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Article

International pellet watch: Global monitoring of polybrominated diphenyl ethers (PBDEs) in plastic resin pellets

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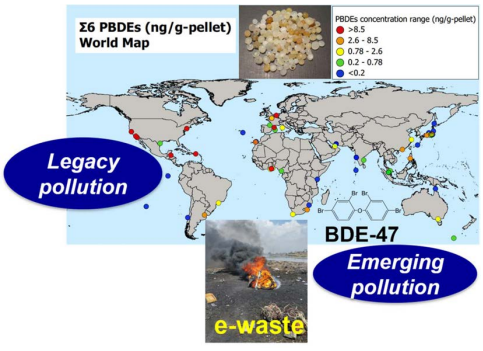
ABSTRACT

Polybrominated diphenyl ethers (PBDEs) were measured in plastic resin pellets collected from 65 beaches across 27 countries worldwide. They were detected at 49 locations at concentrations of the sum of 49 congeners of up to 46 ng / g-pellet and a median of 2 ng / g-pellet. These values are one to two orders of magnitude lower than those of polychlorinated biphenyls (PCBs) (median, 51 ng / g-pellet). This difference can be attributed to lower production of the Penta-BDE technical mixture, which is



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used extensively in some countries, and lower availability of brominated flame retardants for equilibrium partitioning than PCBs. Tetra-, penta-, and hexa-brominated congeners (BDE-47, 99, 100, 153, 154) were dominant over a deca-substituted congener (BDE-209) in many samples; this was significantly detected in pellets from some locations. Results indicate that pellets reflect the pollution status of PBDEs in the dissolved phase in seawater. From the ranking of the summed concentrations of six major PBDE congeners (Σ_6PBDEs), we propose five levels of pollution categorization (ng/g-pellet): no (<0.2), slight (0.2–0.78), moderate (0.78–2.6), high (2.6–8.5), and extreme (>8.5) local pollution. The USA and neighboring countries were categorized as extreme (17–36 ng/g-pellet), western Europe and Japan were categorized as high (≤8.8), and most Asian and African countries were categorized as slight (<0.8). Notably, extreme or high pollution levels were also observed in countries with no history of PBDE production, such as Ghana (Σ_6PBDEs up to 16 ng/g-pellet), the Philippines (7.5), and Hong Kong (7.7). Scrapped electrical and electronic waste might explain these anomalously high values.

Key words: e-waste; legacy pollution; microplastics; passive sampling; citizen science

INTRODUCTION

The extensive and widespread use of chemicals has polluted the Earth's surface. Chemical compounds with persistent, bioaccumulative, and hazardous characteristics are of great concern, and some are internationally regulated as persistent organic pollutants (POPs) by the Stockholm Convention (UNEP, 2017). Their distribution is heterogeneous and their concentrations vary widely. Therefore, understanding the spatial and temporal distribution of individual POPs through monitoring is essential for assessing their threat, modeling their behavior, and regulating and evaluating their effectiveness. International Pellet Watch (IPW), launched in 2005, uses plastic resin pellets to observe the global status of POPs (Takada, 2006; Ogata et al., 2009; Takada and Yamashita, 2016).

Plastic resin pellets are the industrial feedstock for all plastic products. A small but significant proportion of pellets is unintentionally spilled during their manufacturing, transportation, and handling. Polyethylene (PE) and polypropylene (PP) pellets are two major polymers that are lighter than water and can be carried by surface runoff, streams, and rivers to the ocean. Owing to their persistent nature, pellets are distributed on beaches worldwide. While floating at sea, the pellets sorb and concentrate hydrophobic organic pollutants from the surrounding water (Mato et al., 2001). In IPW, pellets are collected from beaches and sent to the Laboratory of Organic Geochemistry at the Tokyo University of Agriculture and Technology, where POPs in them are analyzed. The usefulness of IPW as a tool for global POP monitoring was demonstrated by analyzing polychlorinated biphenyls (PCBs) around the world and the correlation of their spatial patterns with those revealed by the traditional monitoring protocol, i.e., Mussel Watch (Ogata et al., 2009; Takada and Yamashita, 2016). Because of low sampling and shipping costs, IPW can be applied worldwide. Uniquely, citizen science can contribute to IPW as non-specialists can easily collect pellets (Thiel et al., 2017; Zettler et al., 2017). The analytical results can be used to inform people of the hazardous nature of microplastics (plastic particles <5 mm in size), increasing public awareness of plastic pollution (Yeo et al., 2015). The participation of citizens has increased the coverage of monitoring. To date, pellets from 300 locations in 40 countries have been analyzed, and the pollution status of POPs—i.e., PCBs and organochlorine pesticides (dichloro diphenyl trichloroethanes; DDTs and hexachlorocyclohexanes; HCHs)—has been revealed (Ogata et al., 2009; Karapanagioti et al., 2011; Mizukawa et al., 2013a; Hosoda et al., 2014; Yeo et al., 2015; Takada and Yamashita, 2016). The target compounds of IPW have been expanded to include polycyclic aromatic hydrocarbons (PAHs) and hopanes (Mizukawa et al., 2013a; Yeo et al., 2017; Alidoust et al., 2021).

This report focuses on polybrominated diphenyl ethers (PBDEs), which are brominated flame retardants that have been widely used since the 1970s. PBDEs are added to electrical equipment, textiles, and other industrial plastic products to suppress flammability. According to UNEP (2010), the total global production of PBDEs from 1970 to 2005 was 1.3 to 1.5 million tons. Depending on the congener composition, three types of PBDE mixtures were commercially produced: Penta-, Octa-, and Deca-BDE technical mixtures. Congener profiles of the technical mixtures have been characterized by La Guardia et al. (2006). Penta-BDE technical mixtures are mainly contain tetra- and penta-BDEs with hexa- and tri-BDEs as minor or trace components. Octa-BDE technical mixtures are a complex mixture of hexa-BDEs to nona-BDEs with deca-BDE (BDE-209) present as a trace component. Deca-BDE mixtures predominantly contain deca-BDE with nona-BDEs as trace components. The major homologs in penta- and octa-BDE mixtures were listed as POPs in 2009 because of their neurotoxicity (Eriksson et al., 2001; McDonald, 2002), thyroid hormone disruption (McDonald, 2002), and immunotoxicity (Frouin et al., 2010). Deca-BDE production has dominated global production (1.1–1.25 million t from 1970 to 2005), whereas the production of penta-BDE mixtures (91,000–105,000 t) and Octa-BDE mixtures (102,700–118,500 t) has been more modest (UNEP, 2010). Deca-BDE can be debrominated to lower-brominated congeners (Söderström et al., 2004; Eriksson et al., 2004; Kajiwara et al., 2008; Kwan et al., 2013a, 2013b; Mizukawa et al., 2013b), which are toxic; therefore, deca-BDEs were listed as POPs and banned by the Stockholm Convention in 2017.

PBDEs are emitted to the environment via various routes from multiple sources, including industrial wastewater from factories that use PBDEs (e.g., La Guardia et al., 2007), sewage effluent (e.g., Kim et al., 2013), house dust containing PBDEs from the wear of consumer products, and urban runoff (e.g., Melymuk et al., 2014). Facilities that recycle electronic waste (e-waste), dismantling sites (e.g., Luo et al., 2009), and leachate from landfill sites (Li et al., 2012; Kwan et al., 2013a) are also important PBDE sources. Because of their persistence,

PBDEs released into the environment are carried to the ocean, where they can be detected in seawater (Oros et al., 2005; Wurl et al., 2006), biota (Ramu et al., 2007), and sediments (Kwan et al., 2013b). Hence, monitoring PBDEs is important to understand their distribution and fate in marine environments.

