versus Secondary Ingestion

Primary ingestion occurs when plastic items are consumed directly, whereas items ingested indirectly via contaminated prey are termed secondary ingestion. Secondary ingestion was first recorded in the 1970s, when pellets of indigestible prey remains regurgitated by terns were found to contain small plastic pellets apparently derived from their fish prey [44]. Given the recent focus on microplastics and their possible role in transferring persistent organic pollutants through marine food webs, there is growing interest in secondary ingestion (e.g. [45]). However, it is not easy to discriminate between plastics ingested directly from those in prey species. The size of ingested particles may give some indication, because prey size tends to be related to body size. As a result, animals that mainly consume plastics directly such as albatrosses and petrels show a strong correlation between the size of plastic items and body size (Fig. 2). A similar pattern occurs within species that change body size with age. For example, the average mass of plastic items found in the digestive tracts of loggerhead turtles (*Caretta caretta*) increases with body mass (Fig. 3). As turtles grow, their larger gape size allows them to manipulate and eat larger food items [48].

Plastics ingested in prey are likely to be smaller than items ingested directly, because they are scaled to the size of the prey species. One of the best examples of this comes from *Arctocephalus* fur seals, which weigh 30–180 kg, but excrete small plastic fragments mainly 2–5 mm across (average ~10 mg; [49]). The fur seals feed predominantly on myctophid fish (Myctophidae), which are known to ingest small plastic particles (e.g. [9, 50, 51]). Indeed, knowledge of a species' diet also gives useful cues as to whether plastic is ingested directly or through prey. For example, predatory species such as the bald eagle (*Haliaeetus leucocephalus*) obtain plastic from eating contaminated seabirds such as parakeet auklets (*Aethia psittacula*) [52]. Habitual predators of seabirds that contain large plastic loads, such as

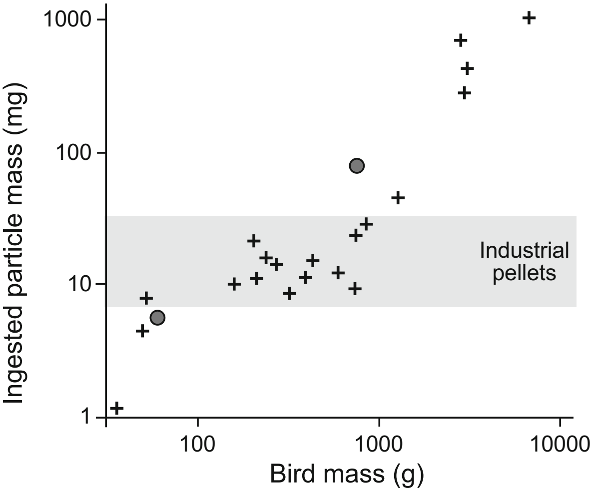

Fig. 2 The relationship between ingested plastic particle mass and body mass in 22 species of seabirds in the 1980s (*plus symbol* Procellariiformes, *filled circle* Charadriiformes). *Grey shading* shows the approximate size range of industrial pellets, which dominated plastic ingested by mid-sized seabirds at that time. Note the log–log scale (adapted from [23, 25])

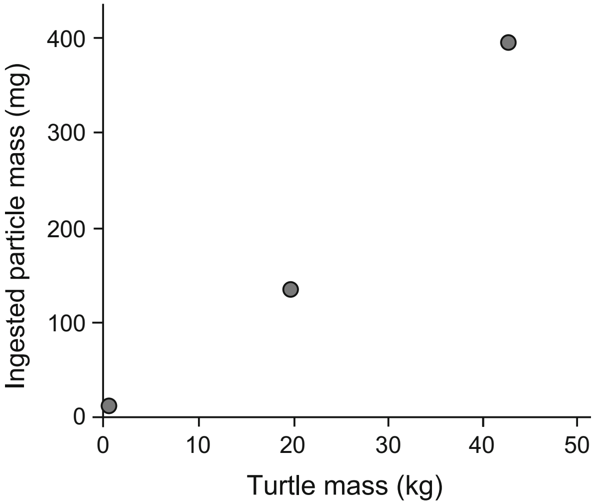

Fig. 3 The increase in the average mass of plastic particles ingested by loggerhead turtles (*Caretta caretta*) of different body masses (post-hatchlings based on unpubl. data from South Africa, juveniles from [46] and subadults/adults from [47])

brown skuas (*Stercorarius antarcticus*), regularly ingest plastic in this way (e.g. [53]). However, skuas do not accumulate large plastic loads because they regularly regurgitate indigestible prey items (see Sect. 4). This trait enables the use of skuas as monitors of regional or temporal changes in plastic ingestion among their prey species [54, 55].

2.2 Accidental Ingestion

Primary ingestion may be deliberate (plastic items mistaken for prey items) or accidental. Accidental ingestion of plastic items typically occurs in indiscriminate feeders such as filter feeders (e.g. baleen whales, goose barnacles, mussels) and detritivores (e.g. lugworms, sea cucumbers), which are likely to consume plastic and other marine debris within the size range of their target prey [56–60]. Aggregation of plastic particles with other organic material may also promote ingestion of plastic items smaller than those targeted by the animals [61]. However, filter feeding doesn't necessarily result in increased amounts of ingested plastic compared to more selective feeders. For example, the prions (*Pachyptila*) are small, Southern Ocean seabirds that differ primarily in bill size, with the larger-billed species having bill lamellae to filter out small zooplankton [62], yet plastic ingestion tends to be greater in the non-filter-feeding species that surface pick prey individually [23, 25]. Similarly, a higher proportion of toothed whale species has been recorded to eat plastic than baleen whales [1], although there have been few dedicated surveys of small plastic items in baleen whale gut contents [56]. Harbour seals (*Phoca vitulina*) also apparently consume small plastic particles and other debris accidentally while feeding on fish, probably mainly on the seabed [63].

The likelihood of accidental ingestion can be increased when plastic is directly associated with prey species. For example, *Phoebastria* albatrosses in the North Pacific Ocean often eat flying fish egg masses, which stick to floating debris [64], and all plastic eaten by post-hatchling and juvenile turtles in the North Atlantic Ocean had *Halobates micans* eggs or goose barnacles *Lepas* spp. [65]. However, in order to make a strong case for this association being the primary factor driving ingestion (as opposed to misdirected foraging, Sect. 2.3), it would be important to show that the incidence of eggs or epibionts on ingested plastic is greater than that on plastic in the environment.

Finally, some plastic items might be ingested accidentally during play. Marine mammals frequently investigate floating items, contributing to their risk of being entangled [66], and this curiosity has been suggested to be a contributing factor to plastic ingestion [1, 67].

2.3 Direct Ingestion

For many vertebrate taxa, it appears that most plastic is ingested deliberately as a result of misdirected feeding behaviours. Schuyler et al. [68] subdivide this into two hypotheses: confusion with prey items and indiscriminate feeding behaviour, but the latter is a behavioural trait that increases the likelihood of the former. Deliberate ingestion has been observed directly (photographs of birds and turtles feeding on debris at sea, e.g. [1]), demonstrated experimentally (turtles; [24]) and inferred from bite marks on plastic debris (birds and fish; e.g. [69, 70]). Often, though, deliberate ingestion has been inferred from the apparently nonrandom composition of ingested plastic, in terms of colour, shape and type of plastic (e.g. [23, 25, 46, 52, 68, 71, 72]). This requires comparable data on the frequency at which plastic particles of different sizes, types and colours occur in the environment where the animals forage to provide the appropriate null models (e.g. [58, 73]).

To assess colour selectivity, the environmental data need to be specific to each type of plastic ingested, because colour frequencies differ between, e.g. industrial pellets, fibres and plastic fragments [23, 25]. In practice, such data are seldom available. A less satisfactory option is to use debris stranded on beaches in the region (e.g. [68, 72]); this might not represent what is available at sea for two reasons: first, the material on beaches may have accumulated over a long period, with potential differences in longevity and turnover rates linked to colour and type of item (see [74]), and second, it presumably includes some fragments that break down in situ, affecting the composition of litter items (e.g. [75]). The colour of ingested plastic items might also be modified by staining while in the digestive tract [1, 23, 25], which might partially explain the predominance of dark-coloured items ingested by many seabirds (e.g. [52, 71]). A final complication pertains particularly to inferring selection of the types of plastic ingested. Here, simply showing a difference in the frequency between ingested and environmental plastics is insufficient, because differential retention times also have to be considered (see Sect. 4).

For example, seabirds appear to avoid ingesting expanded polystyrene, but this might result at least in part from faster throughput rates of this material in seabird digestive tracts [23, 25].

Despite these caveats, there is evidence for selection based on colour and type of plastic by at least some seabirds and turtles. Seabirds tend to preferentially ingest coloured plastic items [23, 25, 52, 76]. This conclusion is supported by experimental trials showing that many seabirds are more likely to investigate brightly coloured items than grey or black items, with red and orange being especially favoured [77]. Turtles apparently prefer flexible plastic items (e.g. [46, 68, 72, 78]), presumably because these resemble jellyfish and other gelatinous zooplankton [79]. Experimental trials with green and loggerhead turtles found some colour preference, with translucent items least often ingested [24]. Comparisons with beach debris suggested that juvenile green turtles prefer translucent items and avoid blue items (which might be hard to detect visually; [68, 72]), with smaller individuals being less selective than larger animals [72]. However, post-hatchling loggerhead turtles consistently prefer white and blue items and avoid translucent items [8]. Among fish, several studies have reported the predominance of pale-coloured plastics [9, 80], but these colours tend to dominate plastics in the environment [1]. Carson [70] reported fish to bite blue and yellow plastic items more than other colours, whereas fish sampled in the English Channel mainly consumed black items [81]. We are only just starting to gather information on the incidence of plastic ingestion among fish; more data are needed to understand why they ingest plastic. It is worth noting that selectivity also could result from secondary ingestion, if the prey species containing plastics favour particular types of debris.

Further evidence that most debris ingested by seabirds results from misdirected foraging decisions or is consumed accidentally while scavenging at the sea surface comes from the fact that almost all plastic ingested by birds floats [23, 25, 52, 71]. All plastic eaten by turtle post-hatchlings also floats [8, 79, 82], which is consistent with their pelagic lifestyles (e.g. [79]). As hard-shelled turtles mature, they switch to a more benthic diet, at which stage they start to consume plastic and other marine debris items that sink in seawater [82]. This typically results in a decrease in the incidence of plastic ingestion [72, 83]. However, in southern Brazil, the largely benthic-feeding Franciscana dolphin (*Pontoporia blainvillei*) has a higher incidence of ingested plastic than the pelagic-feeding Guiana dolphin (*Sotalia guianensis*), and 57% of adult green turtles (*Chelonia mydas*) contain plastic apparently ingested while feeding on benthic vegetation [84]. Perhaps surprisingly, mesopelagic fish generally also eat plastic that floats [80]. However, ballasting of floating plastic items by epibionts might cause these items to sink out of surface waters [85, 86] and also make them more likely to be eaten.

The predominance of floating plastic among items ingested has implications for the likelihood of plastic ingestion. Floating debris tends to aggregate in drift lines that form due to downwelling at surface convergence fronts. These same physical processes also concentrate planktonic prey for marine predators (e.g. [18]), and drifting predators such as post-hatchling turtles [79, 87], increasing the risk of plastic ingestion and entanglement in marine debris.

3 Recording Plastic Ingestion

Estimating the extent and severity of plastic ingestion requires collecting plastic that has been ingested by organisms and then summarising the information across populations, species or communities. Both of these steps present methodological challenges.

3.1 Collecting Plastic Ingested by Animals

Most studies of plastic ingestion to date have focused on the consumption of meso- and macro-debris (particles mostly >1 mm long). In principle such items are fairly easy to detect. They typically remain confined to the digestive tract, and so in the case of dead animals, one can simply dissect out the digestive tract to examine the contents of its various sections (oesophagus/crop, stomach(s), intestines). Plastic tends to occur in the stomachs of seabirds and marine mammals, and is only occasionally found in the intestines, whereas the opposite is true for turtles. Most studies wash the gut contents through a fine sieve (≤ 1 mm mesh) to separate out hard particles. Then, these can be further separated by floatation, because most ingested plastics either float or are close to neutrally buoyant, compared to more dense prey remains (e.g. otoliths, fish bones, squid beaks) and other debris (sand, stones). If necessary, a gradient extraction technique can be applied, especially if most of the ingested debris is denser material ingested from the seabed [63].

The main issue with sampling larger plastic items is to get sufficient samples to obtain a robust estimate of the incidence and amount of plastic ingested. Historically, many studies used destructive sampling, often in conjunction with diet sampling (e.g. [20, 52, 71]). This is still feasible for many fish species, especially those caught commercially, but it is hard to justify ethically for seabirds, turtles and marine mammals, many of which are listed as threatened species. Most studies of these taxa now rely on animals found dead, such as stranded individuals (e.g. [88, 89]), or those killed accidentally (e.g. night-strike victims or individuals caught on fishing gear [90, 91]), or by other predators (e.g. post-hatchling turtles in fish stomachs [48] or seabirds eaten by subantarctic skuas [53]).

The other option is to sample for ingested plastic non-destructively. Some species regurgitate indigestible prey items (see Sect. 4), and these pellets can be examined for plastic (e.g. albatrosses, giant petrels, gulls, terns and skuas; [23, 25, 92]). Faecal samples also can be examined for any plastic items that are excreted (e.g. seals; [49, 63]). Such samples typically provide an index of plastic ingestion that are not directly comparable to assessments based on the examination of gut contents, but they can provide a useful tool to monitor large-scale temporal or spatial changes in ingestion patterns (e.g. [55]).

Another nondestructive approach is to induce animals to regurgitate or excrete ingested debris. The development of stomach-flushing techniques for seabirds (e.g. [93]) revolutionised nondestructive sampling of seabird diets, and can be used to sample plastic items in bird stomachs, but it typically fails to recover all ingested plastic, especially from petrels and storm petrels, which store most plastic in the muscular ventriculus (hind stomach) that is separated from the proventriculus (fore-stomach) by a narrow, angled constriction [94]. The proportion of plastic regurgitated probably varies among the taxa but with experience double flushing can recover 80–90% of plastic from some petrels [19]. This proportion can be improved still further by administering emetics such as syrup of ipecac, but this caused some mortality among Leach's storm petrels (*Oceanodroma leucorrhoa*) [95].

Marine turtles excrete ingested plastic anything from 6 days to 6 months after ingestion, depending on the size and nature of the plastic item [24, 47, 96]. This allows plastic loads to be determined for animals taken into captivity (e.g. [82]). Hoarau et al. [47] found that excreted plastic loads are not significantly different from loads measured from dead animals, but the power to detect a significant effect is compromised by the high individual variance in plastic loads (see below), and Schuyler et al. [97] argued that excreted plastic loads are not directly comparable with necropsy data. Dosing turtles with mineral oils can promote plastic excretion [10], but large items may be hard to pass through the cloaca [8]. There was no difference in plastic loads among post-hatchling loggerhead turtles that died after 0–52 days in a clean environment, suggesting that excretion had little influence on plastic loads in these young animals [8].

A problem specific to sampling plastic ingestion by fish and zooplankton is the issue of ingestion occurring in the net after capture [50]. Appropriate controls are needed to estimate the magnitude of this bias [50]. Other potential biases might result from specific sampling methods, such as stranded animals or animals that die from disease, which might affect their foraging behaviour [63]. There is often a tendency for stranded animals to have a higher incidence of ingested plastic or larger plastic loads than animals sampled at sea (e.g. [23, 25, 48]), but this is seldom statistically significant [89, 98] at least in part because of the high individual variance in plastic loads. Stranded animals tend to be in poorer condition than animals sampled at sea (e.g. [99]) and thus, more likely to ingest unusual prey items.

Detecting small ingested microplastics (<1 mm), and especially items <0.2 mm, poses similar logistical challenges as sampling microplastics in sediment samples (e.g. [100]). Separating plastics from other organic materials becomes increasingly difficult as particle size decreases. Various digestion techniques have been tested with some degree of success [101–103]. However, great care is needed to avoided contamination by environmental microplastics during processing, especially microfibres [60].

