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PBDEs in the marine environment: Sources, pathways and the role of microplastics☆

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ABSTRACT

Brominated flame retardants (BFRs) are an important group of additives in plastics that increase resistance to ignition and slow down the rate of burning. Because of concerns about their environmental and human health impacts, however, some of the most widely employed BFRs, including hexabromocyclododecane (HBCD) and commercial mixtures of penta-, octa- and deca- (poly)bromodiphenyl ethers (PBDEs), have been restricted or phased out. In this review, the oceanic sources and pathways of PBDEs, the most widely used BFRs, are evaluated and quantified, with particular focus on emissions due to migration from plastics into the atmosphere versus emissions associated with the input of retarded or contaminated plastics themselves.

Calculations based on available measurements of PBDEs in the environment suggest that 3.5 and 135 tonnes of PBDEs are annually deposited in the ocean when scavenged by aerosols and through air-water gas exchange, respectively, with rivers contributing a further ~40 tonnes. Calculations based on PBDE migration from plastic products in use or awaiting or undergoing disposal yield similar net inputs to the ocean but indicate a relatively rapid decline over the next two decades in association with the reduction in the production and recycling of these chemicals. Estimates associated with the input of PBDEs to the ocean when "bound" to marine plastics and microplastics range from about 360 to 950 tonnes per year based on the annual production of plastics and PBDEs over the past decade, and from about 20 to 50 tonnes per annum based on the abundance and distribution of PBDEs in marine plastic litter. Because of the persistence and pervasiveness of plastics in the ocean and diffusion coefficients for PBDEs on the order of 10^{-20} to 10^{-27} m^2 s^{-1}, microplastics are likely to act as a long-term source of these chemicals though gradual migration. Locally, however, and more important from an ecotoxicological perspective, PBDE migration may be significantly enhanced when physically and chemically weathered microplastics are exposed to the oily digestive fluids conditions of fish and seabirds.

1. Introduction

Many plastics contain additives, or substances that are mixed with the base polymer during manufacturing that improve performance or modify the physical or chemical properties of the final product (Pfaendner, 2006). Flame retardants are an important group of functional additives in electrical plastics, soft furnishings, fabrics and some paints that increase resistance to ignition, slow down the rate of burning and generate less heat compared with the unmodified material (Troitzsch, 1983). Because of their ability to capture free radicals released during combustion, halogenated compounds have had widespread use in plastics as flame retardants, with organobromine compounds more popular than organochlorines because of their higher free radical trapping efficiency and lower decomposition temperature (Alaee

Table 1
Physico-chemical properties of tetrabromobisphenol-A, hexabromocyclododecane, and the commercial mixtures of penta-, octa- and decabromodiphenyl ethers, and their typical concentrations used in flame-retarded plastics. Note that the properties of the commercial mixtures are based on data for individual congeners identified by the CAS numbers, and that water solubility and K_{ow} are reported for 20–25 °C. EPS = expanded polystyrene; XPS = extruded polystyrene; PUF = polyurethane foam. Sources of information: Alaee et al. (2003); Papazoglou (2004); Maley et al. (2015); Jang et al. (2017); US EPA (2017); Hennebert (2020); Öko-Institut (2020).

BFR	abbreviation	CAS number (congener)	molecular formula	Br content, %	molecular weight	water solubility, mg L^{-1}	log K_{ow}	relative density	% for flame retardancy	Sb added
tetrabromobisphenol-A	TBBPA	79-94-7	$C_{15}H_{12}Br_4O_2$	58.6	543.9	1.26	5.90	2.17	4–33	✓
hexabromocyclododecane	HBCD	25637-99-4	$C_{12}H_{18}Br_6$	74.7	641.7	0.066	5.62	2.24	0.26–30 for EPS/XPS; > 0.1 in PUF	
pentabromodiphenyl ether	pentaBDE	32534-81-9 (BDE99)	$C_{12}H_5Br_5O$	70.7	564.7	0.0133	6.64–6.97	2.25–2.28	10–18	✓
octabromodiphenyl ether	octaBDE	32536-52-0 (BDE203)	$C_{12}H_2Br_8O$	79.8	801.4	<0.001	6.29	2.76	12–15	✓
decabromodiphenyl ether	decaBDE	1163-19-5 (BDE209)	$C_{12}Br_{10}O$	83.3	959.2	<0.001	6.27	3.00–3.40	5–30	✓

et al., 2003). Antimony, Sb, and usually as antimony trioxide (Sb_2O_3), is often used as a synergist that further improves the efficiency of brominated flame retardants (BFRs) by forming additional radical scavenging compounds in the gas phase (Papazoglou, 2004). (Note that this is in addition to the more general contamination of certain plastics and fibres, and mainly polyethylene terephthalate, PET, by antimony as catalytic residue from the manufacturing process itself.)

Because different plastics have different processing and ignition temperatures, there is no universal BFR (or BFR concentration) that is suitable for all materials, and more than 70 products have been developed. However, only five have been widely used in plastics whose properties are given in Table 1: tetrabromobisphenol A (TBBPA); hexabromocyclododecane (HBCD); and the commercial mixtures of polybrominated diphenyl ethers (PBDEs) (pentabromodiphenyl ether, pentaBDE; octabromodiphenyl, octaBDE; decabromodiphenyl ether, decaBDE) (Gallen et al., 2014). TBBPA is a reactive BFR that is covalently bonded in electronic plastics, including epoxy resin printed circuit boards, and in some paints and synthetic textiles, although it has also been used as an added (non-bonded) BFR in acrylonitrile butadiene styrene (ABS) and, to a lesser extent, high impact polystyrene (PS) (Öko-Institut, 2020). HBCD is a non-aromatic compound with sixteen stereoisomers, three of which dominate commercial mixtures of the compound (α-, β- and γ-HBCD). It has a poor thermal stability but is a very effective retardant at low concentrations and without Sb_2O_3 in expanded, extruded and high impact PS foams that are used in the construction, electronic and upholstering sectors (US EPA, 2014). DecaBDE has been used in a wide range of thermoplastics and thermosets and octaBDE has been used to retard ABS in electronic casings; pentaBDE is generally blended with phosphate esters but without Sb_2O_3 to retard polyurethane foam (PUF) and other thermoset resins (Papazoglou, 2004). Amongst the most important congeners of PBDEs are BDE47 (2,2′,4,4′-tetrabromodiphenyl ether), BDE99 (2,2′,4,4′,5-pentabromodiphenyl ether), BDE183 (2,2′,3′,4,4′,5′,6-heptabromodiphenyl ether) and BDE209 (2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether).