The chemical structure and nature (such as hydrophobicity) of PBDEs are similar to those of PCBs. Thus, similar to PCBs, PBDEs are sorbed onto and concentrated in pellets from ambient seawater. PBDEs in plastic pellets have been measured in several countries. Taniguchi et al. (2016) measured PBDEs and other POPs in pellets collected at 41 locations from 15 cities in Brazil and detected PBDEs at 10 locations. Camacho et al. (2019) analyzed plastic debris, including pellets, from the Canary Islands and found PBDEs in all pellet samples. PBDEs were also detected in pellets from central Chile (Pozo et al., 2020). However, the spatial coverage of measurement campaigns is limited, and the global pollution status of PBDEs in pellets has not been reported thus far. Thus, we analyzed pellet samples collected from 65 beaches in 27 countries around the globe to understand the global pollution status of PBDEs and establish criteria for the categorization of the pollution status of PBDEs in pellets. In addition, we analyzed PCBs in the pellet samples and compared them with PBDEs to reveal the unique features of PBDE pollution.

MATERIALS AND METHODS

SAMPLE COLLECTION AND TREATMENT

Within the IPW framework, samples are collected by volunteers and the analytical results of each sample are shared with the collectors via e-mail and a map on the IPW website. Beached plastic resin pellets were collected from 65 locations across the globe (Table 1). Sampling locations included large cities in the industrially and economically developed countries of USA, Japan, and Europe; cities of industrially developing nations such as the Philippines, India, and Ghana; and remote, undeveloped areas, such as the Galápagos Islands (Ecuador), Macquarie Island (Australia), the Canary Islands (Spain), Easter Island (Chile), Hulhumae (the Maldives), and Praia de São Lourenço (Portugal). Details of places and dates of collection are listed in Table 1. Samples were collected using stainless steel tweezers or clean hands and wrapped in aluminum foil and sent to the laboratory in Tokyo. Upon arrival, the pellets were kept frozen at −30°C until sample analysis. The sorting and analytical procedures followed Ogata et al. (2009). Polymers were identified through near-infrared spectrometry (Plascan-WTM OPT Research Inc., Tokyo, Japan) as PE, PP, and others. Yellowing PE pellets with a yellowness of ≥40 were analyzed. From each location, five pools of pellets (each comprising five randomly selected pellets) were analyzed to determine the median concentrations of PBDEs and PCBs. To assess PBDE levels of virgin pellets, we also analyzed two types of commercial virgin PE pellets (Nippon-Chuko, Tokyo, Japan and DJC, Yokohama, Japan).

CHEMICAL ANALYSIS OF MICROORGANIC POLLUTANTS IN PELLETS

The procedures for analyzing microorganic pollutants in pellets are divided into three steps: extraction, cleanup, and instrumental analysis. The pellets were soaked in hexane thrice for 24 h each (total 72 h). The extracts were combined and spiked with isotopically labeled surrogate standard for PBDEs and PCBs (^{13}C-labeled BDE-3, 15, 28, 47, 99, 153, 154, and 183; ^{13}C-labeled CB-28, 52, 101, 153, 138, 180, and 209) and 4'-fluoro-2,2',3,3',4,5,5',6,6'-nonabromo-diphenylether. They were roto-evaporated, redissolved in 2 mL of dichloromethane (DCM), and purified via gel permeation chromatography (2 cm i.d. ×30 cm, CLNpak EV-2000; Showa-Denko, Tokyo, Japan) in DCM as an eluent at a rate of 4 mL/min. The fraction with a retention time of 14 to 25 min, containing PBDEs and PCBs, was roto-evaporated just to dryness, redissolved in 0.4 mL of hexane, and transferred onto a fully activated silica gel column (0.45 cm i.d. ×18 cm). Fraction I, containing aliphatic hydrocarbons, and Fraction II, containing PBDEs and PCBs, were eluted first with 4 mL of hexane and then with 10 mL of 25% DCM in hexane. PCBs and lower-brominated PBDE congeners in Fraction II were determined via gas chromatography–ion-trap mass spectrometry (GC–IT/MS); higher-brominated PBDE congeners were determined via GC using an electron capture detector (ECD). The instrumental conditions are described in Hirai et al.'s (2011) work. Forty-nine PBDE congeners (mono- to deca-brominated; BDE-1, 2, 3, 7, 8/11, 10, 12/13, 15, 17/25, 30, 32, 33/28, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 179, 181, 183, 184, 188, 190, 196, 197, 203, 206, 207, 208, 209) were quantified. The sum of six peaks comprising seven congeners (BDE-33/28, 47, 99, 100, 153, 154) is expressed as Σ_6PBDEs here. Thirty-eight PCB congeners ranging from di- to deca-chlorinated biphenyls (CB-8, 18, 28, 44, 49, 52, 66, 74, 87, 99, 101, 105, 110, 118, 128, 138, 146, 149, 151, 153, 156, 157, 158, 167, 170, 172, 177, 178, 180, 183, 187, 189, 194, 195, 199, 196/203, 206, 209) were quantified. The sum of 13 PCB congeners (CB-66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206) is expressed as Σ_{13}PCBs here.

QUALITY ASSURANCE AND QUALITY CONTROL

Extraction efficiency was confirmed by analyzing additional hexane in which the pellets were soaked. The pellets had been already extracted thrice with hexane and we detected significant quantities of BDE209 and BDE47 via normal analysis. The fourth extract revealed <3% of BDE-209 and <0.1% of BDE-47, indicating that triple-soaking extraction is sufficient to extract PBDEs from the pellets. The reproducibility of this analytical procedure (i.e., column chromatography and instrumental determination) was confirmed by analyzing four aliquots from a single extract of pellets from Tokyo Bay, Japan, for PCBs and PBDEs, which was prepared for quality assurance and quality control (QA/QC). The relative standard deviations of the concentrations were <9% for PCBs and <11% for PBDEs. Recovery was tested by spiking the aliquots of the extracts with concentration-certificated standards; recoveries were 70% to 124% for PCBs and 70% to 144% for PBDEs. PBDE concentrations were corrected against the recovery of isotopically labeled surrogates, which were spiked before cleanup similar to that performed in normal pellet analysis. No recovery correction was performed for PCBs to maintain consistency with PCBs in the IPW samples in IPW website, some of which were determined using GC-ECD without isotopically labeled standards. A signal-to-noise ratio of <3 (non-significant

