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Plastic Additives in the Ocean

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2.1 Function of Plastic Additive Classes

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

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

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

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

Source: “Typical loadings” are the max and min ranges reported by Geyer et al. 2017, Zweifel et al. (2001), Hahladakis et al. (2018), Andrady and Rajapaske (2019), and Ambrogi et al. (2017).
^aThese are market sizes for all applications, not just in plastics.

^bThe majority of alkylphenols (APs) found in the environment are degradation products of surfactants, not plastic additives.

^cIf phosphites are used, the loadings can be higher than the range indicated.

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

2.2 Functional Additives

2.2.1 Plasticizers

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

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

2.2.2 Flame Retardants

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

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

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

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

Source of data: Zero Breast Cancer. (2014). “Phthalates: The Everywhere Chemical.” Retrieved October 8 2020, from https://www.niehs.nih.gov/research/supported/assets/docs/j_q/phthalates_the_everywhere_chemical_handout_508.pdf.
Note: Several phthalates have been banned by the European Union (EU) or the United States for use in toys or childcare articles at concentrations >0.1% (ZBC 2018).

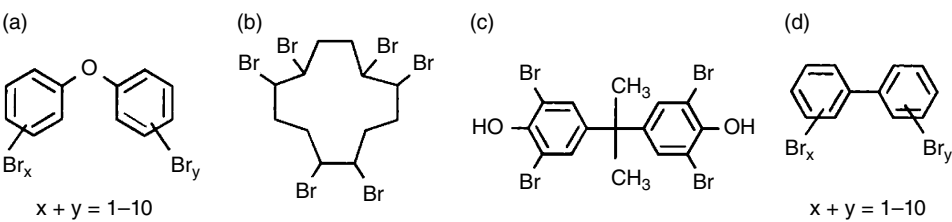


Figure 2.1 Chemical structures of (a) PBDE, (b) HBCD, (c) TBBPA, and (d) PBB.

and van der Meer 2020). Metal hydrate FRs are typically aluminum trihydroxide and magnesium hydroxide that hydrates decompose under high heat to release water, preventing propagation (Innes and Innes 2002).
FRs have a high propensity to migrate out of the plastic into surrounding environments. Some FRs are used as mixtures of congeners, such as commercial PBDEs, with certain congeners more toxic than others. Although some commercial PBDEs (penta-BDE, octa-BDE, and deca-BDE) have been phased out (Sharkey et al. 2020), they will remain in the environment for many years because of their persistence.

2.2.3 Antioxidants

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

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

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

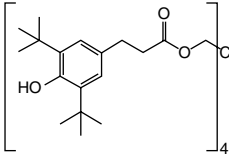
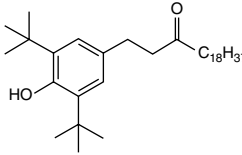
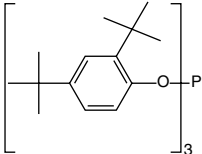
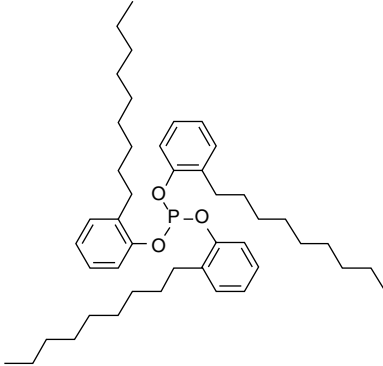
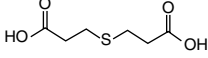
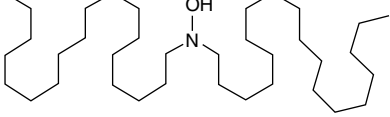
2.2.4 Heat Stabilizers

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

2.2.5 Impact Modifiers

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

Table 2.3 Examples of common antioxidant additives used in plastics.

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

elastomeric and rubbery and have a lower modulus than the host polymer system. When effectively dispersed into the polymer matrix, the rubbery phase of the IM acts to absorb or dissipate the energy from impact in order to stop craze or crack propagation. IMs can be grafted to the polymer during polymerization or physically blended during compounding. Styrenic oligomers/ copolymers, such as ABS and methyl methacrylate-butadiene-styrene, make up the largest category of IMs, accounting for about 45% of the market (Markarian 2004). These along with acrylics that command 30% of the market and are used mostly in PVC. Elastomers, including

ethylene-propylene-diene terpolymer (EPDM) and thermoplastic elastomers, make up about 10% used with polyolefins. The remainder is made up of chlorinated polyethylenes (CPE) and other types. IMs, such as ABS, EPDM, and CPE, are also “stand-alone” plastic products. These materials are used as IMs in their oligomeric forms (i.e. MWs of 5000–20 000 g/mol; Ambrogi et al. 2017). Similar to plasticizers and FRs, IMs are often used at relatively high concentrations in the plastic formulation. However, since most IMs are large molecules, leaching from the plastic into the environment has not been a major concern.