Because of environmental and human health concerns, including both acute and chronic toxicities and propensities to persist and bioaccumulate (de Boer et al., 1998; Breitholtz and Wollenberger, 2003; Darnerud, 2003; Stieger et al., 2014; Gu et al., 2017), many BFRs have been voluntarily phased out or restricted. For instance, the Restriction of Hazardous Substances (RoHS) Directive, effective since 2006, sets maximum concentrations of PBDEs of 0.1% by weight in any component of new electrical and electronic equipment produced for the EU market (European Parliament and Council, 2003; BIS, 2011), with many nations outside the EU subsequently adopting similar, customised regulations (Horn, 2016). HBCD and PBDE congeners in commercial pentaBDE, octaBDE and decaBDE mixtures are also officially recognised as persistent organic pollutants according to the Stockholm Convention and as such measures must be taken to eliminate inputs to the environment (United Nations Environment Programme, 2019; Sharkey et al., 2020).

Despite these restrictions, and the introduction of "safer" but physically and chemically similar "novel" BFRs, such as decabromodiphenyl ethane (DBDPE), bis(2,4,6-tribromophenoxy) ethane (BTBPE) and tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPA-DBPE) (Xiong et al., 2019), legacy BFRs remain in products in use and stockpiled in the technosphere and at e-waste facilities (Sindiku et al., 2015). One consequence of their presence in electronic waste is the inadvertent or illegal recycling into new plastic products (Vojta et al., 2017; Turner, 2018). Typically, this results in the wide contamination of articles with BFRs at levels well below those required for flame retardancy (between 4 and 33% by weight for hard plastics according to Table 1). A particular health concern in this respect is the detection of traces of restricted BFRs in food-contact materials (Puype et al., 2017), kitchen utensils (Kuang et al., 2018) and children's plastic toys (Chen et al., 2009; Fatunsin et al., 2020). In order to prevent BFR contamination of new products, the EU has introduced concentration limits of 1000 mg kg^{-1}, with plans to reduce these to 500 mg kg^{-1}, for PBDEs and HBCD above which
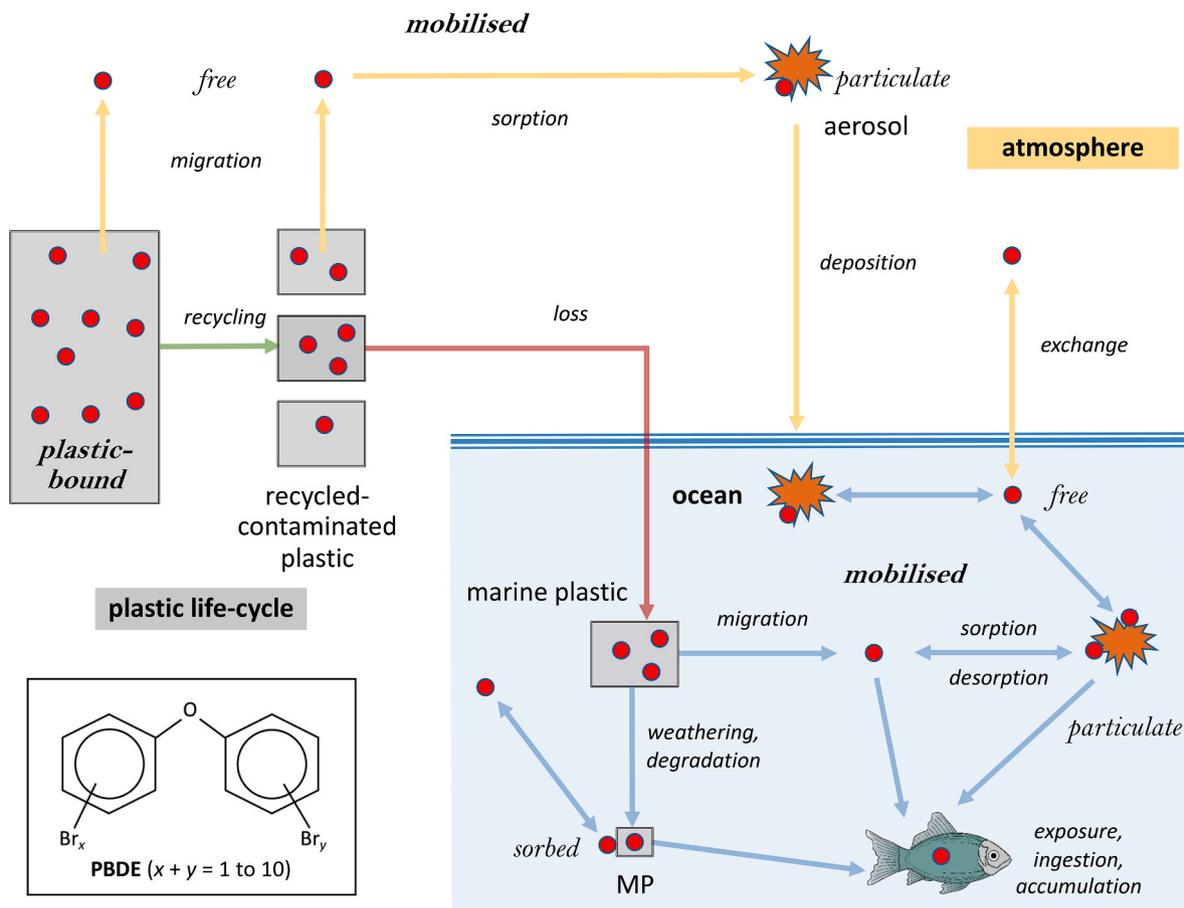
Fig. 1. Molecular structure of PBDEs and conceptualisation and definition of the terms, associations and processes referred to in the discussion. Red dots represent PBDE molecules which can be encountered in plastics (in grey boxes and "bound"), or occur as free or sorbed molecules that have migrated into the environment (mobilised) and are free or are sorbed to aerosols and particulate matter (orange stars) or microplastics (MPs). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
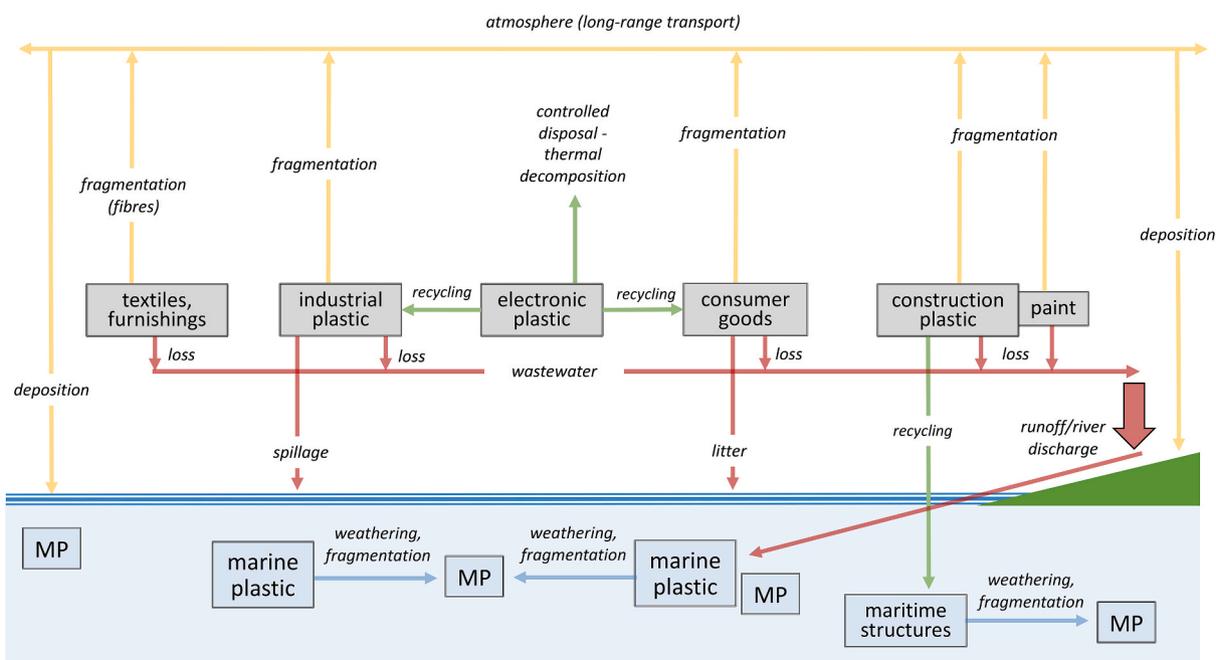
Fig. 2. Environmental pathways of PBDE-bearing plastics in different sectors and their inputs to the marine environment. MP = microplastic.