3.2 Summarising Plastic Ingestion

Several different measures are used to report the occurrence of plastic ingestion by marine organisms. At a community level, studies often report the proportion of species in different taxa or guilds that have been recorded to ingest plastic (e.g. [1, 66]). Here, all that is needed is the presence/absence data for each species, although this measure is sensitive to the number of individuals examined, especially if only a small proportion of individuals contain ingested plastic. It is also important that records of individuals lacking ingested plastic are based on careful examination of gut contents to avoid false negatives [1].

A more sensitive measure of plastic ingestion is the proportion of individuals within each population or species that contains plastic (frequency of occurrence), which is often termed the incidence of ingested plastic. This measure ranges from 0 to 1 and is readily compared among populations or species using goodness-of-fit tests. However, some studies uncritically report changes in incidence rates without testing their significance. For example, Lavers et al. [19] reported that "ingestion of plastic debris has increased from 79% in 2005–2007 [104] to 90% in 2011", even though the sample sizes (56 and 38, respectively) are too small to infer a significant increase ($\chi^2 = 1.21$, $df = 1$, $P = 0.27$).

Incidence measures fail to report the magnitude of plastic loads within individuals. These are usually reported as the average number, mass or volume of plastic per individual. Each measure has its merits, and ideally all three should be reported, although for most species mass and volume are similar (given little variance in plastic densities, volume (cm^3) only exceeds mass (g) to any great extent when items with air spaces, such as cigarette lighters or sealed bottles, are ingested). Some studies report loads per individual containing plastic, not the population average (calculated across all individuals). The former measure gives an idea of the severity of the problem within affected individuals, but for most purposes the population average is preferred [1].

A significant issue with load data is their very high variance and strong right skew (Fig. 4) in all taxa studied, including fish [105] and barnacles [58]. Studies typically report average loads ± standard deviation (or standard error of the mean), even though the mode and median are better indicators of central tendency in strongly skewed data. The very high variance among individuals also reduces the power to detect temporal or spatial changes in plastic loads, and studies attempting to do so have had to resort to extreme smoothing of the data (e.g. running averages over 5 years; [89, 106]). In general, plastic loads correlate with the incidence of plastic ingestion (i.e. individual loads are greater in species where a high proportion of individuals contain at least some plastic; [23, 25]), which suggests that plastic incidence can be a useful measure at least for species where the incidence is well below 100%. For species with a very high incidence of plastic ingestion, the best approach is to assess the proportion of individuals that exceed a specific plastic load (e.g. the 0.1 g threshold set for northern fulmars in northwest Europe; [89]).

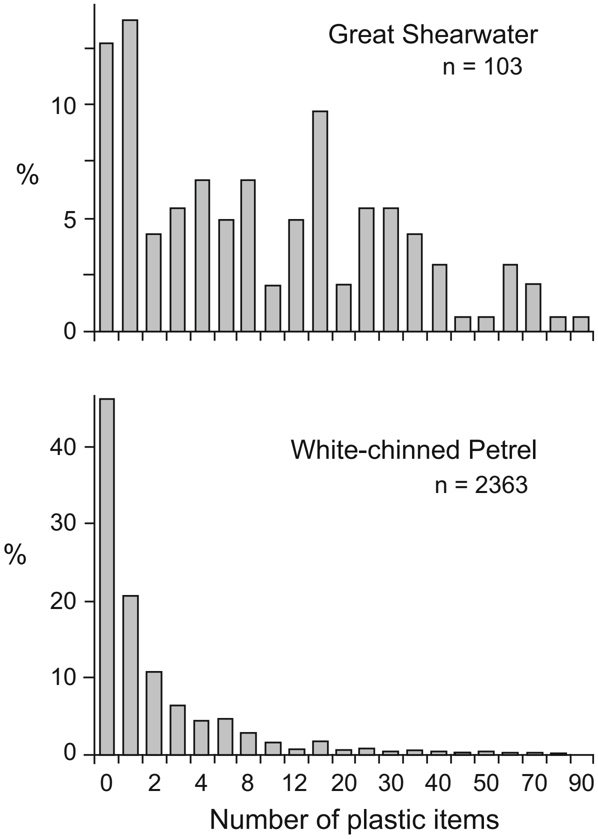

Fig. 4 The frequency of occurrence of plastic loads in seabirds with high (great shearwater (*Ardenna gravis*), 87%) and moderate plastic incidence (white-chinned petrel (*Procellaria aequinoctialis*), 56%), showing the strong right skew irrespective of the incidence of ingestion. Note the uneven *x*-axis scale

Finally, it is important to note that under-reporting of absence data is likely to bias all these measures to some extent [107].

4 Factors Affecting Plastic Loads

The amount of plastic in the digestive tract of an organism is a balance between its ingestion rate and removal via excretion and/or regurgitation. Thus, two quite disparate sets of factors determine plastic loads in animals (and the related incidence of plastic ingestion): (a) exposure to plastic and the likelihood of ingestion and (b) the retention time of plastic items once ingested. Both have to be considered when comparing data across species or modelling patterns of ingestion (cf. [83, 108]). The likelihood of ingestion depends on the type of animal, its age and condition (including reproductive status); these factors are considered in Sect. 5. In this section I assess how temporal and spatial changes in the exposure to plastic combine with differences in gut retention time to determine plastic loads.

4.1 Temporal Changes in Exposure

Plastics are man-made materials that have only been produced in substantial quantities since the 1950s. There has been rapid growth in production since then, with currently almost 300 million tonnes produced annually [109]. This rapid growth in production, coupled with the long lifespan of plastic items, has created a long-term temporal change in the risk of exposure to plastic ingestion, which is reflected in changes in the incidence and amount of plastic ingested by marine organisms. For example, plastic ingestion by seabirds and turtles increased from the early records in the 1960s through the 1970s and 1980s [6, 110]. Since the 1980s, ingestion rates have tended to stabilise or have even decreased in some cases [6, 89, 95, 111], although there have been changes in the composition of plastic ingested at least among seabirds [55, 106, 112]. The use of linear models to infer current trends in ingestion rates (e.g. [108]) should exclude the initial period of rapid increase up to the 1980s. For example, leatherback turtles (*Dermochelys coriacea*) show a strong increase in plastic ingestion when data from 1885 to 2007 are analysed, but there is no significant trend for 1985–2007 [97]. Loggerhead and Kemp's ridley turtles (*Lepidochelys kempii*) also show no clear trend over the last three decades, but ingestion has increased in green turtles and appears to have decreased in hawksbill turtles (*Eretmochelys imbricata*) over this period [97].

4.2 Spatial Differences in Exposure

A substantial proportion of plastic production is used in single-use applications in countries with inadequate solid waste management systems [113]. The concentration of plastic consumption in densely populated areas, coupled with fairly predictable dispersal patterns for low-density plastics entering the sea [114–116], results in striking regional heterogeneity in the distribution of floating plastic [117, 118]. As a result, the amount of ingested plastic varies among populations of the same species in relation to the abundance of plastic in their foraging ranges. This is perhaps best demonstrated by the marked decrease in plastic ingestion rates among northern fulmars with increasing latitude in both the North Atlantic and North Pacific Oceans [106]. Another nice example comes from Laysan albatrosses (*Phoebastria immutabilis*) feeding in different regions of the North Pacific, which deliver vastly different amounts of plastic to their chicks [119].

Regional differences in marine turtle ingestion rates are less clear-cut. For example, estimates of the incidence of plastic ingestion by juvenile loggerhead turtles in the Mediterranean Sea range from 20 to 76% [46, 82, 120–122]. However, there appear to be regional differences in ingestion rates linked to differential exposure among fish. Off northwest Europe, the incidence of plastic in fish decreased from the English Channel [81] through the southern North Sea (south of 55°N) to the northern North Sea [123]. Within the same species, the incidence of

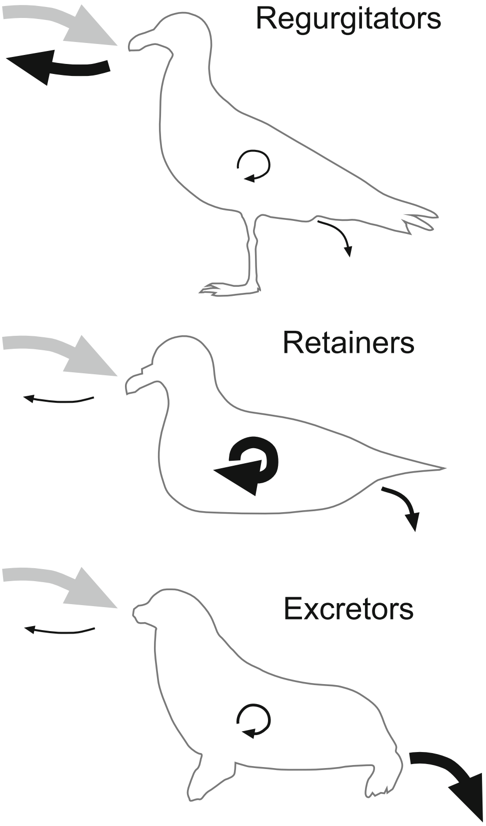

Fig. 5 Three pathways for ingested plastic in animals: gulls, terns and skuas rapidly regurgitate most ingested plastic; petrels, phalaropes and some auks retain ingested plastic in their stomachs until it is eroded to a small enough size to be excreted, whereas fur seals probably excrete most ingested plastic

plastic ingestion was 5 (whiting (*Merlangius merlangus*)) to 30 times greater (horse mackerel (*Trachurus trachurus*)) in the English Channel than in the North Sea [81, 123].

4.3 Retention Time in Organisms

Marine animals have two main ways of dealing with indigestible prey items; they can regurgitate them or excrete them. Depending on the structure of the digestive tract, excretion may take some time, especially if only very small particles can be excreted, as is the case for many seabirds ([52, 124], but see [106]). In these species, plastic items might be retained in the stomach for protracted periods until they are finally small enough to be excreted [42, 125]. We can thus recognise three types of organisms (Fig. 5): species that regurgitate most plastic shortly after ingestion (e.g. gulls, terns and skuas), those that excrete most plastic (e.g. fur seals and at least some auks; R. Yamashita pers. comm.) and those that store plastic in their

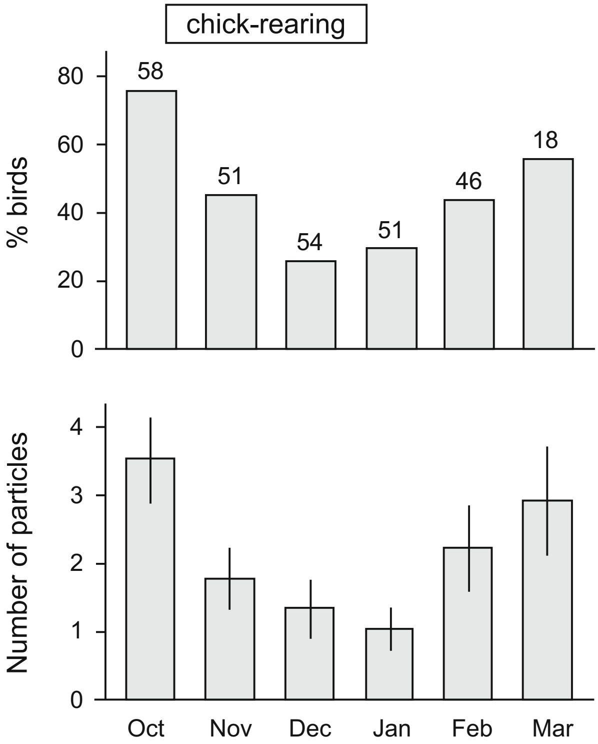

Fig. 6 The effect of intergenerational transfer from adults to chicks on plastic incidence (sample size above each bar) and plastic loads per bird (mean ±1 SE) in white-faced storm petrels (*Pelagodroma marina*) over the breeding season on Inaccessible Island. The bar at the *top* of the figure shows the chick-rearing period (from [125])

digestive tract for protracted periods (e.g. petrels, phalaropes and some auks). Other species fall between these extremes. Marine turtles probably excrete most ingested plastic, but this takes substantially longer than the passage of food items, with the retention time depending on the size and nature of the plastic item [24, 47, 96], so turtles lie between the ‘excretor’ and ‘retainer’ strategies in Fig. 5. Similarly, albatrosses regurgitate indigestible prey remains at least occasionally [23, 25, 92], falling between the ‘retainer’ and ‘regurgitator’ strategies.

The challenge is to determine the relative importance of these different pathways, which can differ within as well as among species. For example, petrels are generally not thought to regurgitate indigestible stomach contents once they pass into the ventriculus, where most plastic occurs in these birds [1, 89]. However, adult petrels can transfer plastic to their chicks, resulting in a decrease in plastic loads over the chick-rearing period (Fig. 6, [126–129]; although some authors think that all plastic fed to chicks is collected by adults during the breeding season [19]). This probably explains the larger plastic loads often reported among juvenile petrels, as they obtain plastic from both parents [128]. However, Hutton et al. [104] reported that some flesh-footed shearwater (*Ardenna carneipes*) chicks regurgitated pellets of indigestible prey remains like albatross chicks, so retention of parental loads might not invariably be the case. An analogous periodic offloading may occur in lobsters, which replace part of the gut lining as well as their exoskeleton during growth moults, resulting in less plastic in recently moulted individuals [43].

Assuming regurgitation does not occur, the time plastic items remain in the stomachs of ‘retainer’ species such as petrels is a function of the rate at which items wear down in the stomach and the size of particles that can pass through the pyloric sphincter into the small intestine [125]. Wear rates almost certainly depend on the type of plastic and the shape/thickness of the item, and retention periods are likely to be related to the original size of the item ingested unless it breaks down into multiple small fragments (e.g. bags and flexible packaging) rather than gradually wearing down (hard plastic fragments). Systematic changes in the types of plastic ingested (e.g. the switch from industrial pellets to fragments of user items over the last few decades) could influence gut retention periods, affecting the way in which ingested plastic loads track the abundance of plastic in the environment [125].

Retention times are thus critical to interpreting plastic loads in marine animals. Studies attempting to predict ingestion rates can ignore retention time if this is relatively constant among the taxa being compared (e.g. marine turtles, [83]), but not when the taxa exhibit gross differences in retention times, as is the case with seabirds [108]. Unfortunately, plastic retention times are poorly known for many taxa. Among marine mammals, *Arctocephalus* fur seals probably rapidly excrete the very small plastic items (<10 mm) they ingest in their myctophid prey, and dolphins excrete plastic objects up to 120 mm long [84]. However, harbour seals contain very small plastic items (average <100 mg), yet those in the intestine are an order of magnitude smaller (6 mg) than those in the stomach (93 mg; [63]), suggesting some retention in the stomach of even very small particles in this species. I could find no references to plastic retention times in whales or sirenians.

Given the great diversity of fish and invertebrates recorded to ingest plastic (Sects. 5.4 and 5.5), it is likely that they exhibit a range of strategies for coping with plastic similar to that observed among seabirds. The size and type of plastic item also play a role in retention times. Feeding trials show that cod (*Gadus morhua*) gut retention times are longer for plastic items than food items (1–7 days), retaining small (<1 mm) particles for up to 10 days and 2 mm particles up to 20 days [130]. Lobsters retain plastic fibres in the gut for weeks [43], whereas mysids, copepods, isopods and sea urchin larvae rapidly excrete plastic microspheres [131–134]. In lobsters, the fibres combine with filamentous food items to form dense fibre ‘balls’ that are too large to excrete and which remain tightly bound together even after prolonged starvation (or experimental digestion of algae with cellulases; [43]).

A worrying aspect with very small micro- and nanoplastics is their potential to migrate out of the digestive tract into other tissues, where they can be retained for weeks [28, 29]. In experimental trials, mussels (*Mytilus edulis*) and oysters (*Crassostrea virginica*) retained microparticles (10 μm) for longer than nanoparticles (0.1 μm), probably because the nanoparticles were transferred to the animals’ digestive gland, although most items of both sizes were excreted within a few days [61]. However, mussels still contained some 3–10 μm particles in their haemolymph at least 7 weeks after exposure [28], and shore crabs (*Carcinus* *maenas*) retained 10 μm particles for up to 2 weeks after ingestion and 3 weeks after uptake from the gills [29].

