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

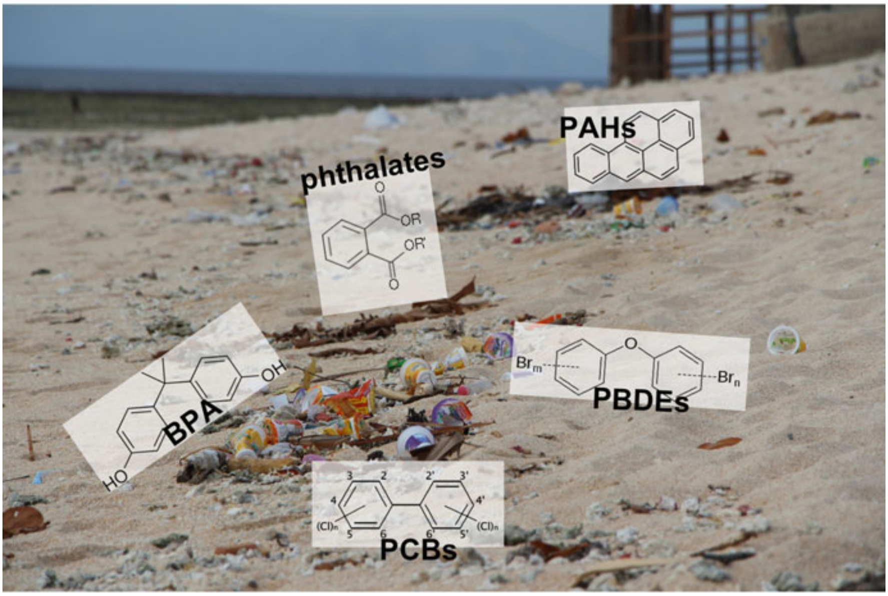

Fig. 1 Cocktail of contaminants associated with plastic debris in the environment. Plastic debris on a beach in Indonesia. The image shows the chemicals that may be associated with this plastic debris, including chemical ingredients (polybrominated diphenyl ethers (PBDEs), phthalates, and bisphenol-A (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).

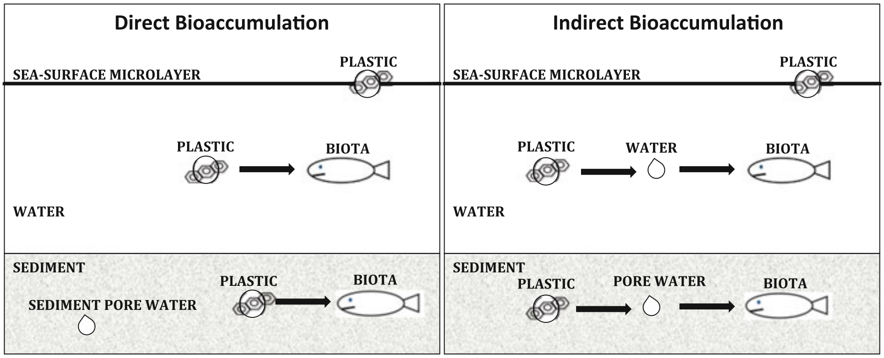

Fig. 2 Mechanisms for the bioaccumulation of chemicals from plastic debris. The diagram depicts different pathways for how chemicals may transfer to biota in aquatic habitats. Bioaccumulation may occur directly via ingestion of plastic (*left*) or indirectly via desorption of chemicals from plastic into 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

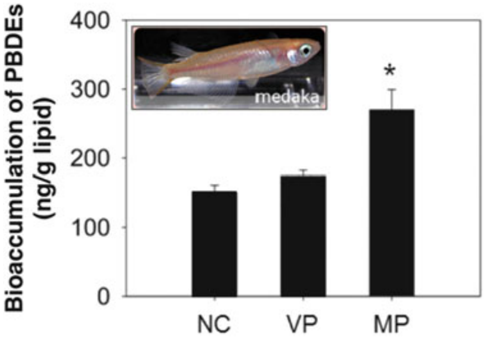

Fig. 3 Laboratory experiments demonstrated that plastic may be a relatively important source of some hazardous chemicals to fish. Japanese medaka that was fed with plastic deployed in the marine environment (MP) accumulated significantly greater concentrations of PBDEs (BDE#47, 49, 99, 100, 153, 154, 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

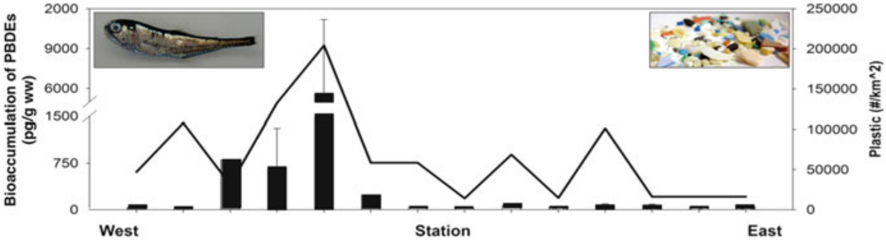

Fig. 4 *Field experiments* suggest that plastic debris is a source of some hazardous chemical contaminants to wild-caught fish. The density of plastic (*solid line*) is significantly correlated ($P < 0.01$, $R^2 = 0.23$) with the concentration of the sum of PBDEs (BDE#7, 8, 10–13, 15, 17, 25, 28, 30, 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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