Table 1 Sample information of the pellet samples

Sampling year	Country	Area / City	Sample Code	Latitude		Longtitude	
	North & Central America						
2011	USA	New Jersey	USA #1	N	40.47816	W	74.01627
2012	USA	Los Angeles	USA #2	N	33.87857	W	118.41025
2012	USA	San Francisco #1	USA #3	N	37.76813	W	122.27640
2016	USA	San Francisco #2	USA #4	N	37.76889	W	122.27806
2014	USA	Texas	USA #5	N	27.58750	W	97.21722
2018	USA	California	USA #6	N	32.76078	W	117.25422
2016	Puerto Rico	Cataño	Puerto Rico	N	18.45878	W	66.13762
2013	Belize	Calabash Caye	Belize	N	17.28260	W	87.81142
	Europe						
2010	France	2010 Normandy	France #1	N	49.48730	E	0.09838
2017	France	2017 Normandy	France #2	N	49.48731	E	0.09839
2015	France	Biarritz	France #3	N	43.46068	W	1.57837
2017	France	Saint-Jouin-Bruneval	France #4	N	49.64710	E	0.15433
2015	Spain	Barcelona	Spain #1	N	41.38175	E	2.19503
2014	Spain	Mallorca Island	Spain #2	N	39.31472	E	3.00505
2014	Netherlands	Hook of Holland	Netherlands	N	51.97872	E	4.11806
2014	Italy	Sardinia Island	Italy	N	41.24318	E	9.40088
	South America						
2012	Brazil	São Paulo	Brazil	S	24.01389	W	46.27278
2008	Argentina	Buenos Aires	Argentina	S	34.51900	W	58.46930
2008	Chile	Concepción	Chile #1	S	36.72797	W	73.12796
	Asia						
2009	China	Hong Kong	China #1	N	22.26968	E	113.99898
2014	China	Shanghai	China #2	N	30.83083	E	121.94083
2011	Malaysia	2011 Port Dickson	Malaysia #1	N	2.41481	E	101.85908
2016	Malaysia	2016 Port Dickson	Malaysia #2	N	2.41475	E	101.85908
2016	Malaysia	Malacca	Malaysia #3	N	2.22025	E	102.17525
2016	Philippines	Manila	Philippines	N	14.46478	E	120.88283
2007	India	Chennai	India #1	N	13.05947	E	80.28631
2015	India	Colva (Monsoon)	India #3	N	15.27613	E	73.91416
2017	India	Caranzalem	India #2	N	15.46844	E	73.80531
2017	Indonesia	Jakarta	Indonesia	S	6.12056	E	106.84917
2016	Japan	Futtsu	Japan #1	N	35.30936	E	139.80050
2013	Japan	2013 Odaiba	Japan #2	N	35.63175	E	139.77731
2016	Japan	2016 Odaiba	Japan #3	N	35.62861	E	139.77632
2015	Japan	Hyogo	Japan #4	N	34.71397	E	135.35206
2017	Japan	Zamami	Japan #5	N	26.23347	E	127.29081
2017	Japan	Toyama	Japan #6	N	36.79168	E	137.07093
2016	Japan	Fujimae	Japan #7	N	35.07845	E	136.84949
2017	Japan	Shizuoka	Japan #8	N	34.91676	E	138.36169
2016	Japan	Shonan	Japan #9	N	35.31572	E	139.46739
2017	Japan	Hayama	Japan #10	N	35.26104	E	139.57716
2017	Japan	Shobuda	Japan #11	N	38.28952	E	141.06593
2017	Japan	Teshio	Japan #12	N	44.86690	E	141.74114
	Africa						
2013	South Africa	Cape town	South Africa #1	S	33.87769	E	18.48806
2012	South Africa	Durban	South Africa #2	S	29.86559	E	31.01738
2014	Equatorial Guinea	Playa de Arena Blanca	Equatorial Guinea	N	3.52718	E	8.58075
2013	Mozambique	Maputo	Mozambique	S	25.92347	E	32.64008
2011	Kenya	Killifi	Kenya	S	3.61381	E	39.88017

2015	Ghana	Sakumono	Ghana #1	N	5.61171	W	0.04408
2015	Ghana	Atorkor	Ghana #2	N	5.77474	E	0.82041
2015	Ghana	Saltpond	Ghana #3	N	5.19874	W	1.06449
2015	Ghana	Korle	Ghana #4	N	5.53067	W	0.21970
2015	Ghana	Independence Square #1	Ghana #5	N	5.54443	W	0.19329
2010	Ghana	Independence square #2	Ghana #5'	N	5.54520	W	0.19061
	Oceania						
2014	Australia	Victoria	Australia #1	S	38.10015	E	145.12456
2017	Australia	Queensland	Australia #2	S	11.64344	E	142.85764
	Middle East						
2018	Iran	Ramchah	Iran #1	N	26.88461	E	56.15119
2018	Iran	Dowlat Park	Iran #2	N	27.18778	E	56.34511
2018	Iran	Kite beach	Iran #3	N	26.81536	E	56.10600
2010	UAE	Dubai	Dubai	N	25.19994	E	55.23650
	Remote Island						
2014	Ecuador	Galapagos	Ecuador	S	0.76098	W	90.33382
2001	Australia	Macquarie Island	Australia #3'	S	54.64903	E	158.82007
2013	Spain	Canary Islands #1	Spain #3'	N	28.67780	W	14.00930
2015	Spain	Canary Islands #2	Spain #4'	N	29.11619	W	13.55322
2011	Chile	Easter Island	Chile #2'	S	27.07394	W	109.32299
2015	Maldive	Malé	Maldive	N	4.21569	E	73.54539
2018	Portugal	Praia de São Lourenço	Portugal #1	N	36.98947	W	25.05514

peaks) on solvent injection into GC–IT/MS or GC-ECD was considered as the limit of detection (LOD). The LOD was normally 0.08 ng/g for lower-brominated congeners such as BDE-47 and 0.3 ng/g for higher-brominated congeners such as BDE-209 (Table S1). A procedural blank using only the solvent was run with every set analyzed (five pools). Analytical values $<3\times$ the corresponding blanks were considered to be below the limit of quantification (LOQ). The LOD and LOQ were usually 0.2 and 0.7 ng/g-pellet for Σ_{13}PCBs, and 0.08 and 0.2 ng/g-pellet for Σ_6PBDEs (Table S2). As pellet blanks, two types of virgin PE pellets were analyzed; no significant PBDE congeners were detected in either pellet.

RESULTS AND DISCUSSION

CONCENTRATIONS AND CONGENER PROFILES OF PBDEs IN PELLETS

Of the 65 collection locations, PBDEs were significantly detected (>0.7 ng/g) at 49 sites (Fig. 1). The concentration of total PBDEs (sum of 49 congeners from mono- to deca-BDEs) reached 46 ng/g-pellet (USA #1), with a median of 2.0 ng/g-pellet (Table 2). Higher PBDE concentrations were observed in pellets collected from the USA, western Europe, and Ghana. The spatial patterns of PBDE concentrations are discussed in the next section.

The congener profiles at all 65 locations and their concentrations are presented in Fig. S1 and Table S3, respectively. Typical congener profiles found in some countries are shown in Fig. 2. Lower- (mono- to hexa-) brominated congeners were dominant over higher (hepta- to deca-) ones at most places (35 of 51). Of these, BDE-47 (Br_4) was the most abundant congener at 25 sites. The prevalence of other relatively abundant lighter compounds, including BDE-99 and 100 (Br_5), BDE-49 and 66 (Br_4), and BDE-154 and 153 (Br_6), was also noted in pellets from Chile (Pozo et al., 2020), Brazil (Taniguchi et al., 2016), and the Canary Islands (Camacho et al., 2019). The congener profiles in pellets were similar to those found in penta-BDE technical mixtures (Fig. S2), and the predominance of tetra- and penta-BDEs (mainly BDE-47 and 99) is consistent with that observed in seawater and bivalves (de Wit, 2002; Bervoets et al., 2004; Bodin et al., 2007; Mizukawa et al., 2009). In other environmental media, the congener profile of pellets collected from Tokyo Bay is more similar to that of dissolved-phase seawater and oyster than that of sediment, in which only BDE-209 was detected (Fig. 3). This suggests that pellets adsorb penta-BDE-derived congeners from the dissolved phase of seawater. Despite much higher production of deca-BDE technical mixtures, BDE-209 was detected in pellets at a limited number of locations. This predominance of lower-brominated congeners accounts for the less availability of BDE-209 for equilibrium partitioning owing to its higher molecular weight and bulky molecular structure (Bao et al., 2011). Di- and tri-brominated congeners (e.g., BDE-7, 15, 17, 28) were not detected in the pellets but were significantly detected in seawater and oysters (Fig. 3). Less-hydrophobic compounds such as di- and tri-brominated diphenyl ethers may be less sorbed onto hydrophobic sorbent pellets. In the case of organisms, the possibility of debromination to lower-brominated congeners as metabolism can also be considered.