5 The Incidence of Plastic Ingestion by Marine Organisms

Ever since the first seabirds were found to ingest plastic in the early 1960s, there has been a steady increase in the range of animals recorded to ingest plastic items [109]. Kühn et al. [1] list 233 organisms known to ingest plastic, but this is already out of date (e.g. [56, 135]). In the last 20 years, the number of vertebrates recorded to contain plastic has increased by 63% ([1], compared to [66]), with the greatest increase among fish (33–92 species) and marine mammals (26–62 species); seabirds (111–164 species) and marine turtles (6–7 species) have shown more modest increases – although in the case of turtles, all species are now known to ingest plastic. Increased awareness of the problem and the resultant greater numbers of species checked for ingested plastic largely account for this recent growth in numbers of affected species.

In this section, I summarise the proportions of species known to ingest plastic as a function of the number of species actually examined, as well as in relation to the total diversity in each family. These proportions suggest that ingestion rates probably are appreciably higher than currently reported. However, in order to gain a better estimate of the magnitude of the plastic ingestion issue, it is important that researchers report negative as well as positive records of ingestion. Early studies tended to report the incidence of ingestion in all species examined (e.g. [23, 25, 52, 71]), but relatively few recent studies do so (e.g. [136, 137]), potentially leading to an inflated perception of the scope of the problem [107].

In order to highlight the taxa that tend to have the largest plastic loads, and thus, are most likely to suffer adverse effects from plastic ingestion, I also report the proportions of individuals within species in each family found to ingest plastic. However, given all the caveats discussed in the preceding sections, the values reported should be regarded as only a crude indication of the taxa most at risk of accumulating large plastic loads.

5.1 Seabirds

At least 165 species of the 367 species of marine birds (45%) have been recorded to ingest plastics (Table 1). However, limiting the analysis to species actually checked for plastic, the proportion is 78% (and this figure does not control for sample size; species where only a few individuals have been examined might well ingest plastic occasionally). The proportion of examined species containing plastic was lowest in pursuit divers (sea ducks, divers, penguins and cormorants) and terns (Table 1). All other families had records of plastic ingestion for more than 50% of examined

Table 1 Numbers (N) of seabird species reported to ingest plastic items, the proportions of each family (or subfamily) affected (expressed as a function of all species and of those species specifically checked for ingestion) and the mean incidence of ingestion per species (restricted to species with at least ten individuals examined, with the range of values among species in parentheses)

Taxon	N ingesting plastic	N species (*n* examined)	% ingesting (checked)	% incidence (range)
Sea ducks Anatidae	1	14 (4)	7 (25)	<1 (0–1)
Divers (loons) Gaviidae	1[a]	5 (3)	20 (33)	<1 (0–1)
Penguins Spheniscidae	5	18 (12)	28 (42)	3 (0–27)
Albatrosses Diomedeidae	17	21 (18)	81 (94)	16 (1–88)
Southern storm petrels Oceanitinae	5	9 (6)	56 (83)	34 (0–82)
Northern storm petrels Hydrobatidae	6	15 (7)	40 (86)	26 (0–92)
Petrels Procellariidae	56	90 (59)	62 (95)	36 (0–96)
Diving petrels Pelecanoididae	2	4 (3)	50 (67)	1 (0–2)
Frigatebirds Fregatidae	1	5 (1)	20 (100)	<1 (0–1)
Cormorants Phalacrocoracidae	6	40 (13)	15 (46)	3 (0–15)
Gannets and boobies Sulidae	5	10 (8)	50 (63)	1 (0–3)
Tropicbirds Phaethontidae	2	3 (3)	67 (67)	4 (0–9)
Phalaropes Scolopacidae	2	3 (2)	67 (100)	46 (23–68)
Gulls Larinae (Laridae)	25	54 (30)	46 (83)	15 (0–33)
Terns Sterninae (Laridae)	7	45 (19)	16 (37)	2 (0–5)
Skuas Stercorariidae	6	7 (6)	86 (100)	14 (5–23)
Auks Alcidae	14	24 (18)	58 (78)	10 (0–59)

[a] Kühn et al. [1] list three divers as having ingested plastic, but two of these records refer to ingestion of fishing gear [138], which are more likely by-catch than plastic ingestion

species. However, the average incidence of ingested plastic within each family provides a more sensitive indicator of the taxa that are most susceptible to accumulate large plastic loads. The petrels, storm petrels and phalaropes had the highest average incidence of ingested plastic, followed by the albatrosses, gulls, skuas and auks (Table 1). More than 50% of individuals contained plastic in 20 seabird species that have been well sampled ($n > 30$ birds): 15 petrels (seven shearwaters (*Ardenna*/*Calonectris*/*Puffinus*), three prions, two fulmarine petrels, one *Procellaria*, one *Pterodroma* and the blue petrel (*Halobaena caerulea*)), 2 storm petrels (fork-tailed (*Oceanodroma furcata*) and white-faced (*Pelagodroma marina*)), 2 albatrosses (Laysan and black-footed (*Phoebastria nigripes*)), 1 phalarope (red (*Phalaropus fulicarius*)) and 1 auk (parakeet auklet). There is no clear regional concentration of these species, with eight from the Southern Hemisphere, six from the Northern Hemisphere, five trans-equatorial migrants and one widespread species.

Plastic is most often found in surface-feeding seabirds with generalist diets; deep-diving species with more specialised diets tend to ingest plastic less frequently [23, 25, 52, 71]. Plastic is more frequently found in small seabirds than large species, perhaps as a result of more generalised diets among small species [23, 25]. Within species, juveniles typically contain more ingested plastic than adults, due to intergenerational transfer in species that regurgitate food to their chicks as well as juveniles probably being less discriminating foragers [52, 73, 128]. Plastic might also be ingested more when natural food is scarce [1] or when animals are in poor condition [23, 25].

In addition to seabirds, some freshwater birds have been recorded to eat plastic, such as ducks (*Anas platyrhynchos* and *A. rubripes*) and swans (*Cygnus olor*); these waterfowl contain plastic appreciably more often than marine ducks [139, 140]. Among the Charadriiformes, the bar-tailed godwit (*Limosa lapponica*), a scolopacid shorebird that feeds in muddy and sandy intertidal habitats when not breeding, also has been recorded to ingest plastic particles [141]. And on subantarctic Marion Island, a small number of lesser sheathbills (*Chionis minor*; Chionidae) also ingest plastic items [142]. Sheathbills live in close association with seabirds, raising their chicks on meals stolen from seabirds, and presumably obtain plastic either directly in stolen meals or while scavenging for scraps in seabird colonies. Stomachs of the flightless Inaccessible Island rail (*Atlantisia rogersi*; Rallidae) also have been found to contain small plastic fragments (unpubl. data).

5.2 Turtles and Other Marine Reptiles

All seven species of marine turtles have been recorded to ingest plastic items [1, 143]. Sea snakes are much less well studied than turtles, and so far none of the roughly 63 species has been recorded to contain plastic [1]. Most turtle studies have been on green and loggerhead turtles, although reasonably large samples ($n > 30$) of all species have been examined for ingested plastic except for the flatback sea turtle (*Natator depressus*) [83]. All species of marine turtles are particularly vulnerable during their early life history stages, when they are pelagic and feed largely on jellyfish and other gelatinous zooplankton [72, 82]. However, there are relatively few data on ingestion rates among the smallest, post-hatchling age class; most studies have focused on juvenile and adult turtles. Bjorndal et al. [144] reported a higher incidence of plastic ingestion among juvenile female (83%) than male (42%) green turtles stranded in Florida, but this has not been found by subsequent studies. A meta-analysis of ingestion risk confirmed that pelagic-stage turtles are most likely to ingest plastic and identified key regions globally where the threat of ingestion is greatest [83]. It found that olive ridley turtles (*Lepidochelys olivacea*) are the most likely to contain plastic and that Kemp's ridley turtles are significantly less likely to ingest plastic than the four other well-studied species (green, loggerhead, hawksbill and leatherback turtles).

Plastic is found in three times more individuals than natural debris (wood, feathers and pumice) in stranded green and loggerhead turtles, indicating the pervasive nature of plastic ingestion [48]. Plastic ingestion is well known to cause mortality in turtles, primarily through blocking the digestive tract (e.g. [78, 145, 146]), and false satiation also may have sublethal impacts [13]. These impacts are particularly worrying given the wide range of threats faced by marine turtles globally and their poor conservation status (all species listed as threatened; www.iucnredlist.org).

5.3 *Marine Mammals*

At least 64 species of marine mammals have been recorded to ingest plastics: 8 of 13 baleen whales, 41 of 65 toothed whales and dolphins, 4 of 19 phocid seals, 8 of 13 otarid seals and 3 of 4 sirenians ([1, 56], PGR unpubl. data). A relatively high proportion of stranded cetaceans contain macroplastic items, but these animals often are in poor health, which might contribute to the wide range of inappropriate items ingested [147]. Cetaceans sampled at sea seldom contain large, conspicuous debris items, with the exception of sperm whales (*Physeter macrocephalus*) and beaked whales, which are thought to ingest plastic and other debris when feeding on benthic prey [147, 148]. Excluding stranded animals, the highest incidence of ingestion recorded to date for a cetacean (23%) occurred in the Franciscana dolphin off the east coast of South America [84, 149]. If dolphins, like gulls, usually excrete most ingested plastic [84], this suggests that these animals regularly ingest large amounts of plastic. Denuncio et al. [149] reported a tendency for individuals caught in estuaries to contain plastic more often than those caught in marine habitats, but the pattern was not strongly supported ($\chi^2 = 2.47$, $df = 1$, $P = 0.12$).

The incidence of microplastics (<5 mm) in large whales is poorly known, as it is only recently that these small particles have been searched for in whales. To date, microplastics have been found in both baleen [56] and toothed whales [148]. In the case of the toothed whale (a True's beaked whale (*Mesoplodon mirus*)), it was unclear whether this was derived from their prey or was ingested accidentally [148].

Few seals have been recorded to regularly ingest plastic debris, but careful examination of gut contents probably will find more plastic than has been reported to date ([63], but see [107]). Like seabirds, young seals might be at greater risk than adults, presumably because they are less discriminating foragers. Most harbour seals found to consume plastic were young animals, <3 years old [63].

Relatively little has been published in the primary literature on the ingestion of plastic by sirenians [1, 150, 151], even though it is known to cause fatal impacts [152–154]. As in the case of marine turtles, this is particularly worrying given the poor conservation status of all sirenians.

5.4 Fish

Much less is known about the frequency of plastic ingestion by fish than air-breathing marine vertebrates. This is partly due to the much greater species richness of fish than air-breathing marine vertebrates (cartilaginous fish ~1,050 species, bony fish ~30,000 species, of which roughly half are marine). At least 18 species from five orders of sharks and rays (Elasmobranchii) and 75 species from 16 orders of ray-finned fish (Actinopterygii) have been recorded to ingest plastic [1, 135], but observations that much beached litter bears fish bite marks [70] suggest that plastic ingestion may be widespread among fish species.

The region with the highest general incidence of plastic ingestion by fish reported to date is in the English Channel, where all ten species examined contained plastic particles, at an average incidence of 36% (range 24–52%; [81]). There was no difference in the incidence or amounts of plastic between five midwater and five benthic species. By comparison, relatively few fish in the Mediterranean Sea contained plastics; Anastasopoulou et al. [136] found plastic in four of nine species of sharks and rays, but only one of 17 ray-finned fish species. Plastic ingestion can be frequent in estuarine fish found in urban areas [135, 155] and is not confined to marine fish; three fish species sampled in European rivers and lakes have been found to contain microplastics [140, 156].

One group that has been relatively well studied is the lantern fish Myctophidae, a family of small, extremely abundant midwater fish. Plastic has been found in 12 of 24 myctophid species sampled in the Pacific Ocean, with six species having plastic in at least one third of individuals [9, 50, 51]. This is particularly worrying because myctophids are key components of many marine food webs, forming the prey base of many predatory fish, squid and vertebrate predators. Additional data are required from other regions to assess how widespread a problem plastic ingestion is in this family. Consumption of contaminated myctophids is thought to account for the relatively high incidence of plastic in *Arctocephalus* fur seals at subantarctic Macquarie Island [49], but there is no evidence of plastic in the diets of these fur seals at other south temperate and subantarctic islands [107].

5.5 Invertebrates

Very little is known about in situ ingestion of plastic by marine invertebrates, with records from only a few species [1, 60]. However, worryingly high ingestion rates have been recorded in areas where there are high concentrations of microplastic particles. In coastal waters off western Scotland, 83% of lobsters sampled contained fibres and other plastic materials, apparently ingested incidentally along with their food [43]. Small lobsters were more likely to contain plastic than large animals. Similarly, all mussels (*Mytilus edulis*) and lugworms (*Arenicola marina*) sampled along the North Sea coast contained microplastics [60], and sandy anemones

(*Aulactinia reynaudi*) occasionally ingest plastic bags and ropes in urban areas in South Africa (unpubl. data).

In oceanic waters, microplastic particles were found in 34% of goose barnacles (*Lepas anatifera* and *L. pacifica*) sampled in the North Pacific gyre from 2009 to 2012 [58]. Most plastic was found in barnacles collected in the core of the subtropical gyre, with little or no plastic in barnacles from more peripheral locations. There was no evidence of gross impact resulting from plastic ingestion (e.g. intestinal blockage). The incidence of ingestion was greatest in large barnacles, and most items consumed were fairly large (median 1.4 mm, range 0.6–6 mm long), but smaller barnacles may have contained small plastic fragments (<0.3 mm) that were not detected by the visual inspection of gut contents undertaken by Goldstein and Goodwin [58]. Ingested plastic also has been recorded in two squid species [1].

Despite the limited knowledge on in situ ingestion by invertebrates, experimental studies suggest that many invertebrates have the potential to ingest microplastic particles, including a diversity of filter-feeding zooplankton (copepods [11, 30, 157], sea urchin larvae [132], euphausids, mysids, cladocerans, polychaete larvae, rotifers and ciliates [133]), benthic detritivores (sea cucumbers [59], polychaete worms [33], scallops [158], amphipods [159], isopods [131, 134]) and secondary ingestion by scavenger-predators such as crabs [45]. I expect the diversity of invertebrates found to contain plastic in the field to increase rapidly in the next few years, especially in heavily contaminated areas.

6 Conclusions

The amount of plastic found in organisms varies among taxa depending on their foraging behaviour, diet, exposure to plastic and method of dealing with indigestible prey remains (Fig. 5). There is also a great variation in plastic loads among individuals within taxa, depending on their foraging location, age, body condition and, in some species, reproductive status (Fig. 6). Species that exhibit a high incidence of plastic ingestion typically also have the largest maximum body loads, although loads are strongly right skewed, so most individuals contain little plastic relative to the most heavily affected individuals (Fig. 4).

6.1 Implications for Monitoring

The large variance in plastic loads complicates the use of ingested plastic as a tool to monitor long-term changes in plastic abundance. Comparing plastic loads in a single-age class from the same location offers the best approach to reduce this variance [23, 111]. Among seabirds that offload plastic to their chicks, adults pose problems because plastic loads depend in part on past breeding history ([23, 128],

Fig. 6). Comparing ingestion loads among fledglings leaving a specific colony [127] obviates this problem, but clarity is needed as to the likelihood of petrel chicks regurgitating indigestible prey remains before fledging [104]. Similarly, among marine turtles, age/size affects diet and foraging sites and thus, the propensity to ingest plastic items [82, 83], so any attempt to detect regional or temporal changes in loads need to control for this effect. Further information also is required on the relationship between plastic loads in organisms and density at sea [111]; is this linear, and is there a threshold above which the plastic load ceases to increase? Another potential issue with using animals to monitor marine plastics is if long-term changes in the types of plastics ingested (e.g. a reduction in the relative abundance of industrial pellets) affect the residence time of items within animals [125]; we might detect a change in ingested plastic loads independent of changes in the amount of plastic at sea.

In Europe, one of the Ecological Quality Objectives (EcoQOs) for the North Sea is to have <10% of northern fulmars containing >0.1 g of ingested plastic in their stomachs [89]. Although the 'acceptable' proportion of animals above the threshold was an arbitrary policy decision [89], it is similar to 'background' levels recorded in fulmars in the Canadian High Arctic [106, 160, 161], thus providing a plausible target for cleaning up more polluted regions. Ideally, the threshold amount for such targets should be based on some perception of risk, and the acceptable proportion of individuals affected should be set so as to have negligible population-level impacts. However, there is little evidence as to what constitutes a 'safe' plastic load; it depends on the threat being posed. A relatively large volume of plastic is needed to cause significant reductions in food intake due to false satiation, whereas only one particularly awkward item might be sufficient to perforate or block the digestive tract. Among turtles, as little as 1–2 g of ingested plastic is sufficient to block the gut of juvenile green turtles 30–40 cm long, weighing 2–6 kg (~0.05% body mass; [99]).