recycling is not permitted unless the BFR content has been destroyed or transformed (European Commission, 2014, 2016; 2019). Unintentional Trace Contaminant (UTC) limits for HBCD of 100 mg kg^{-1} and commercial mixtures of penta-, octa- and decaBDE of 10 mg kg^{-1} each have also recently been introduced for new plastic articles (European Commission, 2016, 2019).

Because of the "migration" of brominated compounds from retarded and recycled-contaminated products throughout their life cycle, and the littering and improper management and disposal of plastics more generally, the marine environment is an important receptor of BFRs. To this end, the present article critically and quantitatively examines the sources and pathways of PBDEs, the most widely produced group of legacy BFRs, in the ocean. Commercial mixtures and individual congeners of PBDEs have received considerable attention in the scientific literature and recent studies suggest that, despite restrictions, they remain the most important BFRs in plastics in societal circulation and lost to the environment (Abbasi et al., 2019; Fatunsin et al., 2020; Liu et al., 2021). Note that novel BFRs, and in particular, DBDPE, and other legacy BFRs that are restricted but have had more limited or specialised usage (e.g., HBCD and polybrominated biphenyls) are referred to for comparative purposes or where information assists the discussion.

Throughout the paper, PBDEs that have migrated into the environment and remain in free molecular form or that have sorbed to geosolids, like sediments, soils and aerosols, are referred to as "mobilised" and are distinguished from PBDEs that remain physically "bound" (but not bonded) to the plastic itself. However, the interactions and interdependencies of mobilised and bound forms are addressed, with particular attention paid to the role of marine plastics and microplastics (operationally defined with an upper size limit of 5 mm) in this context. As an aid to the paper, Fig. 1 conceptualises and defines some of the important terms, associations and processes that are central to the arguments and discussion, while Fig. 2 illustrates the environmental sources and pathways of specific types (or use sectors) of PBDE-bearing plastics.