Ten locations, including USA #1, France #2, Brazil, Japan #6, Japan #7, and South Africa #2, showed a predominance of higher-brominated congeners, mainly BDE-209 (Fig. S1). This could be due to particles picked up from resuspended sediment owing to disturbance or plastic recycling. Sediment, soil, and dust are rich in BDE-209 and related higher-brominated

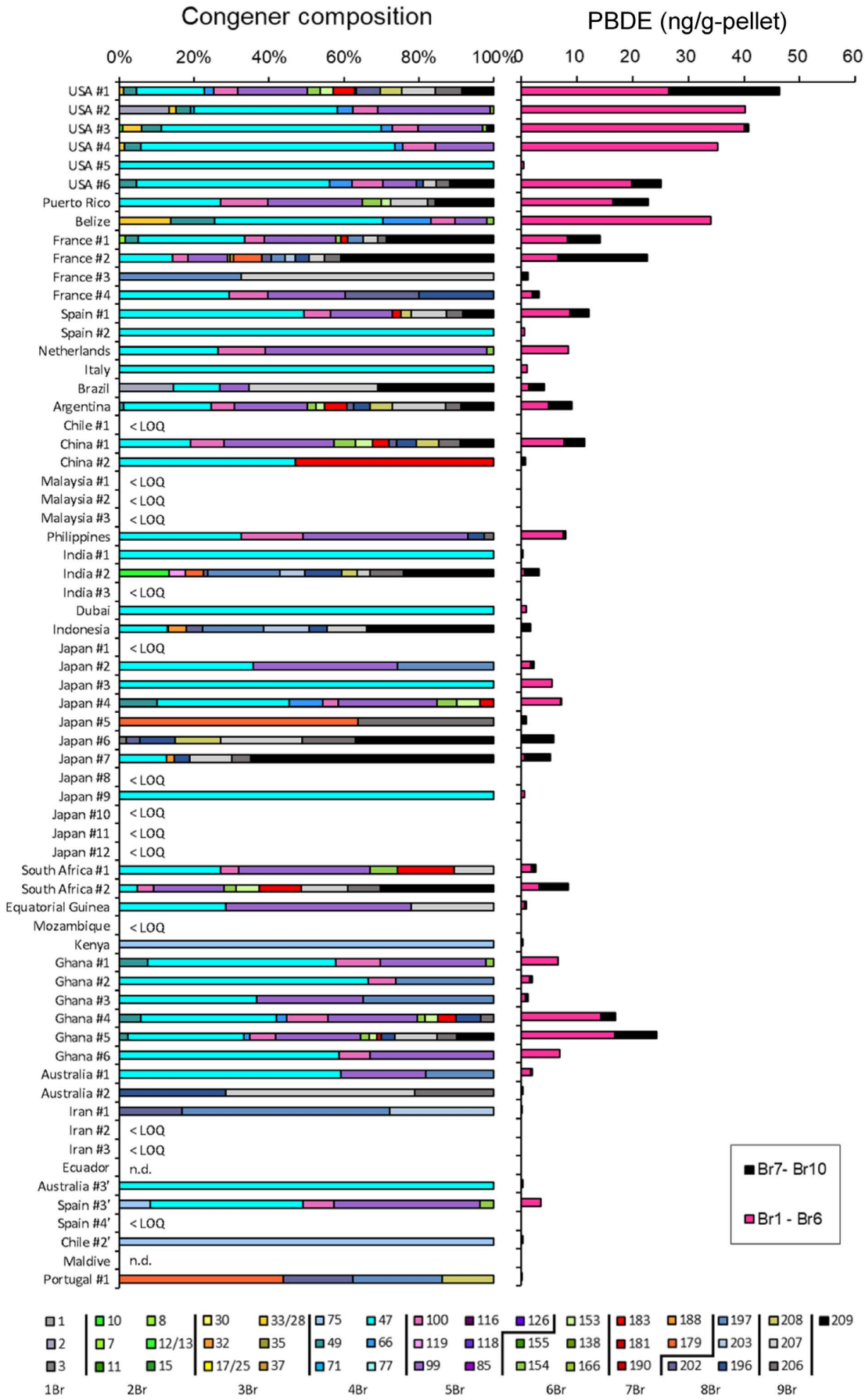

Fig. 1 Congener compositions and concentrations of PBDEs in pellets

Table 2 Concentrations of PBDEs and PCBs in pellet samples

Country	Area/City	Sample Code	Σ_{13} PCBs* (ng/g-pellet)	total PBDEs** (ng/g-pellet)		Σ_6PBDEs*** (ng/g-pellet)		Lower PBDEs**** (ng/g-pellet)		Higher PBDEs***** (ng/g-pellet)		BDE 209 (ng/g-pellet)	
				No LOQ#	+LOQ##	No LOQ#	+LOQ##	No LOQ#	+LOQ##	No LOQ#	+LOQ##	No LOQ#	+LOQ##
North & Central America													
USA	USA #1	New Jersey	432	46	46	24	24	26	27	20	20	4.0	4.0
USA	USA #2	Los Angeles	233	40	42	31	31	40	41	<0.31	1.6	<0.31	0.79
USA	USA #3	San Francisco #1	178	41	41	36	37	40	41	0.76	1.1	0.76	0.76
USA	USA #4	San Francisco #2	104	35	35	33	33	35	35	<0.22	0.13	<0.22	0.13
USA	USA #5	Texas	45	0.46	1.3	0.46	0.46	0.46	0.46	<0.24	0.88	<0.24	0.42
USA	USA #6	Mission Bay Beach	23	25	25	17	18	20	22	5.2	5.4	2.9	2.9
Puerto Rico	Puerto Rico	Cataño	301	23	23	17	17	17	17	6.3	7.5	3.6	3.6
Belize	Belize	Calabash Caye	2.6	34	34	26	26	34	35	<0.14	0.06	<0.14	<0.14
Europe													
France	France #1	2010 Normandy	2230	14	14	7.6	8.0	8.4	9.6	5.8	5.8	4.1	4.1
France	France #2	2017 Normandy	1945	23	23	6.7	6.9	6.7	6.9	16	16.1	9.2	9.2
France	France #3	Biarritz	96	1.3	1.7	<0.08	0.48	<0.08	0.48	1.3	2.1	<0.34	0.64
France	France #4	Saint-Jouin-Bruneval	831	3.3	3.3	2.0	2.1	2.0	2.1	1.3	1.5	<0.22	<0.22
Spain	Spain #1	Barcelona	1243	12	12	8.8	9.0	8.8	9.5	3.3	3.3	1.0	1.01
Spain	Spain #2	Mallorca Island	107	0.69	0.69	0.69	0.69	0.69	0.69	n.d.	n.d.	<0.15	<0.15
Netherlands	Netherlands	Hook of Holland	243	8.5	9.4	8.5	8.6	8.5	8.8	<0.40	0.90	<0.40	<0.40
Italy	Italy	Sardinia Island	46	1.1	1.5	1.1	1.4	1.1	1.4	<1.3	0.37	<1.3	<1.3
Asia													
China	China #1	Hong Kong	61	11	11	7.7	7.7	7.7	8.0	3.7	6.9	1.0	1.0
China	China #2	Shanghai	0.91	0.76	0.76	0.36	0.78	0.36	1.1	0.40	0.40	<0.38	<0.38
Malaysia	Malaysia #1	2011 Port Dickson	1.2	<0.08	0.67	<0.08	0.53	<0.08	0.67	n.d.	n.d.	<0.45	<0.45
Malaysia	Malaysia #2	2016 Port Dickson	0	<0.08	0.64	<0.08	0.04	<0.08	0.09	<0.10	0.55	<0.10	<0.10
Malaysia	Malaysia #3	Malacca	2.7	<0.08	0.81	<0.08	0.23	<0.08	0.23	<0.09	0.58	<0.09	0.28
Philippines	Philippines	Manila	299	8.1	8.1	7.5	7.8	7.5	7.8	0.57	3.9	<0.36	0.55
India	India #1	Chennai	21	0.40	1.6	0.40	0.40	0.40	0.92	<0.33	1.2	<0.33	0.88
India	India #3	Colva (Monsoon)	0.15	<0.08	1.9	<0.08	0.09	<0.10	0.09	<0.29	1.8	<0.29	0.56
India	India #2	Caranzalem	5.2	3.3	3.3	<0.08	<0.08	0.58	0.58	2.7	2.7	0.79	0.79
Indonesia	Indonesia	Jakarta	126	1.7	1.7	0.23	0.23	0.23	0.23	1.5	1.5	0.59	0.59
Japan	Japan #1	Futtsu	671	<0.08	0.42	<0.08	<0.08	<0.08	<0.08	<0.28	0.42	<0.28	<0.28
Japan	Japan #2	2013 Odaiba	340	2.4	2.4	1.8	2.0	1.8	2.2	0.62	0.88	<0.53	<0.53
Japan	Japan #3	2016 Odaiba	473	6.4	6.4	4.5	6.0	5.5	6.8	<1.2	1.1	<1.2	<1.2
Japan	Japan #4	Hyogo	304	7.3	7.3	5.7	5.7	7.1	7.5	0.27	2.0	<0.45	0.55