The value of 0.1 g for northern fulmars evolved from the suggestion that individuals should not contain more than ten plastic items, which is approximately 0.1 g (JA van Franeker in litt.). Despite the arbitrary nature of this threshold, other studies of seabirds have calculated 'equivalent' thresholds to the fulmar EcoQO by scaling in relation to body mass (= 0.0154% body mass, assuming northern fulmars weigh 650 g; [19, 95]). This is modest compared to plastic loads observed in some extreme cases (e.g. 14% of body mass in one flesh-footed shearwater (*Puffinus carneipes*) fledgling, [19]). Laysan albatross chicks found dead (possibly as a result of plastic ingestion) contained average plastic loads of 1.0% body mass, whereas those killed by vehicles contained plastic summing to only 0.5% body mass [22], but this is not to say that 0.5% of body mass is an acceptable plastic load in this species, especially as seabird chicks may be better able to tolerate large loads than adults. It is also important to note that 'safe' loads cannot be applied across species, as plastic loads depend crucially on whether birds regurgitate indigestible prey remains (Sect. 4).

6.2 Implications for the Transfer of Persistent Pollutants

The role of ingested plastics in the transfer of persistent organic pollutants (POPs) is the main theme of this book; the partitioning of POPs between the environment, plastics and marine organisms is covered in another chapter. However, two main points arise from this review that are relevant to this question. One, the strong right skew in plastic loads suggests that large samples are needed to estimate the full range of effects within each species, or there needs to be selective sampling of the most severely impacted individuals within populations. And two, there is a need to know how long an exposure is likely to result in POP transfer, in relation to the wide range of gut retention times for plastics. There are few empirical measures of POP transfer rates from ingested plastics. Koelmans et al. [36, 37] assumed that transfer of POPs is fairly rapid, although it varies with the type of POP. Tanaka et al. [41] showed that leaching of polybrominated diphenyl ether (PBDE) flame retardants is greatly enhanced in oil-rich stomach contents such as those found in petrels, but still took several days to reach equilibrium in the stomach. However, these studies used spherical microplastics [36, 37] of small, hard fragments [41]; transfer rates might be slower from larger items and from flexible items that often become tightly packed. Species that regurgitate most indigestible prey remains such as gulls and skuas probably void most plastics within a day of ingestion, which might be fast enough to result in limited POP transfer, especially as these plastics don't reach the intestine, where most uptake is likely to occur. Very small plastic items also might be excreted within a day or so and, thus, have less chance to contribute POPs than particles that are retained for weeks or months. There is probably also a difference between the release of environmental pollutants adsorbed to plastics and those incorporated during plastic manufacture (e.g. plasticisers, flame retardants and other additives); adsorbed pollutants might reach equilibrium in the gut relatively quickly, whereas additives probably continue to be released as plastic particles erode in the gut. This suggests that long retention times enhance chemical uptake, at least for compounds included in plastics during manufacture. Species with broad, generalist diets that retain indigestible prey items in their digestive tracts for extended periods, such as petrels, phalaropes and perhaps turtles, probably are most likely to obtain large body burdens of hazardous chemicals from ingesting plastic items.

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Transfer of Hazardous Chemicals from Ingested Plastics to Higher-Trophic-Level Organisms

Kosuke Tanaka, Rei Yamashita, and Hideshige Takada

Abstract Field observations of seabirds and whales indicate transfer of chemicals from ingested plastics to the tissue of organisms which have ingested the plastics. To determine the significance of plastic-mediated exposure of chemicals, it should be compared with natural prey-mediated exposure. In case where background pollution is high, plastic-mediated exposure is relatively smaller. However, in remote ecosystem with trace background pollution where marine plastics bring larger amounts of pollutants, plastic-medicated exposure could be significant. In case of additives that are bio-diluted such as BDE209, ingested plastics could be major exposure sources. Leaching experiment using stomach oil indicates that lipophilic nature of digestive fluid is key to facilitate the leaching of hydrophobic chemicals from the plastics and, consequently, the transfer and accumulation of the chemicals in the tissue to biota which have ingested the plastics. Understanding the nature of digestive fluid and biological dynamics of the digestive system is important.

Keywords Biomagnification, Digestive fluid, PBDEs, PCBs, Seabirds, Stomach oil

Contents

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1 Introduction

Ingestion of marine plastic debris by marine organisms has been of great concern. As discussed by Ryan [1], seabirds frequently ingest plastics. Frequency of plastic uptake by some species of oceanic birds has been increasing [2–7]. For example, investigations on short-tailed shearwater showed that the proportion of individuals, ~50%, who had plastics in their digestive tracts in the early 1970s increased to almost 100% by the 1980s until now (Fig. 1). In addition to physical damage such as blockage of food and harm, toxicological effects due to associated chemicals have been of great concern because marine plastic debris carry a variety of hazardous chemicals as discussed by Yamashita et al. [8]. Higher-trophic-level organisms ingest and retain relatively larger plastics such as cm size and mm size depending on their foraging characteristics. Cm-size and mm-size plastics contain both chemicals sorbed from surrounding seawater (e.g., polychlorinated biphenyls: PCBs) and additives (e.g., polybrominated diphenyl ethers: PBDEs). In this chapter, transfer of these chemicals from ingested plastics to higher-trophic-level organisms, mainly seabirds, will be discussed.

2 Transfer of PCBs to Seabirds

To provide the evidence of transfer of contaminants from plastics to seabird tissue, the correlation between contaminant concentrations in tissue of seabirds and the amounts of plastics in their stomachs has been examined in several studies

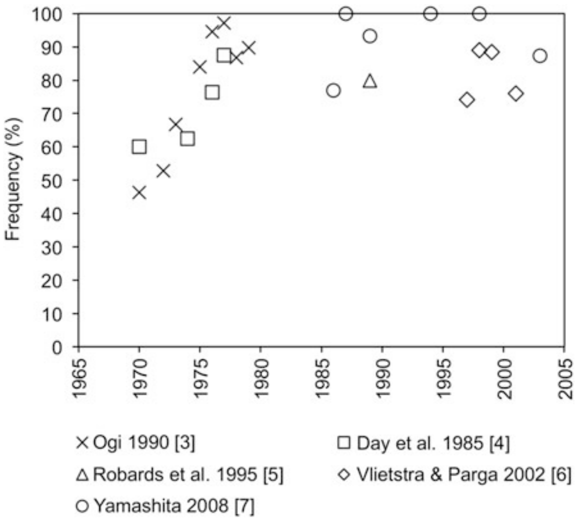

Fig. 1 Temporal changes in frequency of occurrence of plastic ingestion by short-tailed shearwater in the Northern North Pacific (Data from Yamashita et al. [2])

[9–11]. The idea was as follows. If the transfer would take place, more ingestion of plastics would bring more contaminants to the individuals, and higher concentrations of contaminants in their tissue would be observed. Ryan et al. [9] collected 20 female great shearwaters and their eggs from Gough Island, South Atlantic Ocean, in 1984 to examine the correlation of loads of organochlorine compounds, including PCBs with plastic mass in the stomach. Their simple linear analysis detected no significant correlation between PCB load and plastic mass in the stomach. However, on their multivariate analyses, significant correlation was observed between residual variable in PCB load and the plastic mass. This can be explained by that the seabirds are exposed to PCBs not only through ingested plastics but also through their natural prey and PCB load from the prey is variable due to various biological factors.

Similar correlation was observed for short-tailed shearwater collected from Northern North Pacific in 2005 [10]. Twelve birds were collected by catch and dissected to have abdominal adipose and to identify and count plastics in their stomachs. We observed significant correlation of concentrations of lower-chlorinated congeners ranging from Cl_2 to Cl_4 in the adipose with plastic mass in the stomach as shown in Fig. 2. This correlation suggested the transfer of these PCB congeners from ingested plastics to the tissue of seabirds. On the other hand,

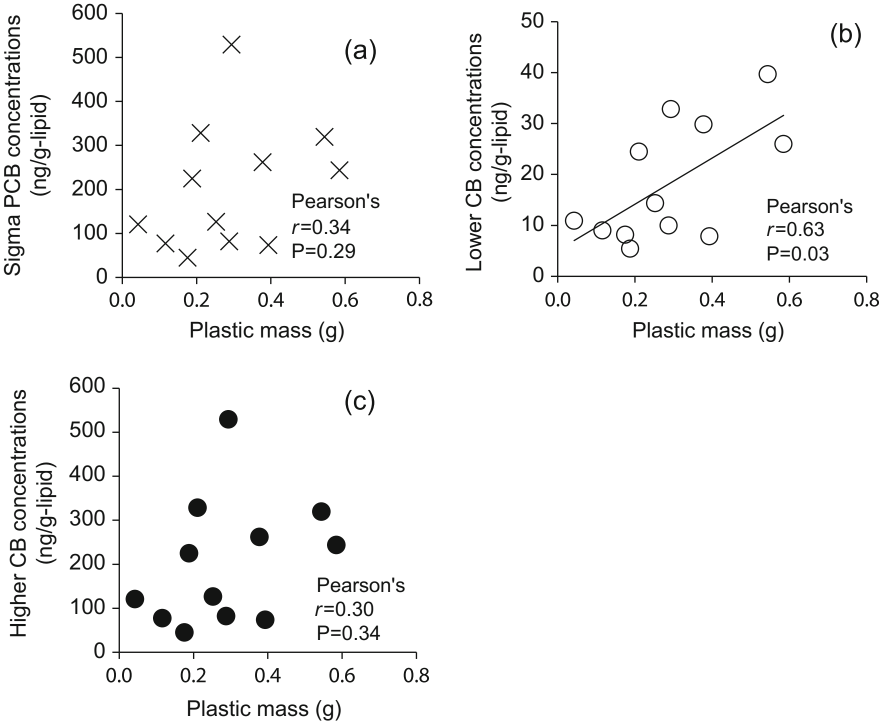

Fig. 2 Relationships between ingested plastic mass and concentrations of (**a**) total PCBs, (**b**) lower-chlorinated congeners (Cl_2–Cl_4), and (**c**) higher-chlorinated congeners (Cl_5–Cl_9) in abdominal adipose tissues of shearwaters that ingested them (Data from Yamashita et al. [10])

correlation with plastic mass was not significant for higher-chlorinated congeners (Cl_5–Cl_8) and sum of PCB congeners. This can be explained by the competition of transfer of PCBs between plastic-associated exposure and natural exposure through food web as follows. PCBs are biomagnified through food web and concentrated in prey of the seabirds, such as fish. Short-tailed shearwater is exposed to PCBs both through ingested plastics and their prey. Biomagnification is more prominent for higher-chlorinated congeners with higher hydrophobicity (e.g., [12]). As the result, higher-chlorinated congeners are rich in fish, whereas lower-chlorinated congeners are depleted in fish, as shown in Fig. 3. Because magnification process does not work for the sorption of PCBs to plastics, lower-chlorinated congeners are relatively rich in plastics in marine environments (Fig. 3). Thus, for the exposure of lower-chlorinated congeners to seabirds, contribution from plastic is higher than that from prey, and, as a result, significant correlation was observed (Fig. 2). On the other hand, in the case of higher-chlorinated congeners, contribution from plastics is lower than from prey and correlation with plastic mass was not significant.

Similar competitive exposure both from plastics and prey was observed on a field experiment in which another species of shearwater was fed with PCB-contaminated plastics. Eight 40-day-old chicks of streaked shearwater (*Calonectris leucomelas*) were used for the experiment. The chicks were kept in cages located at Mikurajima Island, a natural breeding ground of the bird, for 42 days. Among them, five individuals were fed with polyethylene resin pellets collected in Tokyo Bay that contained significant amounts of PCBs. Forty pellets (~1 g) were mixed with their natural prey (Japanese sand lance: *Ammodytes personatus*) and fed to each of the five chicks only at the beginning of the experiment (day 0). As a control, three individuals were fed with the Japanese sand lance without plastic resin pellets. Every 7 days, a preen gland oil sample secreted from the preen gland located at the base

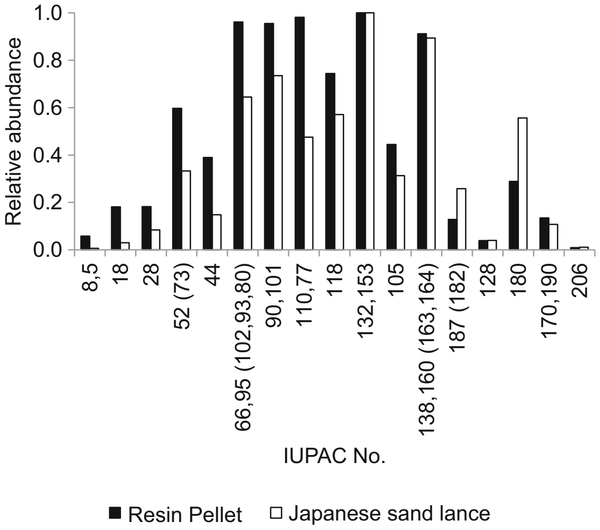

Fig. 3 Pattern of PCB congeners in resin pellets (solid bars) and Japanese sand lance (open bars)

of the tail feathers was collected from the live chicks and was analyzed for PCBs. PCBs are accumulated in the preen gland oil due to their hydrophobic nature, and thus, the PCB concentrations in the oil reflect PCB levels in the internal tissue, and, therefore, it can be used to monitor PCB concentrations in biological tissue of "live" seabirds over time [13]. This approach was applied to the field experiment. Figure 4 displays the average of relative concentrations of PCBs in preen gland oil from the chicks. For each chick, the preen gland oil PCB concentration is normalized to that at day 0 and is averaged for plastic-feeding chicks and control chicks. The PCB concentrations of the lower-chlorinated congeners in preen gland oil increased up to three times from day 0 to day 7 for the plastic-feeding setting, whereas no such increase was observed for control. This difference was statistically significant

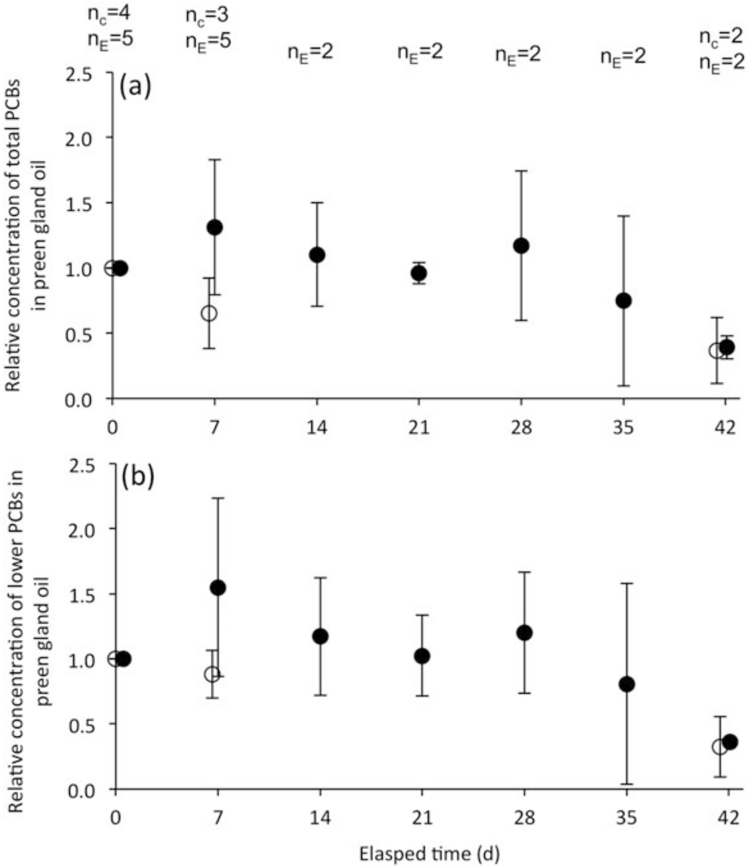

Fig. 4 Temporal change of PCBs in preen gland oil of the chicks: (**a**) total PCBs and (**b**) lower chlorinated congeners. Total PCBs: sum of CB 8, 5, 18, 28, 52, 44, 66, 95, 90, 101, 110, 77, 118, 132, 153, 138, 160, 187, 128, 180, 170, 190, and 206. Lower-chlorinated congeners: sum of CB 8, 5, 18, 28, 52, 44, 66, and 95. PCB concentrations are normalized to those on day 0 on each series. Closed symbols, plastic feeding setting; open circle, control setting

($p < 0.05$, two-tailed t test), suggesting that transfer of PCBs, lower-chlorinated congeners, occurs from ingested plastics to the biological tissue of the organisms which intake the plastics. On the other hand, in the later stage, PCB concentrations in preen gland oil showed no difference between the plastic-feeding and the control settings (Fig. 4, [14]). This is reasonable because plastic resin pellets were fed only at day 0, and, therefore, plastic-associated PCB was exposed at the beginning of the experiment, natural prey-derived PCBs was exposed throughout the experiments, and their contribution was dominant in the later stage of the experiment. Similarly to the field observation, no statistically significant increase was observed for total PCBs whose majority is higher-chlorinated congeners. This can be explained by that higher-chlorinated congeners are richer in natural prey than plastics and PCB exposure from prey is dominant over plastic-associated PCB exposure to the seabirds.