2.2.6 Lubricants

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

2.2.7 Light Stabilizers

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

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

2.2.8 Colorants

Colorants are chemical compounds that not only impart color to plastic materials but can also affect other properties, such as weather resistance, light stability, and transparency of the plastic. Colorants fall into two distinct classes: dyes and pigments; main distinction being dyes are soluble in the plastic matrix while pigments are insoluble. Most commonly used are the azo dyes that make up $>50\%$ of all dyes listed in the Color Index (Ambrogi et al. 2017) and used in textiles, paper,

leather, rubber, or even foodstuffs (Ambrogi et al. 2017). Since organic dyes dissolve in the polymer, they do not scatter but only absorb light. Therefore, even at high concentrations of the dye, the plastic tends to be transparent or translucent. Some dyes such as aromatic amines, are known carcinogens and phthalocyanines have detectable estrogenic activity (Yang et al. 2011).

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

2.2.9 Fillers and Reinforcements

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

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

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

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

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

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

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

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

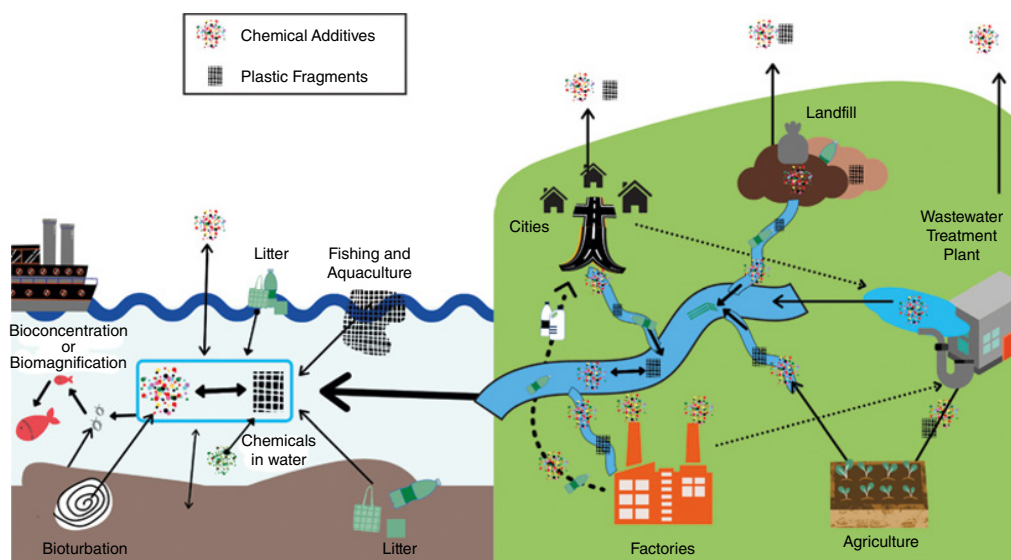


Figure 2.2 Complex sources and transport of plastic additives to, from, and within the ocean.

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

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

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

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

2.3.1 The Simple Release of Additives From Plastics to Water

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

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

Steps 2 through 4, or the migration of additives at the plastic–seawater boundary, are mainly determined by the partition coefficient between plastic and water (K_{pw} ; Endo et al. 2013). Additives with higher K_{pw} (more hydrophobic) will leach slower because they diffuse away from the polymer–water

interface toward the plastic core. Despite its importance, K_{pw} values for most additives in common plastics have not been measured or reported. Fortunately, the water solubility and octanol–water partition coefficient (K_{ow}) can be used as chemical properties to estimate the leaching kinetics of plastic additives in seawater (also see Chapter 9). Table 2.5 provides these properties for a list of additives commonly identified in the marine environment.

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

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

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

2.3.2 The Complexity of Intentionally Added Versus Adsorbed Additives

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

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

Table 2.5 Reported log *K*_{ow} values, water solubility, molecular weight, and LD₅₀ values of common plastic additives.