2. Sources of PBDEs to the marine environment

Evaporative or fugitive migration of BFRs into the atmosphere occurs during the production and use of plastics and during or after their disposal by landfilling, recycling, controlled incineration or open burning (Wang et al., 2010; Gallen et al., 2016; Xu et al., 2021). Surface evaporation of BFRs that are uniformly bound in plastic is rate-limited by internal diffusion within the matrix, with the rate of diffusion related to properties of the plastic, including crystallinity, glass transition temperature, degree of unsaturation, the presence of other additives and any surface and structural modifications arising from weathering, and the size (molar volume) of the compound (Calo et al., 2011; Wei et al., 2019). For PBDEs in unweathered ABS used in electronic casings, Sun et al. (2016) empirically derived diffusion coefficients, D, at 10–30 °C that ranged from about 10^{-20} to 10^{-27} m^2 s^{-1}, with a clear decrease in the magnitude of D with increasing degree of bromination. Based on available information on diffusion and vapour pressures, Redfern et al. (2017) suggest emission factors of various PBDEs from polymers and textiles while in use of between about 10^{-2} and 10^{-7}, while Lassen et al. (1999) suggest that between 0.1 and 0.4% of PBDEs are lost to the indoor atmosphere from various domestic electronic devices through surface evaporation during a ten-year service life. Because diffusion is temperature-dependent and diffusive release fluxes are inversely related to particle size, surface evaporation is predicted to be enhanced during the dismantling, recycling or disposal of plastics where thermal treatment or shredding-pulverisation is involved (Sun et al., 2016).

Bound PBDEs may also be input into the environment with waste plastic itself. Sources here include microplastics and fibres generated by physical abrasion on disposal (Harrad et al., 2019), fibres discharged to wastewater or the atmosphere on laundering (Dalla Fontana et al., 2020; O'Brien et al., 2020), and larger plastics, including occasional electronic articles, arising from losses through littering, spillages and improper management of waste (Shaw and Turner, 2019). Both bound and mobilised PBDEs enter the ocean with atmospheric deposition (including gaseous exchange for mobilised forms), river discharge and treated and untreated wastewater. Additionally, PBDEs may be associated with plastic products or structures that are directly used in or lost to the marine environment. As an example, mm-sized (microplastic) biobeads derived from the recycling of historical and flame retarded electronic waste are often used as filtering media in the treatment of sewage and other wastes (Turner et al., 2019).

In the ocean, plastics and microplastics may act as both a source of mobilised PBDEs through diffusive migration from the matrix into the aqueous phase and a sink for mobilised PBDEs through sorption at the plastic surface, with both associations acting as a potential route of exposure to and accumulation by marine life (Tanaka et al., 2013; Chua et al., 2014; Rochman et al., 2014). Empirical studies reveal that the sorption of PBDEs is dependent on characteristics of the plastic, like crystallinity, surface area and surface structure, as well as properties of the aqueous phase, including temperature and the nature and concentration of organic matter (Xu et al., 2019; Singla et al., 2020).

3. Estimates of mobilised PBDE inputs to the ocean

The atmosphere is able to disperse mobilised BFRs widely, with direct inputs to the ocean taking place through dry and wet deposition of particulate matter and gaseous exchange of free molecules at the air-ocean interface. Fluxes of various PBDEs and other BFRs have been estimated from measurements performed in the atmosphere and surface waters along transects of various oceanic regions. In the eastern Atlantic and the Southern Ocean, Xie et al. (2011) estimated a summed median dry deposition flux for different BFRs of about 0.005 ng m^{-2} day^{-1}, with the largest contribution arising from BDE47, a constituent of commercial pentaBDE. The summed median net deposition flux for air-water gas exchange was about 1 ng m^{-2} day^{-1}, with the dominant contribution from hexabromobenzene (HBB), a restricted polybrominated biphenyl. While the production of HBB has been relatively low compared with PBDEs, it was suspected that significant quantities of the compound may have been derived from the degradation of high molecular weight PBDEs in the tropics or during e-waste burning in Africa.

Lohmann et al. (2013) estimated depositional fluxes for PBDEs in the tropical and subtropical Atlantic Ocean. Gas phase deposition was greatest, and up to about 1 ng m^{-2} day^{-1}, for BDE47, BDE99 (a constituent of commercial pentaBDE) and BDE209 (a constituent of both commercial octaBDE and decaBDE), while dry deposition for the respective congeners was about 0.050, 0.01 and 0.1 ng m^{-2} day^{-1}. In the western coastal Pacific and Arctic Oceans, Möller et al. (2011) estimated gaseous depositions of up to 0.05 ng m^{-2} day^{-1} for BDE47 and BDE99, with dry depositions of up to 0.1 ng m^{-2} day^{-1} in the Arctic and 2.9 ng m^{-2} day^{-1} along the Pacific coast of east Asia. In the East China Sea and northwest Pacific Ocean, Wu et al. (2020) estimated gaseous depositions of PBDEs ranging from about 0.05 to 0.58 ng m^{-2} day^{-1}, with the main contributions from BDE47, BDE99 and BDE209. Dry deposition was dominated by BDE209 and estimates ranged from about 0.85 to 2.7 ng m^{-2} day^{-1} in the coastal zone and from about 0.02 to 0.18 ng m^{-2} day^{-1} in the open ocean. In the German coastal region of the North Sea, Möller et al. (2012) estimated gaseous deposition of up to 0.23 and 0.08 ng m^{-2} day^{-1} for the dominant PBDE congeners, BDE47 and BDE99, respectively, with a total PBDE dry deposition rate of up to 1.4 ng m^{-2} day^{-1}.

Although the estimates and the target BFRs and PBDEs considered in these studies are variable, one of the key observations is the shift in importance of gaseous exchange relative to dry deposition from the coastal zone to the open ocean. Using data from both open ocean and coastal sites, and considering independent results reported in the literature, Lohmann et al. (2013) suggest annual PBDE inputs to the Atlantic Ocean of about 40 tonnes and one tonne for gaseous and dry deposition, respectively. Scaling this up to the global ocean results in respective

estimates of about 135 and 3.5 tonnes.