These results observed in the field and feeding experiments can be modeled as Fig. 5. Higher-trophic-level organisms are exposed to chemicals both from ingested plastics and from natural prey. Both are competing, and importance of plastic-associated exposure depends on magnitude of chemical exposure through natural prey, relative amount of plastics, concentrations of chemicals in plastics, properties of chemicals (e.g., hydrophobicity, susceptibility of metabolism), and biological factors. Hydrophobic and non-metabolizable chemicals such as higher-chlorinated congeners of PCBs are biomagnified through food web, and they are highly concentrated in the prey of higher-trophic-level organisms. For these compounds, contribution from plastic-mediated exposure is relatively small. On the other hand, in case of the chemicals which are not biomagnified, contribution from plastic could be relatively larger. Lower-chlorinated congeners are examples of this case. They are

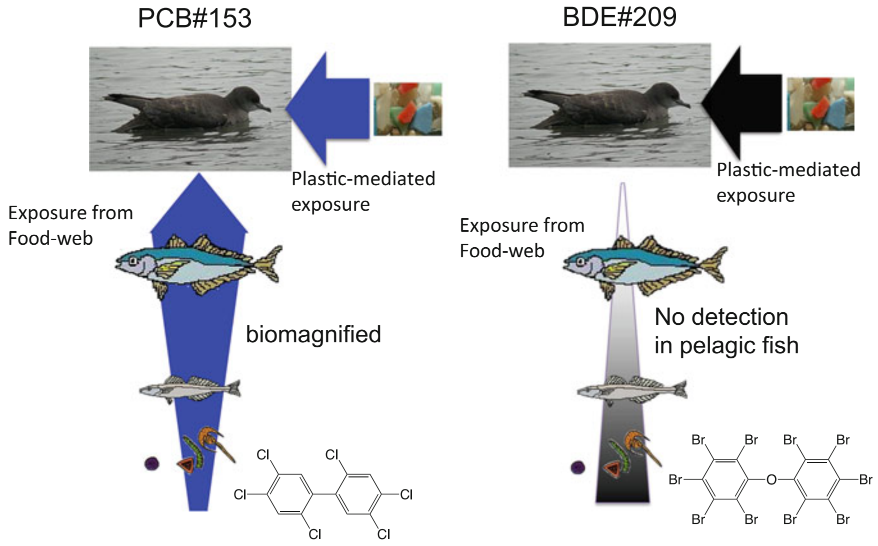

Fig. 5 Models of chemical exposure in seabirds via ingested plastics and food web

more easily metabolized and selectively depleted when PCBs move through the food chain and consequently are less abundant in the fish tissue (natural prey of the seabird). Plastic, however, just concentrate (partition) PCB congeners from seawater (not through the food web), and no metabolic process occurs; therefore lower-chlorinated congeners are not depleted. Lower-chlorinated congeners can be regarded as a sensitive tracer to detect the contribution from plastic-derived PCBs. Furthermore, marine plastics may act as a more important source of phenolic additive-derived chemicals (i.e., NP, OP, and BPA) to higher-trophic-level organisms. Biomagnification of phenolic compounds through the food chain is unlikely as their hydrophilic hydroxyl group makes them easier to be metabolized. Several studies suggest that biomagnification does not play an important role in the transfer of NP to animals and birds at higher trophic levels (e.g., [15, 16]). Thus, ingestion of marine plastics could be a direct and important route of phenolic chemicals to higher-trophic-level animals such as seabirds. In addition, higher-brominated diphenyl ethers (PBDEs) give another evidence of plastic-associated transfer because they are not biomagnified, as discussed in the section below.

3 Transfer of PBDEs to Seabird Tissue

Based on the model of plastic-mediated POP exposure to higher-trophic-level organisms (Fig. 5), PBDEs are selected for further discussion since they are less biomagnified than PCBs [12]. Especially, higher-brominated congeners such as BDE209 and BDE183 are unlikely to undergo trophic transfer, and they disappear in higher-trophic-level organisms. Thus, contribution of plastic-mediated exposure of PBDEs was expected to be dominant over natural-prey-mediated exposure. Thirty individuals of the short-tailed shearwater taken by catch in the Northern North Pacific in 2005–2011 were used. The abdominal adipose, liver, and the plastics in the digestive tracts were analyzed for PBDEs. As examples of their prey, lantern fishes and one squid were also analyzed. In the tissue of 24 among the 30 birds, lower-brominated congeners (i.e., tetra- to hexa-brominated congeners such as BDE47, BDE99, and BDE154) were dominant (Fig. 6). These profiles, with a dominance of lower-brominated congeners, are similar to those found in pelagic fishes (Fig. 6), the prey of shearwaters. These data indicate that these lower-brominated congeners are accumulated in the body of the seabird through the food web. In five birds (WK05-018, WK05-022, OS10-008, WK10-023, WK10-019), however, BDE209 was dominant over lower-brominated congeners, and in another bird (WK05-027), BDE183 was dominant (Fig. 6). Most of these birds had higher concentrations of PBDEs than the other seabirds whose PBDEs were dominated by lower-brominated congeners. This indicates that there is some exposure source of PBDEs rich in these higher-brominated congeners. BDE209 and BDE183 are major components of deca-BDE and octa-BDE technical products, respectively. BDE209 and BDE183 were not detected in the lanternfish (Fig. 6) and squid, which are the natural prey of the short-tailed shearwater and which were collected from the same

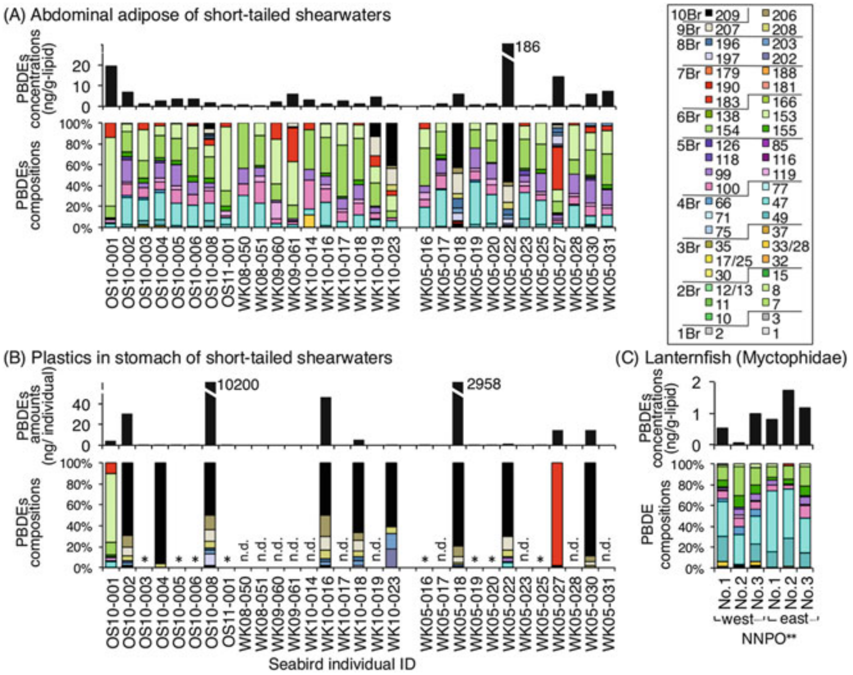

Fig. 6 PBDE concentrations and compositions in (**a**) abdominal adipose of short-tailed shearwaters, (**b**) the plastics in their stomachs, and (**c**) their prey. *n.d.* not detected. *Profile is not shown because only trace concentrations of one congener (BDE47 or BDE71) were detected; ***NNPO* Northern North Pacific Ocean

area as the seabirds. BDE209 and BDE183 were not detected in the other species of pelagic fishes from the northern or southern hemisphere, whereas lower-brominated congeners such as BDE47, BDE99, and BDE154 were abundant [17]. Thus, exposure of the short-tailed shearwaters to higher-brominated congeners through the food web is unlikely. On the other hand, BDE209 and BDE183 were detected in marine plastics [18], where their occurrence was sporadic, because flame retardants are compounded in specific commercial products as discussed in Kwan and Takada [19]. In fact, BDE209 and BDE183 were detected in the plastics found in the stomachs of the five birds (WK05-018, WK05-022, OS10-0008, WK10-023, and WK05-027) that contained mainly BDE209 or BDE183 in the adipose, and their congener profiles (Fig. 6) strongly resemble those in the adipose of the birds (Fig. 6), suggesting the transfer of PBDEs from the ingested plastic to the adipose. For WK10-019, BDE209 was detected in the adipose, whereas not detected in the plastics in the stomach. This may be explained by that plastics containing BDE209 was already excreted, which was supported by the isomer profiles of nona-BDEs [20]. There are the other exposure sources of the higher-brominated congeners such as sediments and benthic organisms, and their contribution could be possible. However, the correlation of detection of higher-brominated congeners between plastics in the digestive tract and tissues cannot be explained by the other exposure route. That is, higher-brominated congeners were detected both in the biological tissue and plastics for the same individuals. Furthermore, among the higher-brominated congeners, BDE183 was dominant both in the tissue and ingested plastic only for the specific bird (WK05-027). These observations cannot be explained by any exposure source of higher-brominated congener other than ingested plastics. In conclusion, fingerprinting of PBDEs in the tissue and the ingested plastics in the short-tailed shearwater provided the evidence of transfer of the chemicals from ingested plastics to the tissue.

4 Transfer of Various Chemical Species from Ingested Plastics to Seabirds

Hardesty et al. [21] utilized phthalates in preen gland oil of seabirds as indicators of transfer of chemicals from ingested plastics to the biological tissue. Phthalates are typical plasticizers. They can be metabolized in the organisms mainly through hydrolysis, and, therefore, they are not biomagnified and some disappear in higher-trophic-level organisms [22]. Therefore, phthalates can be utilized as indicators of exposure to plastics for higher-trophic-level organisms. Hardesty et al. [21] showed positive correlation between number of plastics in the stomach of short-tailed shearwater and the phthalate concentrations in the preen gland oil of the short-tailed shearwater. Correlation was statistically significant for di-(2-ethylhexyl) phthalate (DEHP) while insignificant for dibutyl phthalate (DBP). This is another indication of transfer of plastic-derived chemicals to the tissue of seabirds. However, ubiquitous contamination of whole ecosystem with phthalates should be considered when they are utilized as the indicator of plastic ingestion. In addition, phthalates are applied mainly to polyvinylchloride (PVC) which are not floating on sea surface but are deposited in bottom sediments because of the higher density [23]. Data on the presence and distribution of phthalates in plastic debris in the ocean or in plastics in the stomachs of seabirds is necessary.

Lavers et al. [11] studied the effects of plastic ingestion on the fledging body conditions of flesh-footed shearwater. They examined the correlation between heavy metal concentrations in breast feather of the seabirds and number of plastics in the stomachs. They found significant positive correlation between mass of ingested plastics and chromium and silver in the fledgling breast feather. This is further indication of plastic-associated transfer of chemicals to seabirds. Furthermore, negative correlation was observed between plastic ingestion (mass and/or number of ingested plastics) and some body conditions (i.e., body mass, wing chord, head + bill length), suggesting that plastic ingestion poses sublethal effects on the seabirds. Because the population of this species of seabirds has been decreasing, transfer of organic pollutants to the flesh-footed shearwater and their toxicological effects including endocrine disruption should be studied in future efforts.

5 Other Higher-Trophic-Level Organisms

Regarding transfer of chemicals from plastics to the other higher-trophic-level organisms than seabirds, there have been a very limited number of papers. Large filter-feeding organisms have the potential to ingest relatively large quantities of plastics, because they can take in an enormous amount of water. Fossi et al. [24] used DEHP and its primary metabolite (mono-(2-ethylhexyl) phthalate: MEHP) as tracers of the intake of plastics by the large filter-feeding marine organisms (basking shark and fin whale). They detected significant concentrations of MEHP in the fatty tissue of the sharks and whales as well as in plastics collected from the water column in the area. Based on these findings, they stated that phthalate was transferred from the ingested plastics to the tissue. However, we have to consider the fact that phthalates are the most ubiquitous contaminants among the man-made chemicals. Phthalates have been detected in many components in the ecosystem including zooplankton which is the natural prey of these species of shark and whale. Actually, the authors, themselves, measured the phthalates in Euphausiidae and detected significant concentrations of MEHP. Thus, detection of MEHP in the tissue of the large filter feeders may be derived from plastics ingested, but it is not a definitive evidence of the transfer.

Fossi et al. [24] also proposed that PCB profile could be another indicator of the transfer of chemicals from plastics to the filter feeders. The idea of utilizing the PCB profile to examine chemical exposure from plastics is promising as discussed above (Fig. 3, Yamashita et al. [10]). Fossi et al. [24] showed that CB195 was abundant in plastics in water column (40% of total PCBs) and the shark (10%) and suggested potential utility of CB195 for such indicator. However, CB195 is not abundant but trace congeners (less than 1% of total PCBs) in marine plastics based on our analyses of marine plastics [18]. Actually, no paper reported such high abundance of CB195 in industrial products or environmental media. Thus, detection of CB195 in the tissue of the shark does not provide concrete evidence of transfer of PCBs from the plastics to the tissue.

6 Mechanism of Transfer of Chemicals from Plastics to Higher-Trophic-Level Organisms

Transfer of POPs from prey to tissue of predator takes place through dissolution of POPs into digestive fluid and uptake of the dissolved POPs from intestine. Leaching of POPs from plastics to digestive fluid is the key to consider the transfer and bioavailability of POPs in plastics to organisms. POPs are hydrophobic and rarely dissolved into aqueous digestive fluid. However, organic constituents in the digestive fluid can facilitate dissolution of POPs into the fluid. Teuten et al. [25] studied the desorption of phenanthrene from μm-size plastics (200–250 μm PE, PP, and PVC) by seawater and 15.5 mM aqueous sodium taurocholate, which is a typical component of bile. They demonstrated enhanced desorption by taurocholates by a factor up to 19 times than seawater due to solubilization by the surfactant. Bakir et al. [26] conducted similar leaching experiments for wider range of compounds including DDT and DEHP. They also demonstrated 30 times enhancement of desorption of DDT by sodium taurocholate compared to seawater alone. Both experiments demonstrated the solubilization of hydrophobic contaminants sorbed to μm-size plastics by the bile acid. However, taurocholate is not so hydrophobic and may not be effective to leach hydrophobic additives compounded into polymer matrix of mm-size plastics.

Stomach oil was examined as effective digestive fluid which can leach hydrophobic additives (i.e., BDE209) from mm-size plastic fragments [20]. The stomachs of members of the order Procellariiformes, including short-tailed shearwater, hold oil derived from their diet, mainly fish. Stomach oils are composed mainly of wax esters or triacylglycerol (>70% of total lipids) and could therefore facilitate the leaching of the hydrophobic additives from ingested plastics. Pieces of plastic (2 mm × 3 mm × 3 mm) compounded with deca-BDE were soaked in several leaching solutions. Trace amounts of BDE209 were leached into distilled water, seawater, and acidic pepsin solution. In contrast, over 20 times as much was leached into stomach oil. This enhanced leaching of deca-BDE from plastics into the stomach oil is due to the hydrophobic nature of the stomach oil and solubilization by the oil.