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

Triphenyl phosphate	TPP	Antioxidant	4.59	1900	326.3	1.7
2-Tert-butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol	UV326	Light stabilizer	5.55	0.68	315.8	100 ^b
2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol	UV327	Light stabilizer	6.91	0.026	358	N/A
2-(benzotriazol-2-yl)-4,6-bis(2-methylbutan-2-yl)phenol	UV328	Light stabilizer	7.25	0.015	351.5	>0.083
Nonylphenol	NP	Multiple	4.48–4.80	4.9	220.35	0.31
Styrene	Styrene	Monomer	5.23–5.64	300	104.15	23
Bisphenol A	BPA	Monomer	3.40	120–300	228.29	11.9
Titanium dioxide	TiO2	Colorant	2.23	1.634	79.87	5.5
Carbon black	CB	Colorant	3.97–5.74	Insoluble	12.011	>5,600 ^b
Basic Red 51	BR51	Colorant	N/A	97.91	279.77	0.10
Cadmium	Cd	Colorant, etc.	N/A	N/A	112.41	0.054
Copper	Cu	Colorant, etc.	N/A	N/A	63.55	0.10
Zinc	Zn	Heat stabilizer, etc.	N/A	N/A	65.4	0.928
Calcium carbonate	CaCO ₃	Filler	–2.12	1000	100.09	>>>800

Source:

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

^b 24-hour exposure.

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

Red shades indicate >5 log K_{ow} (concern for bioaccumulation/biomagnification) or LD₅₀ < 1 (concern for acute aquatic toxicity).

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

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

2.3.3 The Complexity of Multiple Compartments

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

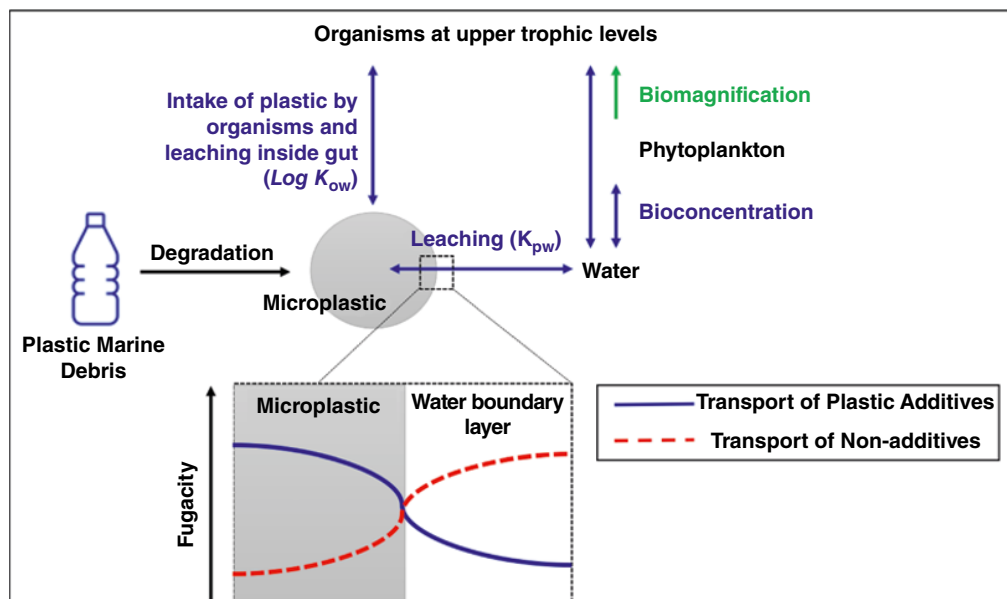


Figure 2.3 Transport and fate of hydrophobic organic chemicals to/from marine plastic particles, seawater, and biota. *Source:* Adapted from Kwon et al. (2017).

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

2.3.3.1 Transport of Plastic Additives to/From Marine Sediment

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

2.3.3.2 Transport of Plastic Additives to/From Marine Biota

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

2.4 Degradation of Plastic Additives in the Marine Environment

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

With phthalates, biodegradation is likely the most important removal process from water (Net et al. 2015). Many phthalates biodegrade into less toxic metabolites, for instance DEP to MEP and phthalic acid (PA) in soils (Cartwright et al. 2000). Both aerobic or anaerobic microorganisms,

including marine-derived fungi, biodegrade phthalates, and higher order animals, also can rapidly biotransform phthalates (Net et al. 2015, Carstens et al. 2020). Paluselli et al. (2019) found that DnBP, DiDP, BzBP, and DEHP were >85% degraded within 49 days of incubation in aerobic seawater. In marine sediments, half-lives of monoalkyl phthalate esters were between (18 ± 4 and 35 ± 10) hours (Otton et al. 2008). Phthalates can also degrade in the marine environment *via* photodegradation and hydrolysis of the ester moiety to PA and the corresponding alcohols via the monoesters. These processes, however, are recognized to be less important than biodegradation (Yan et al. 1995).