Measurements of mobilised PBDEs in river waters allow estimates of ocean inputs from land drainage to be made. These inputs are largely via atmospheric deposition within the catchment, but may also include municipal and industrial wastes in some regions, and in particular where restricted BFRs are still manufactured. In a recent study, Liu et al. (2021) measured various BFRs, including PBDEs, in 36 Chinese coastal rivers. BFRs that were both dissolved and particulate (i.e., sorbed to natural, suspended particles) were considered and the study encompassed rural/remote, urban and industrial (including BFR-production) catchments. The overall median concentration of BFRs was 2.9 ng L^{-1}, with PBDEs contributing 2.6 ng L^{-1} (and BDE209 contributing 2.5 ng L^{-1}), and the concentration range of PBDEs was similar to or greater than corresponding measures in other rivers in Asia, Europe and North America (e.g., Oros et al., 2005; Cristale et al., 2013; Pei et al., 2018; Environment Agency, 2019). Assuming a representative, global concentration for PBDEs in river water of 1 ng L^{-1} that is based on these measures, and a global annual input of river water to the oceans of 38, 500 km^3 (Peucker-Ehrenbrink, 2009), an annual riverine flux of 38.5 tonnes is obtained.

All of the estimates above are subject to limitations and uncertainties, including the neglect of debromination and degradation of some compounds in the atmosphere and ocean, possible inclusion of fine, PBDE-bearing microplastics in particulate samples, and, for riverine fluxes, the assumption that all chemicals sorbed to suspended particles evade entrapment in estuaries through flocculation and deposition. Nevertheless, the total input to the ocean of about 175 tonnes per annum is comparable with estimates of annual atmospheric emissions of PBDEs based on in-use and waste stock inventories and illegal burning of e-waste. Specifically, Redfern et al. (2017) provide an upper estimate of annual atmospheric release of PBDEs of about 30 tonnes (that is dominated by decaBDE) based on data for 2016, while Abbasi et al. (2019) estimate maximum annual emissions of between about 200 and 250 tonnes in the decade 2010–2020 and with BDE47 and BDE209 dominating inputs throughout.

4. Concentrations of BFRs in marine plastics and microplastics

Despite their wide use in a variety of sectors, very little quantitative information exists on BFRs in plastics and microplastics that have been lost to the marine environment. Moreover, in reviews of the distributions and behaviour of BFRs in the marine environment, plastic-bound compounds are generally overlooked (Tanabe et al., 2008; Yogui and Sericano, 2009; Lee and Kim, 2015; Zhang et al., 2016).

Table 2 provides a summary of the concentrations of PBDEs reported in the literature for suspended, stranded (beached) and ingested plastics and determined by gas chromatography-mass spectrometry (GC-MS)

following solvent extraction; note that nearly all samples are polyolefin-based and are, therefore, positively buoyant in seawater. Deng et al. (2021) report a maximum concentration of PBDEs in plastic fragments retrieved from wetland sediments of the Yangtze Estuary of 250 mg kg^{-1}, and indicate that BDE209 is the dominant congener overall, while Tanaka et al. (2019) found 1100 mg kg^{-1} of decaBDE (and mainly BDE209) in a single polypropylene (PP) fragment ingested by a northern fulmar. Although these concentrations appear to be the highest reported in the environmental literature, they are insufficient to effect flame retardancy according to information in Table 1 and, therefore, likely represents plastic contamination by the recycling and blending of retarded plastics. In other studies of PBDEs in plastics and microplastics retrieved from beaches or sampled from the ocean, however, measured concentrations are much smaller. Specifically, concentrations of total PBDEs never exceed 10 mg kg^{-1} and are generally well below 1 mg kg^{-1}, with typical or median values often orders of magnitude lower. Many of these studies attribute the presence of PBDEs to the general contamination of plastics and the sorption of free (mobilised) compounds to the MP surface from surrounding seawater. However, it is unclear why concentrations of PBDEs arising from contamination through recycling-blending should be so low or why sorbed concentrations on similar plastics from the same region should be so variable. Modification of the PBDE content of plastic may occur through environmental processes, including photodegradation (Hirai et al., 2011) or mobilisation from the matrix (Cheng et al., 2020; discussed below). However, inconsistencies in sample processing and analytical constraints must be factored in. Thus, firstly, in many studies microplastics are pooled together, and the resulting "average" concentration may reflect much higher concentrations in specific particles which are diluted by microplastics that are largely BFR-free. Secondly, some studies omit BDE209 from the suite of PBDEs analysed, while other studies suggest that this is the dominant PBDE congener. Thirdly, the efficacy of the extraction protocol has sometimes been queried; for instance, Hirai et al. (2011) acknowledge that they underestimate the concentrations of BDE209 because of the polarity of the solvent employed.

5. Concentrations of bromine in marine plastics and microplastics

A broader, but less sensitive and quantitative assessment of BFRs in marine plastics and microplastics may be gained from X-ray fluorescence (XRF) analysis (Allen et al., 2008; Gallen et al., 2014; Turner and Solman, 2016). Although XRF is unable to discriminate specific brominated compounds, it provides a rapid, non-destructive means of determining total bromine (Br) content and the presence of Sb as a synergist and circumvents some of the drawbacks associated with targeting individual BFRs highlighted above. Table 3 summarises published and

Table 2

Concentration range of total PBDEs and decaBDE (or BDE209) determined in marine plastics and microplastics. Sample description reflects the terminology reported in each case. PE = polyethylene; PP = polypropylene; PS = polystyrene. [a] Often reported as BDE209; [b] excluding BDE209; [c] not stated but beached pellets are usually polyolefin-based.