In members of the order Procellariiformes, stomach oils are generated from prey items such as fish in the proventriculus, where easily digestible organic matter such as proteins and carbohydrates are rapidly broken down, and the remaining oily components separate from the aqueous fraction. The aqueous (lower) phase is emptied first. Then the stomach oil is slowly emptied into the gizzard and then into the intestine where it is gradually digested by pancreatic lipases and bile, and nutrients and some chemicals are absorbed from the intestine into the internal system. Intestinal reflux moves the contents of the intestine back into the stomach. By combining these dynamics of stomach oil in seabirds and the enhanced leaching, mechanism of transfer of hydrophobic chemicals from ingested plastics to the biota is modeled as illustrated in Fig. 7. Plastic fragments become trapped mainly in the gizzard where they come into contact with the stomach oil. This interaction is facilitated by the intestinal reflux. Birds that eat oily prey have a high rate of intestinal reflux and repeatedly shuttle the lipid contents between the stomach and intestines to promote digestion. Thus, mainly in gizzard, hydrophobic chemicals are leached out into the stomach oil. In addition, in the gizzard, plastics are grinded and fragmented into smaller pieces, which also facilitate the leaching of hydrophobic additives from the plastics. During digestion and assimilation of the oil in the intestine, hydrophobic chemicals in the oil are also absorbed into the internal system of the birds via intestine. In this model (Fig. 7), the key is leaching of hydrophobic additives from the plastic by stomach oil. A wide range of seabird species ingest plastic, some of which have stomach oil. Especially the species with stomach oil are able to digest even some kinds of lipids which are hardly digested by birds which do not have stomach oil. The assimilation efficiency of neutral lipids is higher in

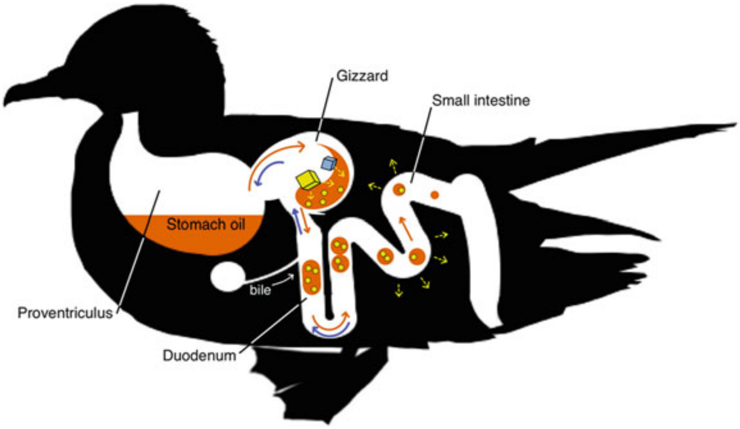

Fig. 7 Conceptual model of interaction of ingested plastics and stomach oil of seabird and resultant absorption of plastic-associated chemicals into the tissue

Procellariiformes (>80%) than the other avian species (e.g., rockhopper penguin; <62%). This means that the birds with stomach oil have not only high potential to extract the chemicals from plastics but also may have high potential to absorb the leached chemicals dissolved in the oil.

7 Conclusions

So far, several indications of transfer of chemicals from ingested plastics to the internal system of seabirds through several field observations and field-based experiments have been recorded. Because plastic-mediated exposure competes with natural prey, no single observation or experiment provided solid evidence of transfer of chemicals from ingested plastics to the organs of the organisms. However, if all the observational and experimental results are combined together, it is obvious that transfer from ingested plastics to the biological tissue certainly occurs for higher-trophic-level organisms. When risk associated with chemical exposure from ingested plastics is evaluated, the plastic-mediated exposure should be compared with that through natural prey. In the case where background pollution is higher such as for PCBs in industrial areas, plastic-mediated exposure could be insignificant. However, in remote areas where background pollution is low and plastics bring higher concentrations of chemicals, plastic-mediated exposure could be significant. Also, plastics could be a significant pathway of additives that are not biomagnified in higher-trophic-level organisms. The lipophilic nature of digestive fluid is key to facilitate the leaching and, consequently, the transfer of hydrophobic chemicals from ingested plastics to the tissues of the organisms. Stomach oil is specific to certain species of seabirds. However, lipids in natural prey or food could facilitate the transfer of hydrophobic pollutants in case of the other organisms including humans.

In future efforts, the extent of contribution of plastic-mediated exposure of variety of chemicals to marine organisms should be surveyed in various ecosystems including remote systems. Also, toxicological effects should be evaluated. In this context, biomarkers should be developed. Lastly, basic environmental chemistry of organic micropollutants should be more deeply and comprehensively understood. For example, our understanding of the distribution and transport of POPs in ecosystem should be enhanced. Especially, metabolism and biomagnification of organic micropollutants and toxicological responses should be studied for high-trophic-level organisms.

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The Role of Plastic Debris as Another Source of Hazardous Chemicals in Lower-Trophic Level Organisms

Chelsea M. Rochman

Abstract Over the last decade, it has become indisputable that small plastic debris contaminates habitats and wildlife globally. Of concern is that this material, which is ingested by hundreds of species across multiple trophic levels, is associated with a complex mixture of hazardous chemicals. Models, laboratory exposures, and field studies have all demonstrated that plastic debris can act as a source for hazardous chemicals to bioaccumulate in animals. This has been demonstrated with several plastic types, including polystyrene, polyvinyl chloride (PVC), polyurethane foam, and polyethylene, and for several different organic chemicals, including PCBs, PAHs, PBDEs, triclosan, and nonylphenol. What remains less certain is the ecological importance of this transfer, i.e., the relative contribution of plastic as a source of chemicals to wildlife relative to other sources. Experimental data suggests that for some chemicals and under certain exposure scenarios, plastic debris may be a relatively important source of chemicals, including at environmentally relevant exposure concentrations. Toxicological studies in the laboratory demonstrate adverse effects from the combination of plastic and hazardous chemicals in fish and lugworms. Further research is warranted to better understand the mechanisms by which plastic-associated contaminants transfer to organisms and if the chemicals are biomagnified in higher trophic level animals leading to ecological consequences or even human health effects via consumption of contaminated seafood.

Keywords Bioaccumulation, Bioconcentration, Hazardous chemicals, Plastic debris, Priority pollutants

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Contents

1 Introduction

Over the last decade, it has become indisputable that small plastic debris contaminates the environment globally [1–5]. Recently, it seems that in each new habitat examined, small plastic debris is found in sediment and/or water collected from bays [6, 7], estuaries and shorelines [2, 8], coral reefs [5], the deep sea [5], freshwater lakes [9], rivers [10], and even in Arctic Sea ice [1]. Moreover, the ubiquitous nature and the quantities of small plastic debris are alarming [4, 11]. Recent studies reveal the presence of small plastic debris on seamounts and in corals from the deep sea globally [5] and another study estimates that there are more than 5 trillion pieces of small plastic debris floating in pelagic habitats globally [4].

The ubiquitous nature of this debris is not independent of wildlife. Research demonstrates that aquatic and terrestrial animals are contaminated with this material via ingestion and entanglement [12–14]. As of 2015, reports of ingestion of plastic debris have been made for 181 species [14]. This includes animals across multiple taxa and trophic levels including invertebrates [15–17], fishes [18–20], reptiles [21], birds [22, 23], and mammals [24, 25]. Because the focus of this handbook is hazardous chemicals associated with plastic debris, the occurrence or hazards of entanglement are not covered here. The occurrence and hazards of ingestion are discussed in this chapter Ryan (2016) because plastics are associated with a cocktail of chemicals [26], some bioavailable upon ingestion [27–31].

In the environment, plastic debris is associated with a complex mixture of chemicals, many considered a priority by the United States Environmental Protection Agency (US EPA) [32] and the European Union [33] because they are persistent, bioacummulative, and/or toxic (Fig. 1). Of all 126 chemicals listed as priority pollutants by the US EPA, 78% are associated with plastic debris [26]. Chemicals in this complex mixture include those that are ingredients of plastic

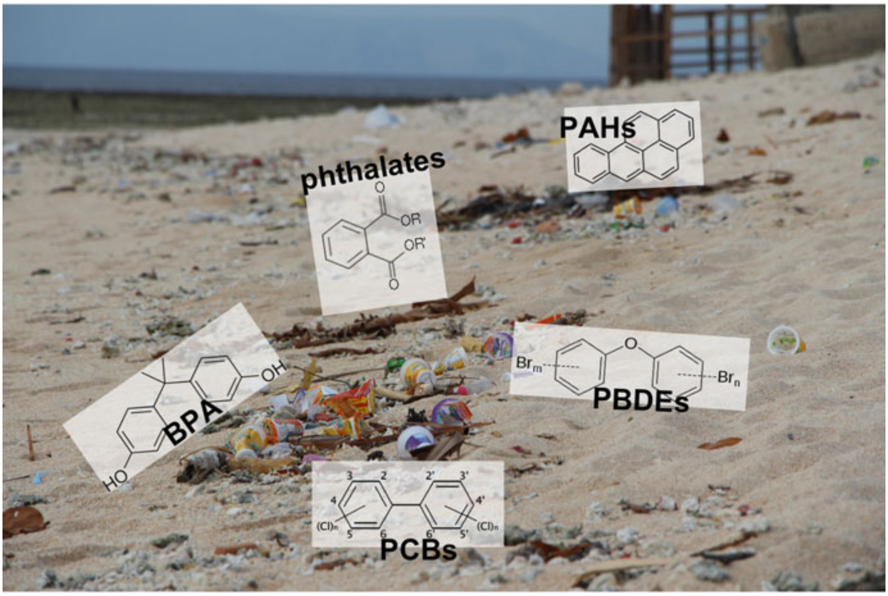

Fig. 1 Cocktail of contaminants associated with plastic debris in the environment. Plastic debris on a beach in Indonesia. The image shows the chemicals that may be associated with this plastic debris, including chemical ingredients (polybrominated diphenyl ethers (PBDEs), phthalates, and bisphenol-A (BPA)), byproducts of manufacturing (polycyclic aromatic hydrocarbons (PAHs)), and those that accumulate from surrounding seawater in the marine environment (polychlorinated biphenyls (PCBs) and PBDEs)

materials (e.g., monomers and additives) [34], byproducts of manufacturing (e.g., chemicals composed during the combustion of the raw material petroleum) [34], and/or chemical contaminants in the ocean that accumulate on plastic from surrounding environmental media (e.g., persistent organic pollutants (POPs) and metals in ambient water or air) [35, 36].

Recent research suggests that several chemicals associated with this "cocktail of contaminants" are bioavailable to whales [37, 38], basking sharks [38], seabirds [39–42], amphipods [31], crickets [27], lugworms [28, 29], and fish [30, 43, 44] as a result of plastic debris. What remains less certain is the ecological importance of plastic as a source of contaminants to wildlife, i.e., the relative contribution of plastic as a source of chemicals relative to other sources such as surrounding water and/or prey. This chapter focuses on role of small plastic debris as a source of chemicals to lower-trophic level organisms and the toxic effects that may result.

2 The Role of Plastics as Another Source of Chemicals for Bioaccumulation

As described above reports [35, 36], plastics are associated with a complex mixture of hazardous chemicals. Because incidences of wildlife interacting with plastic debris are increasing [14], there is concern regarding the role of small plastic debris as another source of hazardous chemicals to bioaccumulate in animals [39]. Because there are several pathways for bioaccumulation, concerns are not primarily about whether contaminants transfer from the plastic to animals, but also how important this may be relative to other sources [45].

Chemical contaminants partition among many matrices in the environment. This process is dependent upon the physical and chemical properties of each chemical and environmental matrix (e.g., sediment, water, organic matter, and living biota). These processes, along with any degradation processes expected for each chemical [46], help determine their environmental fate globally. As such, organisms are exposed to hazardous chemicals via several transport mechanisms, including the bioconcentration of chemicals from ambient media (e.g., water, air, or sediment) and bioaccumulation via ingestion (e.g., environmental particulates and diet) [47]. The introduction of plastic debris to the environment globally provides another source of chemicals to the environment and another media for chemical contaminants already present in the environment to interact with [48]. Thus, plastic may provide another transport mechanism into organisms. This transport may occur directly via ingestion of plastic or indirectly via desorption of chemicals from plastic into other environmental media followed by bioconcentration from water or bioaccumulation via ingestion of a prey item that was contaminated by plastic (Fig. 2).

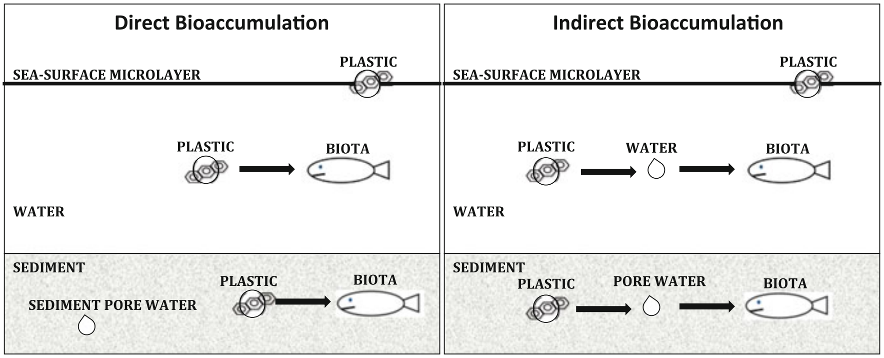

Fig. 2 Mechanisms for the bioaccumulation of chemicals from plastic debris. The diagram depicts different pathways for how chemicals may transfer to biota in aquatic habitats. Bioaccumulation may occur directly via ingestion of plastic (*left*) or indirectly via desorption of chemicals from plastic into other environmental media followed by bioconcentration from the water or bioaccumulation via a prey item that was contaminated by plastic (*right*)

Plastic debris, like other environmental matrices, accumulates and transports chemicals in the environment. Of greatest concern for management appears to be how the transport mechanisms of hazardous chemicals from plastic debris to wildlife differ from other environmental media. In some ways, plastic is unique from non-anthropogenic media, bringing to the environment its own suite of innate chemicals (e.g., monomers and additive ingredients) [34, 45, 49]. In addition, plastic debris has its own unique physical and chemical properties that may influence the complex mixture and fate of chemicals. For example, POPs accumulate on plastic debris at concentrations up to six orders of magnitude greater than ambient water [35], which can be greater than on sediment and suspended particulates [50, 51]. As such, the role of plastic as a source of chemicals for bioaccumulation may differ from other sources of chemicals to wildlife. Testing hypotheses regarding how plastic acts as a source for the transport of chemicals into biota using models, laboratory techniques, and field observations is critical to understanding the hazards associated with plastic debris in the environment.

3 The Weight of Evidence for Bioaccumulation from Plastic Debris

Several experiments and observational studies have measured the role of plastic debris as a source of hazardous chemicals to accumulate in animals. These studies include modeling exercises, laboratory exposures, and observational experiments in nature. Scientists have asked questions about the possibility of chemicals to transfer from plastic to animals and about the ecological importance of this transfer, i.e., the relative contribution of plastic as a source for bioaccumulation relative to other mechanisms. Here, we will discuss the weight of evidence regarding the transfer of chemicals from plastic to animals.

3.1 Modeling Studies

In some studies, modeling approaches have been used to determine how plastics may play a role as a source for the bioaccumulation of contaminants in aquatic habitats. Several models assume that lipids are the primary target for chemicals and use traditional approaches that use mass balance of uptake and loss and thermodynamic models of equilibrium [51, 52]. In this way, whether plastic acts as a source of chemicals to biota depends on the gradient between the chemical concentration in the plastic and lipid [53, 54]. Thus, based on fugacity, when an organism is relatively clean of contaminants, the model assumes that chemicals will transfer into the lipid. However, if an organism has a greater body burden of chemicals than the introduced plastic debris, the models assume that the plastic debris will “clean” the lipid.

As such, results from the models conclude that chemicals from plastic can transfer to animals upon ingestion. Generally, the models predict that chemical body burdens will increase when plastic is the only source of chemicals and the only pathway of uptake [51, 53]. However, the models also find that in a system that is contaminated, plastic debris may not be a relatively important mechanism for the transport of hazardous chemicals because the increase in contaminant levels may be negligible in comparison to other sources [51–55].