Japan	Japan #5	Zamami	2	0.96	0.99	<0.08	0.03	<0.08	0.03	1.0	2.3	<0.17	0.50
Japan	Japan #6	Toyama	10	5.9	62	<0.08	<0.08	<0.08	56	5.9	6.9	2.2	2.2
Japan	Japan #7	Fujimae	76	5.3	5.3	0.67	1.0	0.67	1.1	4.6	5.4	3.4	3.4
Japan	Japan #8	Shizuoka	20	<0.08	0.62	<0.08	0.10	<0.08	0.10	<0.30	0.53	<0.30	<0.30
Japan	Japan #9	Shonan	38	0.68	1.7	0.68	0.68	0.68	0.68	<0.13	1.0	<0.13	0.40
Japan	Japan #10	Hayama	106	<0.08	4.8	<0.08	0.63	<0.08	4.6	<1.1	0.22	<1.1	<1.1
Japan	Japan #11	Shobuda	86	<0.08	1.8	<0.08	0.10	<0.08	0.10	<0.12	1.7	<0.12	0.60
Japan	Japan #12	Teshio	7	<0.08	0.69	<0.08	<0.08	<0.08	0.19	<0.33	0.50	<0.33	0.11
South America													
Brazil	Brazil	São Paulo	901	4.2	4.2	0.85	0.85	1.5	1.5	2.8	3.3	1.3	1.3
Argentina	Argentina	Buenos Aires	168	9.1	9.1	4.9	4.9	5.0	5.1	4.1	4.8	0.80	0.80
Chile	Chile #1	Concepción	53	<0.08	0.87	<0.08	0.18	<0.08	0.18	<0.16	0.68	<0.16	<0.16
Africa													
South Africa	South Africa #1	Cape town	96	2.6	2.6	1.9	2.1	1.9	2.1	0.67	0.81	<0.16	<0.16
South Africa	South Africa #2	Durban	122	8.6	8.6	3.2	3.2	3.2	3.2	5.4	5.4	2.60	2.6
Equatorial Guinea	Equatorial Guinea	Playa de Arena Blanca	84	0.88	0.88	0.69	0.77	0.69	0.77	0.19	0.19	<0.36	<0.36
Mozambique	Mozambique	Maputo	53	<0.08	0.43	<0.08	<0.08	<0.08	0	<0.23	0.43	<0.23	<0.23
Kenya	Kenya	Killifi	19	0.30	0.41	<0.08	0.12	0.30	0.41	<0.27	0.11	<0.27	<0.27
Ghana	Ghana #1	Sakumono	60	6.7	8.9	6.2	6.4	6.7	7.0	<0.40	2.2	<0.40	0.53
Ghana	Ghana #2	Atorkor	19	2.1	2.1	1.5	1.8	1.5	1.8	0.55	1.5	<0.40	0.42
Ghana	Ghana #3	Saltpond	8.8	1.3	1.3	0.84	0.91	0.84	0.91	0.45	1.3	<0.30	0.36
Ghana	Ghana #4	Korle	143	17	17	13	13	14	14	2.6	4.5	<0.40	0.50
Ghana	Ghana #5	Independence Square #1	46	24	24	16	16	17	17	7.6	7.6	2.4	2.4
Ghana	Ghana #5'	Independence square #2	51	7.0	7.1	7.0	7.1	7.0	7.4	<1.2	0.14	<1.2	<1.2

Country	Area/City	Sample Code	Σ_{13} PCBs* (ng/g-pellet)	total PBDEs** (ng/g-pellet)		Σ_6 PBDEs*** (ng/g-pellet)		Lower PBDEs**** (ng/g-pellet)		Higher PBDEs***** (ng/g-pellet)		BDE 209 (ng/g-pellet)	
				No LOQ#	+LOQ##	No LOQ#	+LOQ##	No LOQ#	+LOQ##	No LOQ#	+LOQ##	No LOQ#	+LOQ##
Oceania													
Australia	Australia #1	Victoria	238	2.0	2.0	1.7	1.9	1.7	1.9	0.37	0.48	<0.10	<0.10
Australia	Australia #2	Captain Billy's Landing	1	0.32	0.42	<0.08	0.11	<0.08	0.11	0.32	0.79	<0.00074	0.23
Middle East													
Iran	Iran #1	Ramchah	2.9	0.13	0.13	<0.08	<0.08	<0.08	0	0.13	0.13	<0.20	<0.20
Iran	Iran #2	Dowlat Park	6.9	<0.08	0.44	<0.08	<0.08	<0.08	0	<0.13	0.44	<0.13	<0.13
Iran	Iran #3	Kite beach	5.7	<0.08	0.41	<0.08	<0.08	<0.08	0	<0.005	0.41	<0.005	<0.005
UAE	Dubai	Dubai	2.7	0.95	0.95	1.0	0.95	0.95	0.95	n.d.	n.d.	<0.37	<0.37
Remote Island													
Ecuador	Ecuador	Galapagos	12	<0.08	<0.08	<0.08	<0.08	n.d.	0	n.d.	0	<0.20	<0.20
Australia	Australia #3'	Macquarie Island	12	0.34	0.34	0.34	0.34	0.34	0.34	n.d.	0	<0.40	<0.40
Spain	Spain #3'	Canary Islands #1	7.4	3.6	3.6	3.3	3.3	3.6	3.6	n.d.	0	<0.40	<0.40
Spain	Spain #4'	Canary Islands #2	4.3	<0.08	0.89	<0.08	0.20	<0.08	0.52	<0.20	0.36	<0.20	0.36
Chile	Chile #2'	Easter Island	1.8	0.36	3.1	<0.08	<0.08	0.36	0.36	<0.60	2.7	<0.60	0.93
Maldive	Maldive	Maldive	0.41	<0.3	<0.3	<0.08	<0.08	<0.08	0	<0.30	<0.30	<0.30	<0.30
Portugal	Portugal #1	Praia de São Lourenço	1	0.26	0.26	<0.08	<0.08	<0.08	0	0.26	0.26	<0.23	<0.23