Environment	Sample description	Polymers	DecaBDE[a], mg kg^{-1}	Total PBDEs, mg kg^{-1}	Reference
Suspended					
North Pacific gyre	fragments	PE, PP	<0.001–9.9	<0.001–9.9	Hirai et al. (2011)
North Pacific gyre	fragments (hard)	PE, PP		<0.001–0.19	Chen et al. (2018)
	nets and ropes	PE, PP		<0.001–0.05	Chen et al. (2018)
	pellets	PE, PP		<0.001–0.07	Chen et al. (2018)
Japanese coastal waters and North Pacific	microplastics	PE, PP	<0.001–2.2	<0.001–2.5	Yeo et al. (2020)
Stranded					
Pacific remote beaches	fragments and pellets	PE, PP	<0.001–0.40	<0.001–0.42	Hirai et al. (2011)
Pacific urban beaches	fragments and pellets	PE, PP	<0.001–0.23	<0.001–0.23	Hirai et al. (2011)
Canary Island beaches	fragments and pellets (<25 mm)	PE, PP		<0.001–3.9[b]	Camacho et al. (2019)
Brazilian urban beaches	pellets	PE, PP[c]		<0.001–0.003[b]	Taniguchi et al. (2016)
Yangtze Estuary sediments	fragments (13–170 mm)	mainly PE,PP, PS		<0.001–250	Deng et al. (2021)
Ingested					
Northern fulmar stomach	fragments (2–15 mm)	PP	1100		Tanaka et al. (2019)

Table 3

Percentage of beached plastic and microplastic samples from different categories in which Br was detected by XRF and accompanying concentration ranges (detection limit ranges from about 2 to 20 mg kg^{-1} depending on sample thickness, porosity and composition, and concentrations highlighted in bold denote sufficient quantities of BFRs for flame retardancy in the specific plastic type or group of plastic types identified). The presence of Sb in more than 10% of samples which were Br-positive is indicated, along with dominant polymer types (EPS = expanded polystyrene; XPS = extruded polystyrene; PA = polyamide; PE = polyethylene; PET = polyethylene terephthalate; PP = polypropylene; PS = polystyrene; PUF = polyurethane foam; PVC = polyvinyl chloride). [a] Br detected in one sample only; [b] less than 5% abundance; nd = not determined.

Category (number of samples analysed)	Polymers	% Br detected	Br, mg kg^{-1}	Sb present	Reference
pre-production pellets ($n = 79$)	PE, PP	1.3	12[a]		Turner et al. (2019)
biobeads ($n = 497$)	PE	49.7	5.4–6730	✓	Turner et al. (2019)
foam fragments ($n = 27$)	EPS, XPS	85	12-**11,500**		Turner and Lau (2016)
foam fragments ($n = 39$)	PUF	87	21-**5820**		Turner and Lau (2016)
plastic objects ($n = 93$)	PE, PP, PVC[b]	26	3.5–1840	✓	Shaw and Turner (2019)
secondary plastics ($n = 258$)	PE, PP, PVC[b]	30	3.8–**43,400**	✓	Shaw and Turner (2019)
rope ($n = 153$)	PA, PE, PP, PA	52	3.9–2420	✓	Turner (2017)
pyroplastics ($n = 165$)	PE, PP	73	2.9–346	✓	Turner et al. (2019)
food packaging ($n = 62$)	PE, PET, PS, PVC[b]	0			unpublished
urban paints ($n = 46$)	nd	43	159–1570	✓	unpublished
antifouling paints ($n = 52$)	nd	35	22.2–511	✓	unpublished
lint ($n = 70$)	nd	89	5.5–213	✓	Turner et al. (2019)

unpublished Br results from the author's database for a range of individual plastic and microplastic samples retrieved from beaches of southwest England and samples representative of microplastic inputs to the marine environment. All data were derived from XRF analysis using a Niton He XL3t GOLDD+ operated in a plastics mode and with thickness correction and whose performance was checked with reference plastic discs impregnated with known quantities of Br. Bromine data are shown as frequency of detection and concentration range for different sample categories, with concentrations sufficient for flame retardancy highlighted. Also shown are dominant polymer types and an indication of whether Sb was present in more than 10% of Br-positive samples in each category.

The range of Br concentrations in foamed PS determined by XRF is entirely consistent with the concentrations of HBCD determined in stranded marine EPS fragments from the Asia-Pacific region (up to 14,500 mg kg^{-1}; Jang et al., 2017) given the mass percentage of Br in HBCD, and the lack of detectable Sb amongst foamed samples is in agreement with the incompatibility of antimony-based synergists in such plastics. Qualitatively, lack of detection of Br in microplastic pre-production pellets concords with the lowest levels of BFRs reported for beached polyolefin pellets by Taniguchi et al. (2016) and Camacho et al. (2019). Other types of beached litter (including biobeads, pyroplastics, ropes, and objects and fragments that are usually black in colour), however, exhibit maximum Br concentrations orders of magnitude greater than those reported for total and specific PBDEs above, and include samples in which sufficient Br is present to effect flame retardancy. The data also suggest that BFRs may be widely dispersed amongst additional marine plastics and microplastics that have not yet been considered in this respect, like microfibres derived from laundering and household textiles and where dryer lint may be used as a proxy and a composite, and paint particles derived from certain coatings on maritime and land-based structures.

Given the historical production and usage of PBDEs and their significance in (unfoamed) plastic products in use and in waste stocks (Kuang et al., 2018; Abbasi et al., 2019; Li et al., 2019; Hennebert, 2020; Kajiwara et al., 2022), it is likely that they represent a high proportion of the BFRs in the hard plastics reported in Table 3. For example, a recent comparison of total Br determined by XRF (Niton XL3t He GOLDD+) and summed BFR content (including both legacy and novel BFRs) determined by gas chromatography-mass spectrometry (GC-MS) following solvent extraction has been performed for 23 homogenous consumer plastics (and mainly toys where recycling had been suspected) by Fatunsin et al. (2020). Overall, there was a statistically significant relationship between Br concentration returned by the XRF (y) and BFR content determined by GC-MS (x), with a slope of about 1.4. In all samples, BFRs were dominated by HCBD, various PBDE congeners (and

mainly BDE209) or TBBA, with one or more PBDE congeners detected in all cases and the total BFR content of 14 samples comprising >50% PBDEs. Discrepancies between the XRF and GC-MS approaches were attributed to the presence of brominated compounds used in other pigments, such as copper phthalocynanines where Br may be encountered with similar concentrations of Cu in blue-green plastics (Ranta-Korpi et al., 2014), and, to a small extent, the use of BFRs not targeted by GC-MS.