Modeling approaches are useful for interpreting mechanisms and to help understand the magnitude and directions of results observed in experimental and observational studies. They are also useful for risk assessment. Laboratory and field experiments can provide further information on testing the actual occurrence of transfer and/or the relative contribution as compared to other sources. Thus, all types of studies must be considered when making conclusions about plastic debris as a source of chemicals for bioaccumulation.

3.2 Laboratory Studies

Controlled laboratory experiments can be useful to test hypotheses regarding the potential for plastic to transfer chemicals to organisms and their relative contribution compared to other sources. Different questions lead to various types of experiments falling on a spectrum of environmental relevance. In general, studies that aim to simply understand whether plastic debris can be a mechanism for the transport of chemicals to organisms are less environmentally relevant. They use clean organisms, expose animals to large doses of plastic or chemicals, and/or use less relevant exposure scenarios such as using synthetic gut fluids instead of live animals. In contrast, studies that aim to measure ecological significance tend to use animals that have been previously exposed to contaminants, use an environmentally relevant dose of plastic and/or chemicals, and/or use environmentally relevant exposure scenarios such as exposing animals to plastic debris via the same mechanisms they are exposed in nature (e.g., chronic exposure, dosing with plastics by mixing with sediment or allowing it to float in a tank).

Several studies have tested whether plastics can simply be a mechanism for transport of chemicals to organisms. In a cholesterol-derived bile salt, used to simulated gastric conditions (pH 4 at 38°C), POPs transferred from plastic into gut fluids, and at a much greater rate than in seawater, suggesting that chemicals on plastics can be bioavailable to organisms via direct ingestion [56]. Laboratory studies exposing animals to plastic via dietary exposures have reached the same conclusion. Several studies have demonstrated the bioaccumulation of PBDEs in animals from exposure to plastic, including in crickets [27], amphipods [31], lugworms [28], and fish [30]. In one study, the PBDEs were additive ingredients of polyurethane foam fed to crickets. In other studies, PBDEs were adsorbed onto plastics that were then mixed into the water or sediment with the animals. For the crickets, it is likely that direct bioaccumulation occurred via ingestion, but in other studies, bioaccumulation may have been indirect if the PBDEs from the plastics leached into the water or sediments and then, bioconcentrated in the organism. Another study showed greater concentrations of PCBs in lugworms exposed to contaminated sediment with small amounts of clean polystyrene as opposed to contaminated sediment without plastic, suggesting that the existence of the plastic in the experiment facilitated the transfer of chemicals to lugworms [28]. Lastly, a laboratory study demonstrated that nonylphenol, phenanthrene, and triclosan can desorb from polyvinyl chloride (PVC) and be transferred into the tissues of lugworms [29].

The controlled laboratory studies above all demonstrate that plastics can be a source of chemicals to organisms. Some of these studies also tested hypotheses regarding the importance of plastic as a source for bioaccumulation compared with different media (i.e., water, sediment, and/or food) or in the presence of a contaminated system (i.e., previously contaminated animals and contaminated diet). To measure the importance of plastic as a source for bioaccumulation compared with other media, one study exposed clean amphipods to environmentally relevant concentrations of PBDEs with and without the addition of clean microplastics to see if microplastics mediated greater bioaccumulation of PBDEs than seawater. Similar to what the models described above suggest, organisms that were exposed to PBDEs in the presence of clean microplastics had a smaller body burden of PBDEs than those exposed to PBDEs dissolved in seawater alone [31]. Similarly, a study exposed clean lugworms to PVC microplastics or sand spiked with environmentally relevant concentrations of phenanthrene and nonylphenol to test the relative difference in bioaccumulation between sand and microplastics. They found that, although sand accumulated smaller concentrations of chemicals than the plastics, lugworms exposed to chemicals via sand bioaccumulated >250% more phenanthrene and nonylphenol suggesting that chemicals from sand are more bioavailable than from microplastics [29].

To measure the importance of plastic as a source for bioaccumulation in the presence of a contaminated system, one group of researchers exposed contaminated amphipods to microplastics spiked with environmentally relevant concentrations of PBDEs and to relatively large concentrations of PBDEs [31]. Consistent with model predictions for this exposure scenario, they found no difference between concentrations of PBDEs in animals exposed to clean plastics versus those exposed to microplastics with environmentally relevant levels of PBDEs, and an increase in PBDEs in amphipods exposed to microplastics with concentrations of PBDEs greater than their starting concentrations [31]. In another study, fish that were already contaminated with PAHs, PCBs, and PBDEs via a contaminated diet were dosed with environmentally relevant concentrations of “clean” polyethylene or “dirty” polyethylene with sorbed chemicals from the marine environment. The bioaccumulation of PAHs and PCBs across all treatments was similar, and the effect from the diet could not be separated from the effect from the plastic. In contrast, the bioaccumulation of PBDEs was significantly greater in the fish fed

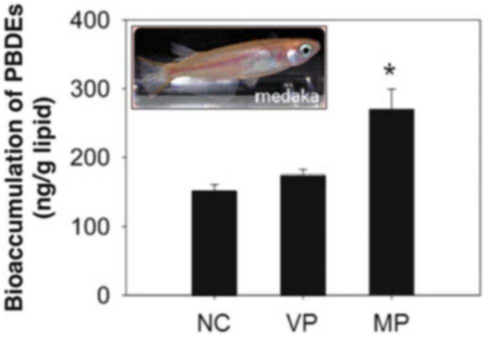

Fig. 3 Laboratory experiments demonstrated that plastic may be a relatively important source of some hazardous chemicals to fish. Japanese medaka that was fed with plastic deployed in the marine environment (MP) accumulated significantly greater concentrations of PBDEs (BDE#47, 49, 99, 100, 153, 154, and 155; $P = 0.0003$, 2-factor ANOVA, $n = 3$) in their tissues than fish fed with virgin polyethylene (VP) and a no-plastic diet (NC) [30]

with plastic having sorbed contaminants from the marine environment, suggesting that in some scenarios and/or for certain animals or chemicals plastic debris may be a relatively important mechanism of bioaccumulation even at environmentally relevant concentrations (Fig. 3) [30]. Another study placed clean polystyrene in the presence of sediments with environmentally relevant concentrations of PCBs for a 1-month period and then added clean lugworms to the system [28]. Lugworms exposed to smaller concentrations of polystyrene had significantly greater concentration of PCBs in their tissues, but lugworms exposed to larger amounts of polystyrene accumulated similar concentrations of PCBs as lugworms that were not exposed to plastic [28]. This result is conflicting, possibly suggesting that adding large amounts of clean plastic to a contaminated environment may have a "cleaning" effect, but that smaller amounts of polystyrene may have actually enhanced the bioavailability of PCBs to lugworms.

Overall, data from laboratory experiments demonstrate without a doubt that the transfer of chemicals from plastics to animals can occur. This has been demonstrated with several plastic types, including polystyrene, PVC, polyurethane foam, and polyethylene, and for several different chemicals, including PCBs, PAHs, PBDEs, triclosan, and nonylphenol. What remains less understood is the relative importance of plastic debris as a source for the bioaccumulation of chemical contaminants in the natural environment where chemical contamination has become ubiquitous in water, sediments, and food webs, globally [57]. The laboratory studies above suggest that the answer is not simple and it likely depends on the exposure concentration, the contaminants of interest, and the biology of the target organism. For further understanding, some researchers have conducted field experiments to see if patterns observed via modeling exercises or in the laboratory could be observed in nature.

3.3 Field Observations

In nature, patterns can be difficult to find in the presence of so many factors and the sources or mechanisms behind a pattern can be difficult to tease apart as well. In this case, animals are exposed to chemical contamination via multiple sources, and thus, it is difficult to demonstrate that plastics are the source of bioaccumulation observed in wildlife. Still, researchers who have conducted observational experiments in nature have suggested that burdens of chemical contaminants in wildlife were introduced by plastic debris. This chapter will only focus on those relevant to lower-trophic level organisms. Recent studies have looked for associations between plastic debris and bioaccumulation in baleen whales [37, 38], basking sharks [38], and fish [43, 44]. Many of these studies are qualitative, suggesting that the presence of plastic in a region and plastic-associated chemicals in an organism provides evidence of plastic-induced bioaccumulation [37, 38, 43]. Others are more quantitative, demonstrating statistically significant correlations between plastic ingestion and bioaccumulation of chemicals in wildlife [44].

Qualitative studies have been observational in nature, noting the large presence of plastic debris in the feeding grounds of animals, the presence of plastic in their gut content and/or the detection of plastic-associated chemicals in surrounding media, and the detection of plastic-associated chemicals in the animal of concern [37, 38, 43]. For example, Fossi et al. [37] noted the large quantities of microplastic in the Mediterranean Sea where fin whales forage, detected phthalates in local plankton samples (i.e., the diet of fin whales) and in the tissue of stranded fin whales. Gassel et al. [43] sampled fish from a region with large contamination by plastic debris and detected plastic and plastic-associated chemicals (BDE-209 and nonylphenols) in fish. While these lines of evidence suggest that chemicals detected in animals may come from plastic debris, bioaccumulation from other sources is quite possible and thus, further evidence is needed to demonstrate that the bioaccumulation observed is a consequence of plastic.

Other studies have quantitatively demonstrated positive correlation between plastic debris and bioaccumulation of hazardous chemicals. Correlative evidence demonstrates that the concentrations of higher-brominated PBDEs in fish [44] are positively correlated with the amount of plastic debris in their habitat. In addition to a positive correlation between the quantities of plastic debris and bioaccumulation of higher-brominated PBDEs (Fig. 4), myctophid fish collected from the South Atlantic in regions of large plastic contamination were found with similar congener patterns of PBDEs in their tissues as those found on the plastic debris in the region. This same study could not find any significant correlation between plastic debris and the bioaccumulation of other contaminants, including bisphenol A (BPA), nonylphenols, and PCBs. Like laboratory studies, this observation also suggests that the answer is not simple and patterns of bioaccumulation likely depend on the exposure concentration, the ecology of the animal, and the contaminants of interest.

As noted above, truly defining the source of bioaccumulation is difficult in nature. Still, observational data from the field suggest that plastic can be a source

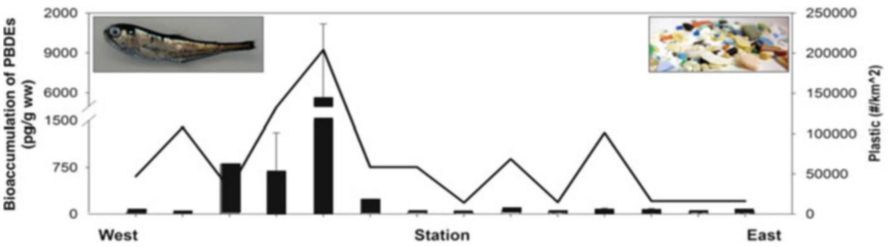

Fig. 4 *Field experiments* suggest that plastic debris is a source of some hazardous chemical contaminants to wild-caught fish. The density of plastic (*solid line*) is significantly correlated ($P < 0.01$, $R^2 = 0.23$) with the concentration of the sum of PBDEs (BDE#7, 8, 10–13, 15, 17, 25, 28, 30, 32, 33, 35, 37, 47, 49, 51, 66, 71, 75, 77 79, 85, 99, 100, 104, 116, 119, 120, 126, 128, 138, 140, 153, 154, 155, 166, 181, 183, 190, 196, 197, 203, 204, and 206–209) in fish (bars). This relationship is explained only by the higher-brominated congeners, BDE#183, 190, 196, 197, 203, 204, and 206–109 [44]

of chemicals to organisms upon exposure and support some of the laboratory experiments showing that in some situations, bioaccumulation of hazardous chemicals from plastic debris is relatively important compared to other sources. Remaining uncertainties and contradictions regarding the relative importance of plastic debris as a source of chemicals for bioaccumulation between modeling, laboratory, and field experiments suggest a need for further research.

4 Biological Consequences of Plastic-Induced Bioaccumulation

Evidence demonstrating that plastic debris can act as another source of hazardous chemicals to wildlife has raised concerns regarding adverse biological effects. While several studies have examined adverse health effects from the ingestion of clean microplastics [28, 58–60], few laboratory studies have tested hypotheses regarding the impacts associated with the complex mixture of plastic and sorbed contaminants to organisms. One study found that the combination of PVC with environmentally relevant levels of sorbed triclosan altered feeding behavior and caused mortality in lugworms [29]. Another study demonstrated that polyethylene deployed in the San Diego Bay, CA (i.e., allowing the plastic to accumulate environmentally relevant concentrations of priority pollutants) caused hepatic stress, including glycogen depletion, lipidosis, cellular death, and tumor promotion, in fish exposed to environmentally relevant concentrations for a 2-month period [30]. Moreover, fish exposed to the combination of polyethylene and priority pollutants showed signs of endocrine disruption via changes in gene expression and abnormal growth of germ cells in the gonads [61]. In both studies, adverse effects were demonstrated from the plastic alone, but organisms suffered greater effects when exposed to the mixture of plastic with sorbed chemical contaminants

[29, 30], suggesting that the combination of plastic debris and priority pollutants may be a multiple stressor in the environment.

5 Broader Implications

5.1 *Ecological Implications*

Plastic debris is associated with a cocktail of hazardous chemicals, some unique to plastic debris and others are ubiquitous in nature. As mentioned previously, 78% of the chemicals listed by the US EPA Clean Water Act as priority pollutants are associated with plastic debris [26]. As such, plastic debris is another source of priority pollutants to the environment and potentially to wildlife, raising concerns regarding how plastic debris may impact the health of ecosystems. Priority pollutants are considered a priority based upon their persistence, toxicity, and their ability to biologically accumulate in organisms and magnify in food webs [39, 62–64]. Ecotoxicological work has shown that priority pollutants can alter the structure and functions of ecosystems. Physiological processes of organisms (e.g., cell-division, immunity, and hormonal regulation) can be disrupted, causing disease (e.g., cancer) [65–67], reducing the ability to escape predation [68] and altering reproductive success [69]. Furthermore, priority pollutants can alter interactions among species (e.g., competition) [70], which may lead to structural [70] and genetic [71] changes in biodiversity [72]. Thus, existing data regarding hazards associated with priority pollutants suggest that there may be ecological consequences to the exposure of plastic debris and thus, further research regarding ecological impacts is warranted.

5.2 *Human Health Implications*

The ubiquity of plastic marine debris and the toxicity of chemicals associated with the material have begun to raise concerns regarding how the ingestion of plastic by animals may influence human health [73]. Plastic debris is found in hundreds of species globally and across multiple trophic levels [14], including in many species of fish [14, 18–20] and bivalves [15] – animals often considered seafood. The presence of plastic debris in seafood [15, 74, 75] raises several questions regarding the bioaccumulation of chemicals from plastics in humans. The weight of the evidence supports the idea that chemicals can transfer from plastic to animals [30, 43, 44]. As such, further research is necessary to test hypotheses regarding whether plastic debris can indirectly transport chemical contaminants to humans via a seafood diet.

6 Conclusion

The scientific understanding is growing, and it has been demonstrated several times that plastics are associated with a complex mixture of hazardous chemicals that can transfer to animals. Still, there remain several gaps in our understanding regarding the cocktail of chemicals associated with plastic debris. To design effective management strategies for mitigating any impacts, policy-makers will benefit from a greater understanding regarding the role of plastic debris in the global transport of chemicals, the bioaccumulation of plastic ingredients and accumulated chemical contaminants in wildlife, and the importance of plastic as a mechanism for food web contamination relative to other sources. Today, while researchers continue to expand our knowledge base, policy-makers can begin to act now with the current information available, as there are no signs that the amount of plastic debris entering the marine environment is decreasing [76, 77]. Recent studies estimate that there are more than 5 trillion pieces of small plastic debris floating in pelagic habitats globally [4] and that with our current behaviors the amount of plastic debris available to enter our oceans will increase by an order of magnitude by 2025 [78].