2.5 Detection in the Marine Environment

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

2.5.1 Plastic Samples

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

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

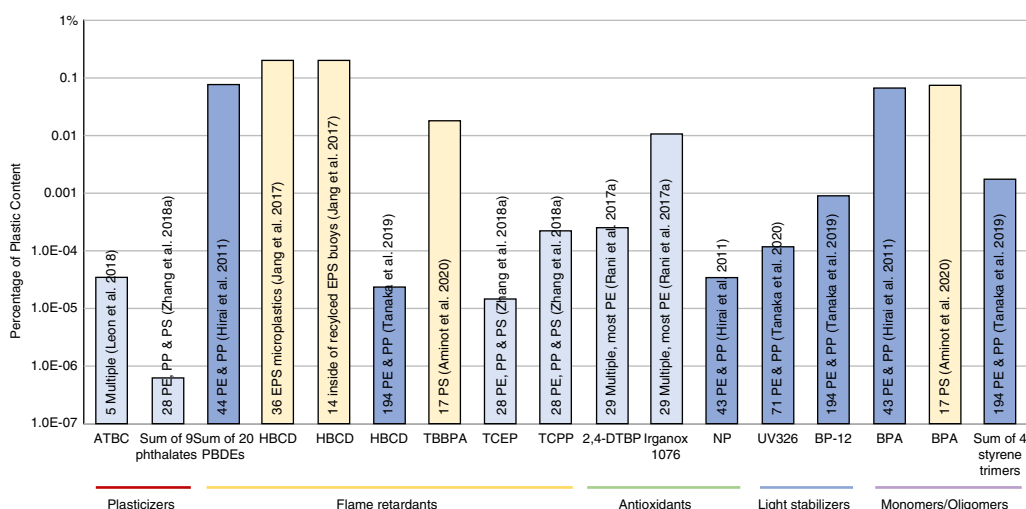


Figure 2.4 Mean concentrations of additives measured in plastics found in the marine environment, shown in logarithmic units of percent content of the plastic sample. *Note:* Sample size, polymer type, and reference are shown inside the bars. Data bars are color coded by polymer of samples (light blue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

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

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

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

2.5.2 Abiotic Samples

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

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

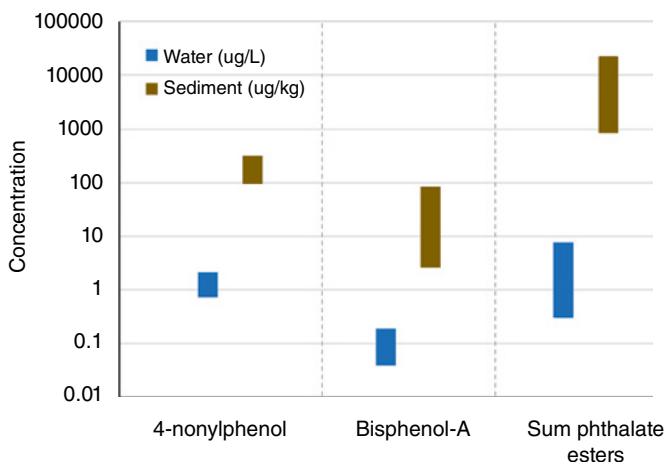


Figure 2.5 Range of concentrations of three plastic additive classes measured in paired seawater and sediment samples. *Note:* Data were taken from de los Rios et al. (2012) for 4-nonylphenol and bisphenol A in natural samples from the Bay of Biscay; and from Zhang et al. (2018b) for phthalates in Bohai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