6. Estimates of BFR inputs to the ocean from marine plastics

Estimates of the annual input of plastic-bound BFRs to the oceans may be derived from lower and upper estimates of the annual inputs of plastic provided by Jambeck et al. (2015) (4.8 and 12.7 million tonnes, respectively). Cheng et al. (2020) assumed that 30% of plastics contain flame retardants at a concentration of 15% by mass and that 10% of these retardants are brominated. On this basis, the range of estimated annual contemporary inputs of BFRs to the ocean is about 20,000 to 60,000 tonnes. These figures appear to be rather high given that the annual market demand of the BFRs listed in Table 1 was about 200,000 tonnes when restrictions were being introduced two decades ago (De Wit et al., 2010). Regarding PBDEs, data for 2010 suggest a global manufacture of plastics based on resin production of 270 million tonnes (Jambeck et al., 2015) and a production of PBDEs of about 20,000 tonnes (Abbasi et al., 2019). These figures yield an average concentration of PBDEs in plastics of 74 mg kg^{-1} and estimates of annual inputs to the marine environment ocean ranging from 360 to 950 tonnes. While, strictly, such estimates would be contemporary for the plastics whose designed lifespans are about decade, these are the types of plastic that are most likely to be encountered (and persist) in the marine environment. However, a limitation is the assumption that the same fraction of plastic produced that is flame-retarded enters the waste stream. In theory, flame retarded plastics, and in particular electronic plastics containing BFRs, are subject to specific disposal routes for recycling or safe decomposition (Fig. 1; Turner, 2018).

Based on data in Table 3 regarding the Br content of common groups of marine plastic litter on a mass basis (and excluding biobeads, pyroplastics, paints and fibrous lint), the median frequency of occurrence is 30% and a median concentration is about 40 mg kg^{-1}. Using a mean Br content of BFRs of 70% (Table 1) and the range of plastic inputs reported by Jambeck et al. (2015) results in an estimated range of annual inputs of BFRs to the oceans associated with plastics of about 80–220 tonnes, or two orders of magnitude lower than the estimates based on the fraction of BFRs in manufactured plastics given above. The contribution of PBDEs to these figures is unknown but an evaluation of their significance may be gained from data reported by Deng et al. (2021) for the Yangtze

Table 4

A summary of estimates of mobilised and plastic-bound BFR inputs into the ocean derived from different approaches along with assumptions and limitations of each approach.

Association	Pathway	BFR type	Annual input, tonnes	Assumptions and limitations	Sources of information
mobilised	atmospheric dry deposition	PBDEs	3.5	extrapolation from Atlantic Ocean data	Lohmann et al. (2013)
mobilised	atmospheric gaseous deposition	PBDEs	135	extrapolation from Atlantic Ocean data	Lohmann et al. (2013)
mobilised	atmospheric emission/ deposition	PBDEs	30	migration from in use and waste plastics containing PBDEs	Redfern et al. (2017)
mobilised	atmospheric emission/ deposition	PBDEs	200–250	migration from in use and waste plastics containing PBDEs	Abbasi et al. (2019)
mobilised	rivers	PBDEs	38.5	limited number of riverine concentrations	Liu et al. (2021) and references therein
plastic-bound	plastic loss	all BFRs	20,000–60,000	global plastic loss and BFR usage in plastic	Cheng et al. (2020)
plastic-bound	plastic loss	all BFRs	80–220	global plastic loss and total Br measurements of buoyant plastic litter	this study
plastic-bound	plastic loss	PBDEs	360–950	global plastic and PBDE production in 2010	Jambeck et al. (2015); Abbasi et al. (2019)
plastic-bound	plastic loss	PBDEs	20–50	global plastic loss and PBDE measurements of buoyant plastic litter	Deng et al. (2021)

coastal zone. Here, the mean, total PBDE content of 123 beached plastic litter samples was about 4 mg kg^{-1} and applying this concentration to the ocean plastic input estimates provided by Jambeck et al. (2015) yields lower and upper figures of about 20 and 50 tonnes, respectively. Although such estimates of total BFRs and PBDEs account for their wide dispersion in plastics as contaminants, they are based on samples from a single region and the regional production and use of different BFRs can vary considerably (Abbasi et al., 2019). Moreover, estimates, strictly, apply to positively buoyant plastics (e.g., EPS and polyolefins) that are readily retrieved from strandlines and surface trawls and neglect denser, negatively buoyant plastics (for example, ABS, polycarbonate, and HIPS) that are known to be used widely and recycled in the electronics sector.

A summary of input estimates of BFRs and PBDEs to the ocean via mobilised and plastic-bound pathways is shown in Table 4. It is likely that inputs of bound BFRs (and PBDEs) lie somewhere between estimates based on plastic production and Br contamination of marine plastic litter, with uncertainties related to the extent of fractionation of flame-retarded waste during disposal and loss to the environment and the degree of BFR contamination in recycled products. Nevertheless, this pathway, overall, appears to be at least as important as that associated with the migration of BFRs from plastics during their designed life cycles and waste disposal. Inputs from both bound and migrated sources are predicted to diminish in the future as BFRs are replaced by non-halogenated alternatives (Malucelli et al., 2014; Aschberger et al., 2017) and more stringent regulations on new and recycled products take effect (Sharkey et al., 2020). However, any reduction to the BFR inventory and shifts in BFR signatures to safer compounds in oceanic plastic may be considerably delayed because theoretical considerations and empirical evidence suggest that terrestrial inputs of plastic may circulate in the coastal zone for decades before being degraded or dispersed offshore (Lebreton et al., 2019; Turner et al., 2021).