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Conclusions of "Hazardous Chemicals Associated with Plastics in Environment"

Hrissi K. Karapanagioti and Hideshige Takada

Abstract The production of plastics increases, their applications are diverse, and land-based management of the end-of-life products is not perfect. These result in increased amounts of plastics to be supplied to the ocean through a variety of routes and plastic pollution to be a serious and urgent problem for the marine environment. Degradation causes plastic to break into smaller pieces and additives to leach. For some chemicals and under certain exposure scenarios, plastic debris can be a relatively important source of chemicals for some organisms. More research is required related to the abundance of floating plastics and microplastics in bottom sediments. Risk from plastic-mediated exposure to chemicals is not yet well-understood. New research points include the study of plastic degradation under environmental conditions, the desorption of additives as well as the effects to the environment and to human health, and the redesign of plastic materials and additives. Finally, an urgent measure to be taken considering long-term impact is the reduction of single-use plastics.

Keywords Additives, Bottom sediments, Degradation, Microplastics, Single-use plastics

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1 Introduction

While editing the present volume, it was obvious that each chapter consisted of two main parts. In each chapter, the authors presented the knowledge that is well-known through a literature review and by focusing on case studies related to plastics in the marine environment. At the same time, the authors through their critical analysis pointed out the topics that are not as well-known or understood at this point, and these are the points that require further attention.

In this chapter, a summary is provided by the editors of this book to determine the main points that are well-known and understood and the points that require further research related to the hazardous chemicals associated with plastics in the marine environment.

2 Research Points Well-Known

All authors agree that the production of plastics is currently increasing. The demand for plastics will continue to increase into the future [1]. At the same time, it is evident that plastics are present in the marine environment, from the shallow water, the continental shelf, till the abyssal plains, in all different sea compartments and basins, and, thus, posing a serious problem for the marine environment [2].

The major land-based sources of plastic debris include wastes from dumpsites in coastal regions, watersheds and rivers, industrial outfalls, littering of beaches, tourism, and recreational use of the coasts [3]. The maritime sources of plastic debris include shipping, fishing, fish farming, offshore mining, and illegal dumping at sea. While most litter is continuously supplied to the oceans, catastrophic events such as floods, cyclones, and tsunamis release large amounts of litter into the oceans.

Degradation of plastics is a dynamic situation with continuous changing parameters [4]. For polyethylene, photodegradation results in oxygen-containing functional groups such as ketones, esters, acids, etc., whereas biodegradation results in the decrease of carbonyl indices if the sample has already been photodegraded by exposure to UV. Studies with environmental samples agree with these findings, but the degradation of plastics is very subjective to the local environmental conditions that are usually a combination of those simulated in laboratory conditions [4].

Ultraviolet (UV) degradation, embrittlement and crushing by waves, thermooxidative degradation, hydrolysis, biodegradation, grazing and shredding by macrofauna, and abrasion along coastlines are mechanisms causing macroplastic to degrade and fragment into smaller pieces (microplastic). In all subtropical gyres, debris types of floating plastics can be generally classified into five categories: fragment, pellet, line, thin film, and foamed polystyrene [3]. Microplastic, i.e., small plastics less than 5 mm [5, 6], has been reported in every location so far examined [7].

The most commonly used polymers in high volume applications are polyethylene [PE], polypropylene [PP], polystyrene [PS], poly(ethylene terephthalate) [PET], and poly(vinyl chloride) [PVC] [1]. Among them, PS, PET, and PVC are heavier than seawater and, therefore, sink to the bottom when they enter to marine environments. Ioakeimidis et al. [2] demonstrated that an important stock of marine plastic litter ($>$10 mm) lies on the world seafloor with great spatial heterogeneity. Larger pieces of PE and PP float on the sea because they are less dense than seawater. However, while floating at the sea surface, microplastics are colonized by microorganisms that form biofilms [8]. This increases the density and reduces the buoyancy of microplastics and may be an important mechanism for their settlement from the water column onto the seabed. Intake of microplastics by zooplankton, bivalves, and small fishes and their excretion in feces also facilitate transport of microplastics into bottom sediments. Recently, microplastics have been detected in sediments in both coastal shallow waters [9–11] and the deep sea [12]. Matsuguma et al. [11] indicated that stocks of PE and PP microplastics were five orders of magnitude higher than those in surface waters. Thus, sediment is a significant sink of macro- and microplastics in marine environments.

Additives are essential components of consumer plastic products. The additives used at high weight fraction in plastics are fillers, plasticizers, and flame retardants, whereas the ones that are used at low weight fraction are colorants, stabilizers, UV absorbers, and lubricants. Some of the additives are endocrine disruptors. Phthalates are predominantly used as plasticizers, and human exposure to them occurs primarily via food and water with the plasticizers being picked up from packaging or from the environment. Exposure to phthalates can result in a range of adverse health outcomes. These are primarily associated with male reproductive development and function (reduced sperm quality, increased sperm DNA damage, and altered male genital organs) [1]. Besides the intentionally added substances, there are other substances that are found in plastics but are non-intentionally added. There are numerous studies reporting the occurrence of both types of substances in various foodstuffs and bottled waters that are in contact with plastic packaging [13].

When plastic wastes are disposed in landfill sites, the additives and monomers leach out from plastics [14]. A wide spectrum of additives ranging from less hydrophobic ones such as bisphenol A to highly hydrophobic ones such as higher brominated diphenyl ethers (BDEs) are detected in landfill leachates. Their leaching is facilitated by acidic and basic conditions and higher temperature in the landfill sites. In addition, anaerobic conditions underground in the landfill sites facilitate chemical transformation of additives, such as debromination of PBDEs. Leached additives can contaminate surface waters and groundwater [15]. On the other hand, preventive options such as sealing and treatment facility can avoid the contamination of surrounding environments. However, they are costly and risky. Thus, landfilling of the plastic wastes is not a suitable management choice.

The additives are also retained and significantly detected in plastics and microplastics in marine environments. The retention and detection are closely related to sorption/desorption mechanism of chemicals to/from plastics. The sorption/

desorption equilibrium of some environmental pollutants has been studied and is well-understood [16]. It is also well-known that HOCs sorb/desorb to all plastic materials but with different rates and different diffusion abilities within the polymer. The main recent finding is that desorption rates of HOCs from plastics can be slow but are increased in the presence of higher animal body fluids, and small plastic particles will uptake or release pollutants much faster than larger pellets [17]. Because of the slow sorption/desorption and leaching, sporadically high concentrations of POPs, both sorbed chemicals and hydrophobic additives, are frequently observed in pellets and the other microplastics with the same size range, i.e., mm size, in open ocean and remote islands [18].

Ryan [19] reviewed plastic ingestion by a wide spectrum of marine organisms ranging from mussels to whales. Seabirds are the most well-examined animals for plastic ingestion. More than 165 species of the 367 species of marine birds examined (45%) were recorded to ingest plastics [19]. Ingestion of plastics by marine organisms can be direct (primary ingestion) or indirect (secondary ingestion via contaminated prey), with direct ingestion being either deliberate (plastic items mistaken for prey items) or accidental (plastics consumed passively by, e.g., filter feeding). Individual-level variation in plastic loads typically is large and strongly right-skewed.

For some chemicals and under certain exposure scenarios, plastic debris can be a relatively important source of chemicals, including at environmentally relevant exposure concentrations [20]. Toxicological studies in the laboratory demonstrate adverse effects from the combination of plastic and hazardous chemicals in fish and lugworms.

3 Research Points Known but Requiring More Research

Unfortunately, so far, we do not have a clear picture regarding the areas where the accumulation of plastics is significant although several ongoing studies try to give a clearer picture [2]. The information regarding the floating plastic is scarce. More studies are needed worldwide in floating marine litter. A harmonized worldwide marine litter assessment should be strongly supported for the different kinds of marine litter items, which are present in the marine environment. There are no universally recognized sampling protocols. Therefore, harmonization and standardization of sampling protocol of microplastics have been conducted by several groups such as GESAMP and G7.

Increasing trends in the abundance of microplastics in bottom sediments have been demonstrated (Fig. 1; [11]). However, increasing or decreasing trends in the abundance of microplastics in surface waters are difficult to ascertain due to the varied input of plastic type, volume, and location [3]. The issue of plastic debris drifting in the middle of the ocean lacks the benefit of visibility, leaving persistent misconceptions to drive mitigation efforts with the most common fallacy being the recovery of microplastics from the open ocean [3], though larger plastic fragments (i.e., precursors of microplastics) can be recovered.

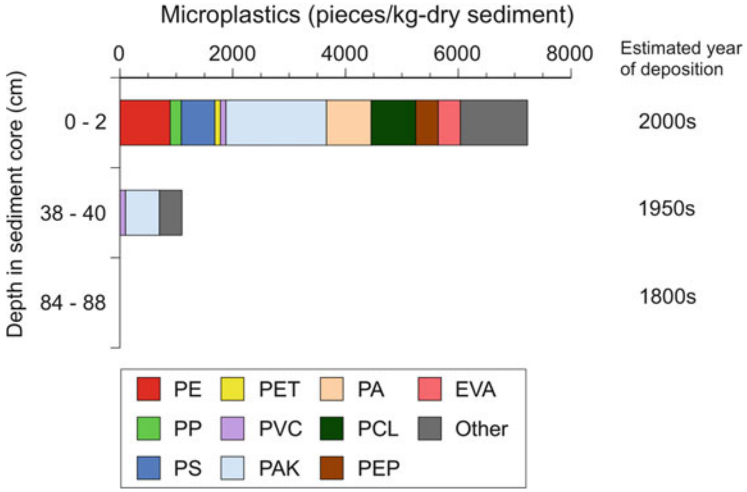

Fig. 1 Vertical profile of microplastics in sediment core collected in the Sakurada-bori Moat at the Imperial Palace in Tokyo, Japan (Modified after Matsuguma et al. [11]). *PE* polyethylene, *PP* polypropylene, *PS* polystyrene, *PET* polyethylene terephthalates, *PVC* polyvinyl chloride, *PAK* polyacrylates, *PA* polyamide, *PCL* polycaprolactone, *PEP* polyethylene-propylene copolymer, *EVA* ethylvinyl acetate

First experiments with nano-sized plastic particles suggest enhanced sorption of a chemical and particle toxicity as well as chemical toxicity [21]. Thus, thorough studies on the relationship between the size and the sorption properties would shed more light on possible mechanisms of enhanced sorption [16]. Also, although the influences of plastic degradation and fouling on sorption capacity have been conceptualized, they remain to be validated and quantified by experiments [16].

Degradation could have both positive and negative influences on sorption capacity and may partly compensate for each other. Considering the variety of HOCs found in the environment, the various types and sizes of plastics found in the stomach of some organisms along with the biodiversity that exist in the marine environment, there remains considerable uncertainty [17].

Retention times of plastic in the organism body are poorly known for many groups of marine animals and may be influenced by particle size, shape, and type of plastic, as well as phylogenetic and age-related differences in how animals handle indigestible prey remains [19]. Retention time in the digestive tract of an animal could be important for the transfer of hazardous chemicals. Long retention times could enhance chemical uptake, at least for compounds included in plastics during manufacturing. Species with broad, generalist diets that retain indigestible prey items in their digestive tracts for extended periods, such as shearwaters, petrels, albatrosses, and perhaps turtles, probably are most likely to obtain large body burdens of hazardous chemicals from ingesting plastic items. This is consistent with the fact that transfer and accumulation of plastic additives in the tissue were observed for short-tailed shearwater [22]. Wider species of marine organisms should be studied to further examine this correlation.

Plastic-mediated exposure of chemicals should be compared with natural-prey-mediated exposure. In case where background pollution is high, plastic-mediated exposure is relatively small. In remote ecosystem with trace background pollution but where marine plastics bring larger amounts of pollutants, plastic-mediated exposure could be significant. Leaching experiment using stomach oil indicates that the lipophilic nature of digestive fluid is key to facilitate the leaching of hydrophobic chemicals from the plastics and, consequently, the transfer and accumulation of chemicals in the tissue of biota which ingest the plastics. Understanding the nature of digestive fluid and biological dynamics of the digestive system as facilitators of the chemical desorption from plastic is important [22]. In addition, more data on additives and POPs in smaller microplastics (i.e., μm-size plastics) from coastal areas and open ocean are necessary [18].

4 New Research Points

Polymer scientists need to redesign materials for each plastic item to minimize the overall environmental footprint, i.e., reduce the use of fossil carbon and reduce the accumulation of waste, for example, by designing so that the eventual end-of-life products can readily be used as raw material for new production [7]. As long as plastics are produced from fossil carbon, incineration of end-of-life products, including waste-to-energy, would cause net emission of carbon dioxide and accelerate global warming. Development and wider utilization of biomass-based plastics would be promoted.

Hazard associated with additives in plastics is another problem to be solved. Alternatives to conventional phthalates that are now considered less toxic have been developed. It is important, however, to ensure their relative merits in terms of toxicity of their breakdown products as well as their leachability from plastic matrices [1]. Although the toxicity of certain compounds is known, the magnitude and variability of human exposure through direct exposure of the additives, i.e., food intake as well as health risk considering possible additives or synergistic effects, require more studies [13]. Indirect human exposure of plastic additives through eating of seafood contaminated with microplastics which may retain toxic additives is another emerging concern which we have to tackle.

Only few degradation studies have been performed in the natural environment. Although there have been some steps toward the understanding of the degradation of plastics in the environment, there are still many questions to answer. How can the changes caused by the environment in plastic affect the environment? How can we classify the degraded plastics? How long does it take for each plastic to degrade? How do smaller pieces of plastics (microplastics) interact with environment? [4]. More specifically, what is the lifespan of plastic marine litter items in the marine environment? [2].

The desorption equilibrium and mechanism of the plastic additives have not been studied and are currently not well-understood [16]. Also, there is limited information on the role of the microbes attached to the plastics and the scale of their contribution to marine biogeochemistry [8]. It is also important to understand if the microplastics are biomagnified in higher trophic-level animals leading to ecological consequences or even human health effects via consumption of contaminated seafood [20].

5 Endnote by the Editors

According to Thompson [7], we already know that marine debris is damaging to the economy, to wildlife, and to the environment and that its sources need to be stopped. If the effect to human can be documented, it will be a stronger evidence for policy to take effective measures. However, if this happens, it would mean that plastic pollution has already irreversibly entered the human food chain. Before this happens, better communication of new science and increased attention to improve waste management and smarter plastic product design should be used as effective measures that are proposed based on scientific merit [3]. We have to take multiple options, e.g., affording economic incentive to reduce plastic wastes, improvement of systems to facilitate the recycling of plastics, environmentally sound waste management, reusable and recyclable products, biodegradable biomass-based materials, etc. Among these, the most simple, direct, and effective option is reduction of single-use plastics. Lastly, we like to conclude this volume with a quoting statement by Dr. Habib N. El-Habr of the United Nations Environment Programme (UNEP) addressing the 6th International Marine Debris Conference held at San Diego, CA, in March 2018, "Improvement of waste management is important. However, considering long-term impact, production of unnecessary single-use plastics should be reduced."

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Erratum to: Food Containers and Packaging Materials as Possible Source of Hazardous Chemicals to Food

Evangelia Manoli and Dimitra Voutsa

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For this chapter, the following belated corrections were received from author:

1. The sentence "Alternatively, the use of natural antioxidants, particularly tocopherol, plant extracts, and essential oils from herbs and spices, is proposed [5, 13, 90]" in fourth paragraph of section 3. Additives in Plastics has been replaced with Alternatively, the use of natural antioxidants, particularly tocopherol, plant extracts, and essential oils from herbs and spices, is proposed [5, 13, 20]
2. Shotyk et al. (2006) in fifth column of table 4 has been replaced with Shotyk et al. (2006) [111]
3. Krachler and Shotyk (2009) in fifth column of table 4 has been replaced with Shotyk and Krachler (2007) [107]

The updated online version for this chapter can be found under
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4. The sentence “TLi et al. [53] reported that 4NP was present in 21 brands of bottled water in all samples purchased from local supermarket in Guangzhou, China, at concentrations ranging from 108 to 298 ng/L;” in fourth paragraph of section 5.2 Alkylphenols has been replaced with “Li et al. [52] reported that 4NP was present in 21 brands of bottled water in all samples purchased from local supermarket in Guangzhou, China, at concentrations ranging from 108 to 298 ng/L”
5. The citation [89] at the end of second paragraph of section 5.6 Antimony has been replaced with citation [110]
6. Year of reference 64 has been changed from 2011 to 2010
7. A new reference “Makris KC, Andra SS, Herrick L, Christophi CA, Snyder SA, Hauser R (2013) Association of drinking water source and use characteristics with urinary antimony concentrations. J Exposure Sci Environ Epidemiol 23(2):120–127” has been added to the reference list

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