*Σ13 PCBs: sum of concentrations of CB66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206.
**sum of concentrations of BDE1, 2, 3, 7, 8/11, 10, 12/13, 15, 17/25, 30, 32, 33/28, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 179, 181, 183, 184, 188, 190, 196, 197, 203, 206, 207, 208, 209.
***Σ6 PBDEs: sum of concentrations of BDE28/33, 47, 100, 99, 153 and 154.
****Lower PBDEs: sum of concentrations of mono- to hexa-brominated congeners.
*****Higher PBDEs: sum of concentrations of hepta- to deca-brominated congeners.
#No LOQ: Values lower than LOQ are excluded.
##+LOQ: Values lower than LOQ are included.
Shaded cells: less than LOQ.
n.d.: less than detection limit (LOD).

congeners (e.g., Fig. 3; de Wit, 2002; Kwan et al., 2013a; Mizukawa et al., 2021). The attachment of these particles on the pellet surface and their bulk extraction with pellets may help detect those higher brominated congeners in the extracts. Flame retardants are added during the manufacture of final products and are therefore unlikely to be found in virgin pellets. Indeed, the virgin pellets we analyzed contained no significant PBDE congeners (Table S4). However, when plastic products containing flame retardants are recycled, the additives are recycled with them. Typically, recycled plastic products are fabricated from recycled pellets. Vojta et al. (2017) reported extremely high concentrations of BDE-209 (up to 17,500 ng/g) in recycled plastic products, which suggest its presence in recycled pellets. Li et al (2020) detected PBDEs in recycled pellets made from e-waste. Both recycled and virgin pellets can be spilled into the environment and carried with runoff into the ocean, resulting in the occurrence of BDE-209 and related congeners in beached pellets at some locations.

Overall, PBDE congener profiles in pellets were similar to those of penta-BDE technical mixtures, with some contribution from deca-BDE mixtures. In addition, some pellet samples had congeners that are absent in the technical products. For example, BDE-49 was detected in 12 samples. This is probably due to the debromination of penta-BDEs, particularly BDE-99, and is consistent with the tendency for BDE-99 to be less abundant than BDE-47 in the pellet samples, with a BDE-47:99 ratio of 2.4 ± 0.8; in contrast, BDE-99 was the most abundant congener in the technical products, with a BDE-47:99 ratio of 0.78–0.96 (La Guardia et al., 2006). This discrepancy can be explained by the debromination or selective degradation of BDE-99 through photolytic, microbial, or anaerobic reactions. Debromination is also suggested for higher-brominated congeners in some pellet samples: nona- and octa-brominated congeners, particularly BDE-202, in some pellet samples (e.g., USA #1 and France #2) indicate the debromination of BDE-209.

Majority locations (pellets) did not show similar congener profiles to those of the octa-BDE technical products, which are dominated by BDE-183 (Fig. S2). Among the 325 analyzed pools (65 locations × 5 pools each), only one pool (Fujimae, pool #5 of Japan #7) was found to have a congener profile similar to that of DE-79 which is an octa-BDE mixture (Fig. S3). This may suggest the minimal contribution of octa-BDE mixtures to marine pollution because of PBDEs. However, this is not consistent with the greater volume of production of octa-BDE mixtures (102,700–118,500 t) than that of penta-BDE mixtures (91,000–105,000 t). Less availability for equilibrium partitioning due to the higher molecular weight and bulkier nature of BDE-183 and associated congeners (Bao et al., 2011) or faster photodegradation of BDE-183 (Fang et al., 2008) could explain the lower contribution of octa-BDE mixtures to PBDE pollution in marine environments.

Concentrations of total PBDEs in pellets (0.08–46 ng/g, median of 2.0 ng/g) were one to two orders of magnitude low-