7. Migration of PBDEs from marine plastics and microplastics

BFRs in marine plastics that are not chemically bonded will be subject to migration into the aqueous phase as free and, subsequently, particulate (sorbed) compounds. As above for surface evaporation into the atmosphere, migration of BFRs into seawater is rate-limited by diffusion within the plastic matrix (Sun et al., 2019). However, migration can be facilitated by additional chemical components in the aqueous phase, such as those encountered in the digestive environments of plastic-ingesting animals.

Cheng et al. (2020) estimate that for microplastic spheres of radius 2.5 mm and $D = 10^{-25}$ m^2 s^{-1} (a median value for nine PBDE congeners

in ABS at 10–30 °C; Sun et al., 2016), only 2.4×10^{-4} % of PBDEs would be released from the plastic matrix into the aqueous phase in the first year, while Sun et al. (2019) predict PBDE migration half-lives (times required for 50% of the initial concentration to be released) of similarly sized ABS spheres to be $> 10^6$ years. By comparison, the US EPA (2019) report a value of D for HBCD in foamed plastics of about 10^{-15} m^2 s^{-1} at 21 °C, with empirical evidence indicating significant leaching over periods of days to months (Al-Odaini et al., 2015; Rani et al., 2017; Aminot et al., 2020; Pan et al., 2021) and ready accumulation by organisms exposed to EPS (Jang et al., 2016; Mukai et al., 2020).

Thus, although earlier discussion implies that plastics may represent the most important source of PBDEs to the ocean, theoretical considerations suggest that atmospheric deposition, either directly or indirectly (through freshwater inputs), is likely to represent the dominant contemporary source of mobilised PBDEs. In the longer-term, however, and as external inputs of PBDEs decline and marine plastic particles become smaller and more weathered, the stock of flame-retarded and contaminated plastic in the ocean is predicted to become the more significant source of these BFRs.

Despite the theoretical constraints on the migration of PBDEs from plastics by diffusion, Tanaka et al. (2013) found that the signature of various congeners in the abdominal adipose tissue of shearwaters was similar to that of ingested microplastics rather than in prey, and Neumann et al. (2021) detected BDE209 in liver tissue of fulmars that had ingested plastics but not in liver tissue of birds without ingested plastic. These observations suggest that PBDEs bound in the ingested plastic matrix may undergo significant migration in the digestive environment of certain animals. Tanaka et al. (2015) explored digestive migration by leaching micronised (2–3 mm) PE containing decaBDE (as BDE209) at about 700 mg kg^{-1} in distilled water and acidified pepsin solution (both at 20 °C), and fish oil and stomach oil extracted from wild seabirds (both at 38 °C). Over a 15-day exposure period, the water-based solutions released traces (generally <1%) of the BFR, while stomach (dietary) oil and fish oil released maxima of about 15% and 50%, respectively. The authors attributed greater release of BDE209 by oil-based solutions to its higher solubility in low polarity extractants. However, Sun et al. (2019) note that leaching of BFRs by oils is more likely to be facilitated by swelling of the plastic matrix and loosening of the polymer chains after penetration of the more hydrophobic components of the oils.

A recent laboratory study exposed various consumer and environmental microplastic fragments to simulated avian solutions (NaCl and acidified pepsin and acidified pepsin amended with fish oil) over a 7-day period at 40 °C (Smith and Turner, 2020). Qualitatively consistent with the observations above, and in the presence of oil, pseudo-first-order and parabolic diffusion rate constants for total Br release from PE (attributed

to the presence of unknown BFRs) dramatically increased, with an overall Br migration at the end of the exposures of about 2%. Sun et al. (2021) also found that leaching of BDE209 from spherical particles of 0.15–2 mm in diameter derived from various contaminated plastics (and up to a concentration of 14,100 mg kg^{-1}) was accelerated in the presence of fish oil under conditions representative of the North Sea cod (10 °C for 7 days), with a maximum D of about 2×10^{-15} m^2 s^{-1} for PP. However, when typical quantities of plastic ingestion were factored in, results from a biodynamic model predicted that accumulation in cod tissue lipid arising from ingestion of retarded or contaminated plastics should be negligible compared with other (e.g., dietary) pathways. Likewise, from experiments performed with contaminated 0.4–0.8 mm granules of electronic ABS, PP and PP under simulated digestive conditions of the lugworm, Sun and Zeng (2022) predicted that the bioaccumulation of PBDEs should be unimportant. Nevertheless, with migration rates being inversely proportional to particle diameter and influenced by physical and chemical breakdown, the authors acknowledge that much finer, weathered microplastics could pose a more significant ecological risk and, therefore, merit further study.

8. Concluding remarks

With PBDEs remaining in electronic plastics and soft furnishings in use and stockpiled for dismantling or recycling, their migration into the environment and input into the ocean via atmospheric deposition and wastewater discharges will continue. However, as these products are destroyed or safely disposed of, inputs of BFRs through this pathway are predicted to diminish considerably over the next decade or two. In the longer term, calculations and considerations above suggest that a more important, latent source of PBDEs is the wide and diverse pool of flame-retarded and contaminated plastics and microplastics that have been directly lost to the ocean or that have some specific use in the maritime sector. Estimates for this source vary widely depending on the data employed and assumptions made, with improvements requiring a better understanding of the concentrations and distributions of PBDEs in marine plastics and microplastics. Regardless of these uncertainties, and based on values of D for common (but unweathered) plastics reported in the literature, this reservoir is predicted to act as a long-term source of mobilised PBDEs but whose general impacts are limited. However, empirical evidence suggests that migration from microplastics into parts of the marine food chain may be greatly facilitated by digestive chemicals (including hydrophobic, oily constituents) that accelerate PBDE dissolution. Migration more generally is predicted to be favoured for microplastics that have undergone considerable physical and chemical weathering but studies involving environmental plastics are lacking.

Credit author statement

AT: conceptualization; methodology; writing – original draft; writing – review and editing; visualization.

Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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