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

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

2.5.3 Biotic Samples

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

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

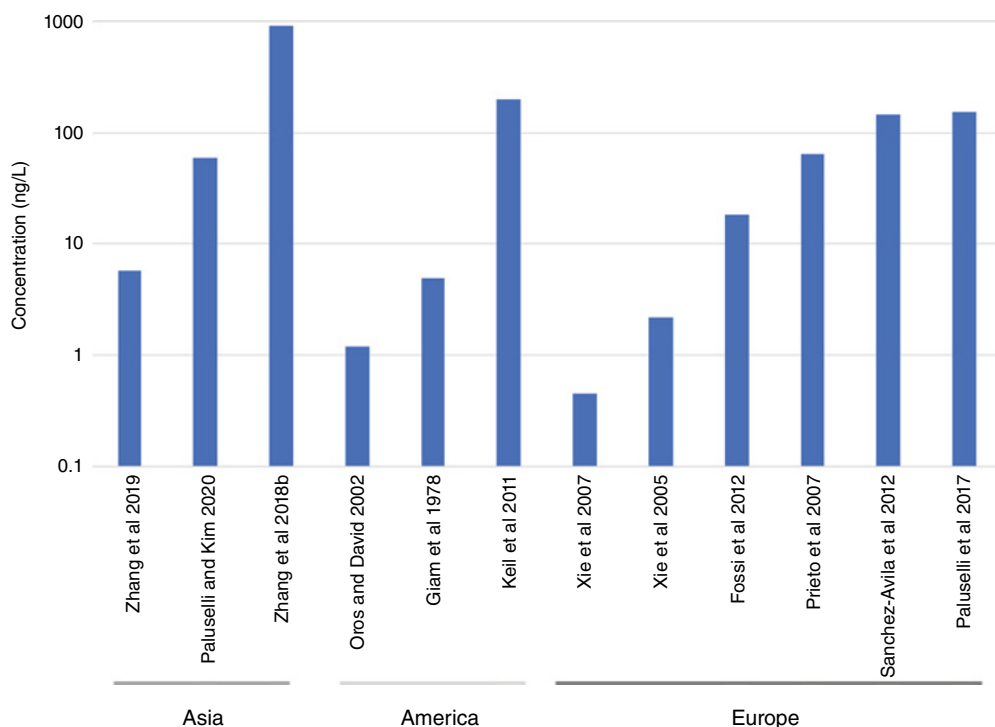
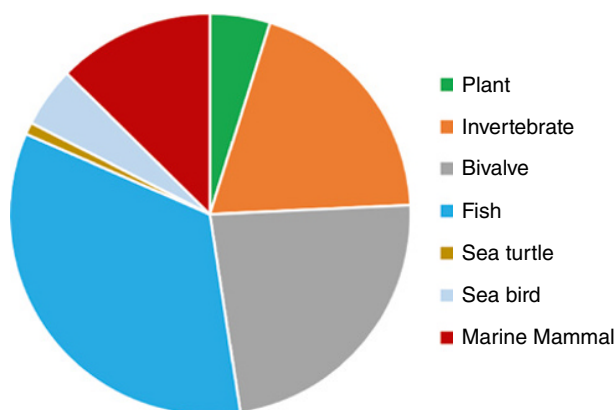


Figure 2.6 An updated spatial comparison of mean concentrations of DEHP measured in marine surface waters from Asia, America, and Europe.

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



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

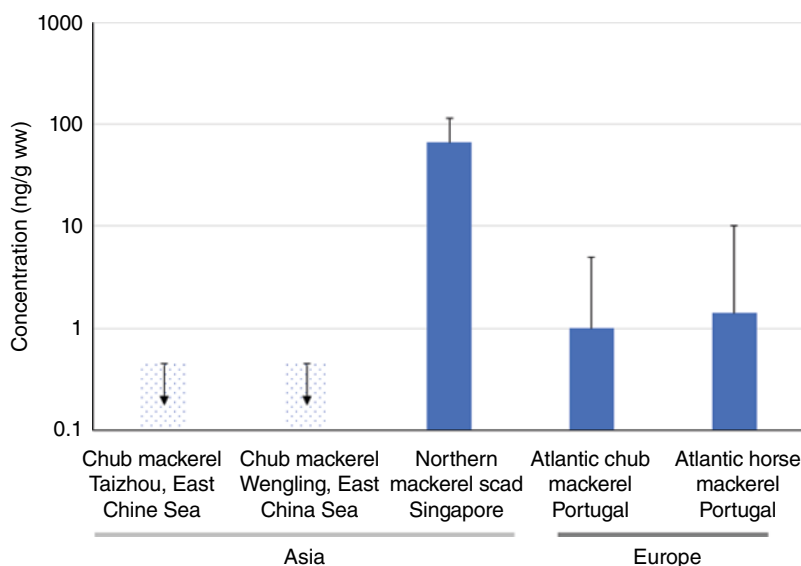


Figure 2.8 Spatial comparison of bisphenol A mean concentrations in muscle tissue from mackerel and scad fish species. *Source:* Data were taken from Gu et al. (2016), Basheer et al. (2004), and Barboza et al. (2020). *Note:* Sample sizes are 1, 4, 5, 50, and 50 from left to right, respectively. Dotted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

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

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

Certain additives can biomagnify in food webs, while others, like plastics themselves, do not (Covernton et al. 2021; Koelmans et al. 2016; Tomy et al. 2008). From our database, 12 studies investigated biomagnification of additives in marine food webs (see Box 1.2 in Chapter 1 for a

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

2.6 Toxicity of Additives

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

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

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

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

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

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

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

Table 2.7 Plastic additives that are endocrine-disrupting compounds.

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

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

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

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

2.7 NIST Disclaimer

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

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