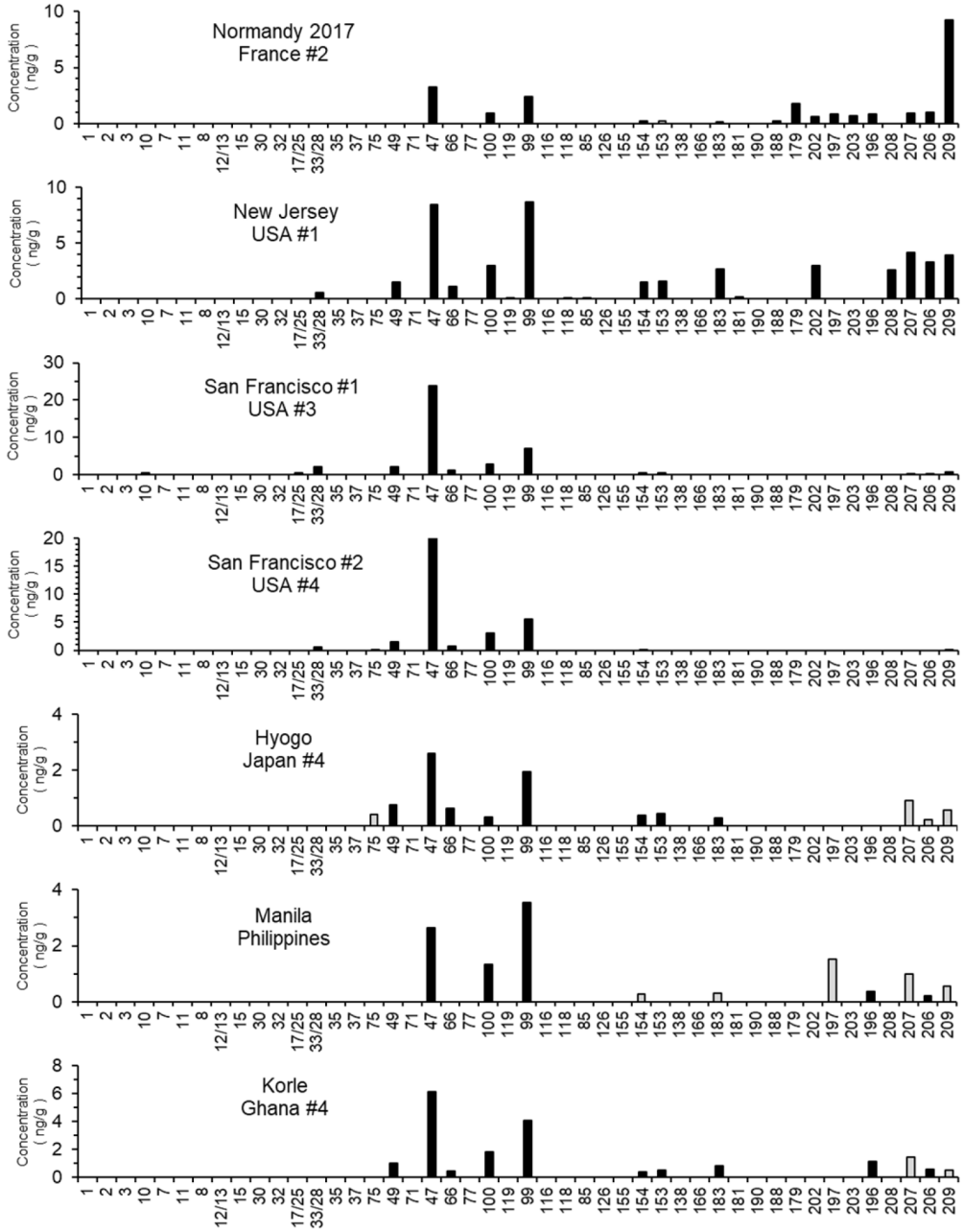

Fig. 2 Typical congener profiles of PBDEs in pellets. Gray bars: < LOQ

er than those of Σ_{13}PCBs (0.15–2,230 ng/g-pellet, median of 51 ng/g-pellet; Table 2). This seems to be inconsistent with the similar levels of PBDE and PCB production: ~1.3 to 1.5 million t of PBDE from 1970 to 2005 (UNEP, 2010) and ~1.3 million t of PCBs until 1993 (Breivik et al., 2002). However, as PBDEs in pellets were mainly derived from Penta-BDE technical mixtures, and their production (~0.1 million t) was one order of magnitude lower than that of PCBs, lower concentrations of PBDEs than that of PCBs in pellets can be reasonably expected. Similar lower concentrations of PBDEs than that of PCBs were observed in seawater (Mizukawa et al., 2009), bivalves (Bayen et al., 2003; Bervoets et al., 2004; Bodin et al., 2007; Mizukawa et al., 2009), mammal tissues (Kunisue et al., 2008), and human breast milk (Malarvannan et al., 2009). Different forms of usage between the two chemicals may also contribute to the lower environmental concentrations of PBDEs: PBDEs are added as flame retardants to long-lived plastic products and textiles and thus are not leached into the environment as easily as PCBs, which are used in insulation oils, lubricants, heating fluids, and pigments. PCBs are thus more easily leached from these products during their use and disposal, resulting in higher environmental concentrations than that of PBDEs.

SPATIAL PATTERN OF PBDEs IN PELLETS

Σ_6PBDEs are used as frequently detected congeners to spatially compare PBDE concentrations in pellets. They are often measured in other PBDE monitoring studies. BDE-209 and related higher-brominated congeners are not included in the sum because they may originate from recycled plastics and the direct attachment of soil and sediment particles, resulting in the spurious detection of higher-brominated congeners in

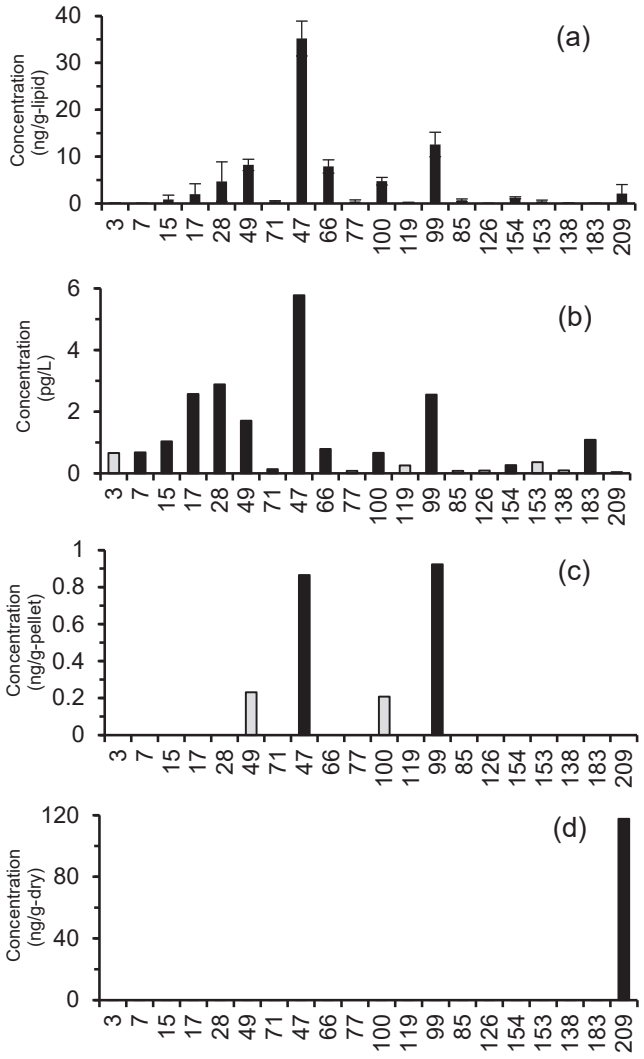

Fig. 3 PBDE congener profiles of (a) bivalves*, (b) filtrates of seawater†, (c) pellets‡, and (d) sediments§ from Tokyo Bay
*Average of values in giant Pacific oyster in Tokyo Bay from Mizukawa et al. (2009, 2013b). Values for Tokyo Bay sediment from Mizukawa et al. (2009). Gray bars: LOD ("not detected").
†Values for the filtrate of surface water of Tokyo Bay from Mizukawa et al. (2021). Gray bars: < LOQ.
‡This study (Odaiba). Gray bars: < LOQ.
§Values for Tokyo Bay sediment from Mizukawa et al. (2009). Gray bars: < LOQ.

samples. Herein, we assayed Σ_6PBDEs.

The results of the assays are shown in the global map (Fig. 4a) and regional maps for Europe (Fig. 4b) and Japan (Fig. 4c). Σ_6PBDEs ranged from n.d. (usually < 0.08 ng/g-pellet) to 36 ng/g-pellet. The samples were categorized into five pollution levels based on their concentrations. Twenty locations exhibited no significant concentrations of Σ_6PBDEs (< 0.2 ng/g-pellet, which is the typical LOQ). This is classified as "no local pollution." The other, higher, concentration levels are categorized based on equal sorting of samples according to Σ_6PBDEs such that each category contains an equal number of samples; they are classified as "slightly polluted" (0.2–0.78 ng/g), "moderately polluted" (0.78–2.6 ng/g), "highly polluted" (2.6–8.5 ng/g), and "extremely polluted" (> 8.5 ng/g). Extremely polluted samples came from the USA, Belize, Puerto Rico, Ghana, and Spain (Fig. 4). Highly polluted sites were identified in China, France, the Philippines, Ghana, Japan, and Argentina. Moderately polluted sites were in Australia, the UAE, Brazil, and other countries in Europe and Africa (Fig. 4). No local pollution and slightly polluted areas were detected mainly on remote islands and in coastal zones in rural regions (Fig. 4).

These concentrations of PBDEs in pellets and the categorizations are consistent with those previously reported for pellets in Brazil (Taniguchi et al., 2016), Chile (Pozo et al., 2020), and the Canary Islands (Camacho et al., 2019). Taniguchi et al. (2016) measured pellets from 41 locations in São Paulo, Brazil, and reported Σ_6PBDEs ranging from 0.76 to 2.67 ng/g-pellet. They analyzed pellets from three locations in Guarujá, São Paulo, where pellets were also sampled for our study. At the three locations, they found Σ_6PBDEs ranging from < 0.76 to 1.61 ng/g, similar to our measurement (0.85 ng/g-pellet). These low levels of PBDE pollution are consistent with the results obtained in crabs and fishes in a neighboring region (Magalhães et al., 2012, 2017). In Chile, Pozo et al. (2020) measured pellets from three sites in San Vicente Bay, where pellets were also sampled for our study; they reported Σ_6PBDEs ranging from 0.03 to 0.45 ng/g-pellet. All samples were categorized as reflective of "no local pollution" or "slightly polluted." This is consistent with our Σ_6PBDEs value of 0.18 ng/g in the pellets collected from the same bay. Camacho et al. (2019) measured PBDEs in pellets from four locations in the Canary Islands and reported the sum of eight BDE congeners (BDE-28, 47, 99, 100, 154, 153, 85, 183) ranging from 0.5 to 3.1 ng/g-pellet. This wide range is similar to our measurement of PBDEs in two locations in the Canary Islands, Σ_6PBDEs of 0.2 and 3.3 ng/g-pellet. These comparisons support that our measurements reflect the global spatial pattern of PBDE concentrations, although our collection of pellets from each country was limited.

High concentrations of Σ_6PBDEs were observed in industrialized countries: USA (17–36 ng/g-pellet), France, the Netherlands, and Japan (< 0.7–8.8 ng/g-pellet). Higher concentrations of PBDEs in pellets collected from USA (Fig. 4a) were anomalous with the measured concentrations of PCBs. PCB concentrations in pellets collected from US coasts were similar to or lower than those collected from the coasts of France, the Netherlands, Italy, and Japan (Fig. 5). This is because the consumption of penta-BDE technical mixtures, which contain tetra- and penta-brominated congeners as the main components, is higher in USA than in Europe and Japan. USA is estimated to constitute 85% of the global consumption of penta-BDE (Abbasi et al., 2015), compared with only 48% of the global historical emissions of PCBs (Breivik et al., 2007). Resulting from the prevalent consumption of penta-BDE technical products in the USA, a greater amount of tetra- to penta-brominated congeners is likely to have been released and accumulated there than in other countries.

Higher concentrations of PBDEs in pellets collected from USA were also consistent with those observed in seawater, sediments, and biota (Oros et al., 2005). Concentrations of BDE-47 in mussels, which have long been used to monitor POPs, obtained from the literature (de Boer et al., 2003; Zhu

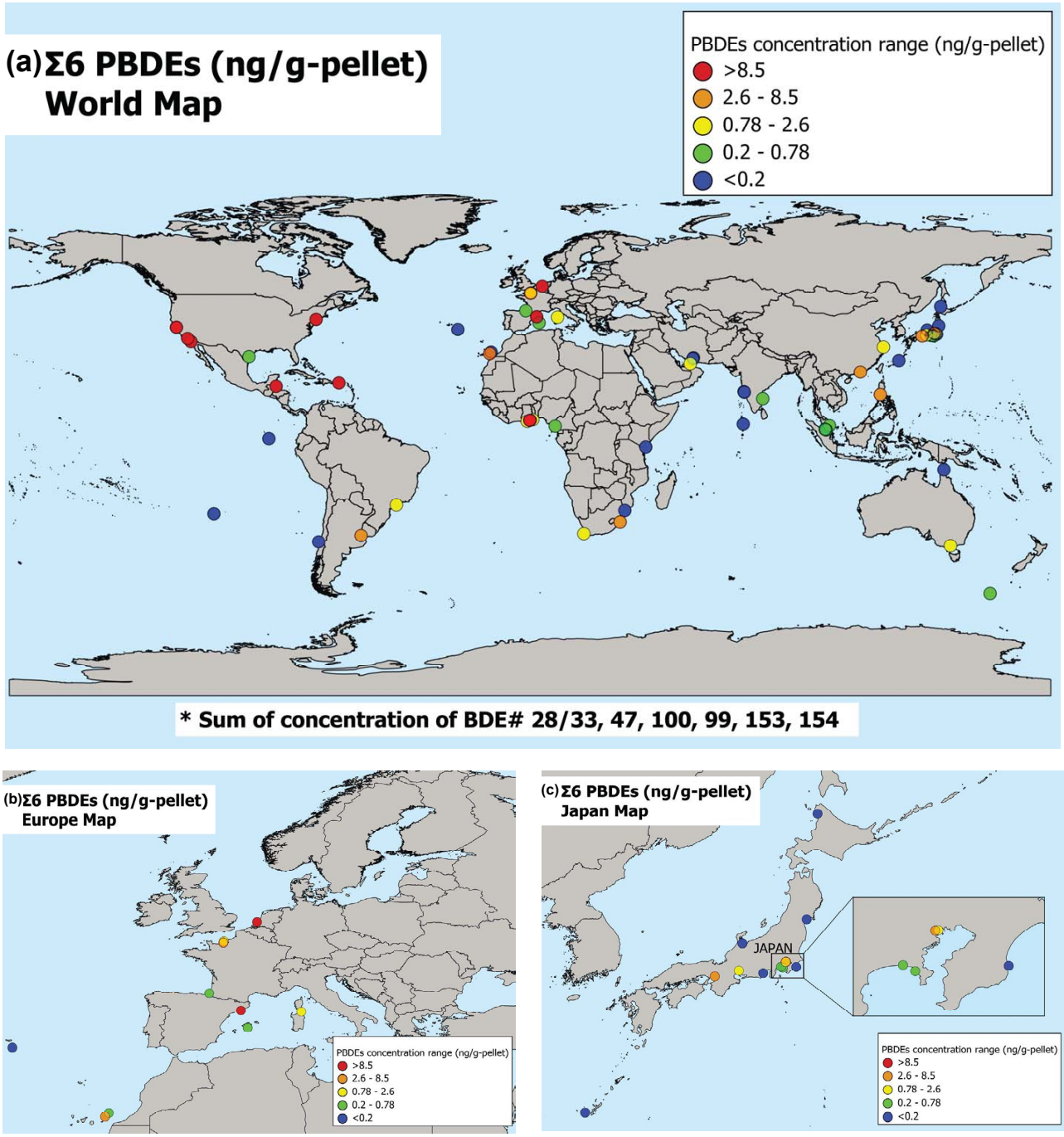

Fig. 4 Concentrations of Σ_6PBDEs in beached plastic resin pellets. Σ_6PBDEs: sum of concentrations of BDE-28/33, 47, 99, 100, 153, and 154. (a) Global, (b) Europe, and (c) Japan

and Hites, 2003; Oros et al., 2005; Johansson et al., 2006; Ramu et al., 2007; Mizukawa et al., 2009; Ueno et al., 2010) are summarized in Table S5. Concentrations of BDE-47 in mussels from USA (1.4–43 ng/g-dry) were one order of magnitude higher than those from Europe (0.58–4.96 ng/g-dry), which were subsequently higher than those from Japan (0.02–0.98 ng/g-dry), China, Malaysia, Indonesia, and India (0.002–0.108 ng/g-dry). This order in other environmental media is consistent with that determined using pellets. Widespread PBDE pollution in the air in the Northern Hemisphere (Jaward et al., 2004; Shen et al., 2006) is also consistent with the occurrence of higher concentrations of PBDEs in pellets collected from the Northern Hemisphere (Fig. 4a). These results indicate that the global spatial pattern of PBDE pollution in pellets is similar to those in other environmental media.

PBDE POLLUTION IN DEVELOPING COUNTRIES

Similar high concentrations of PBDEs to those in Europe and USA were observed in Ghana, Puerto Rico, and Belize, where no PBDEs are produced. Moderately high concentrations were observed in the Philippines, Hong Kong, and Brazil, where no PBDEs are produced. These concentrations can be attributed to imported electrical and electronic equipment (EEE) or e-waste imported (officially and unofficially) from

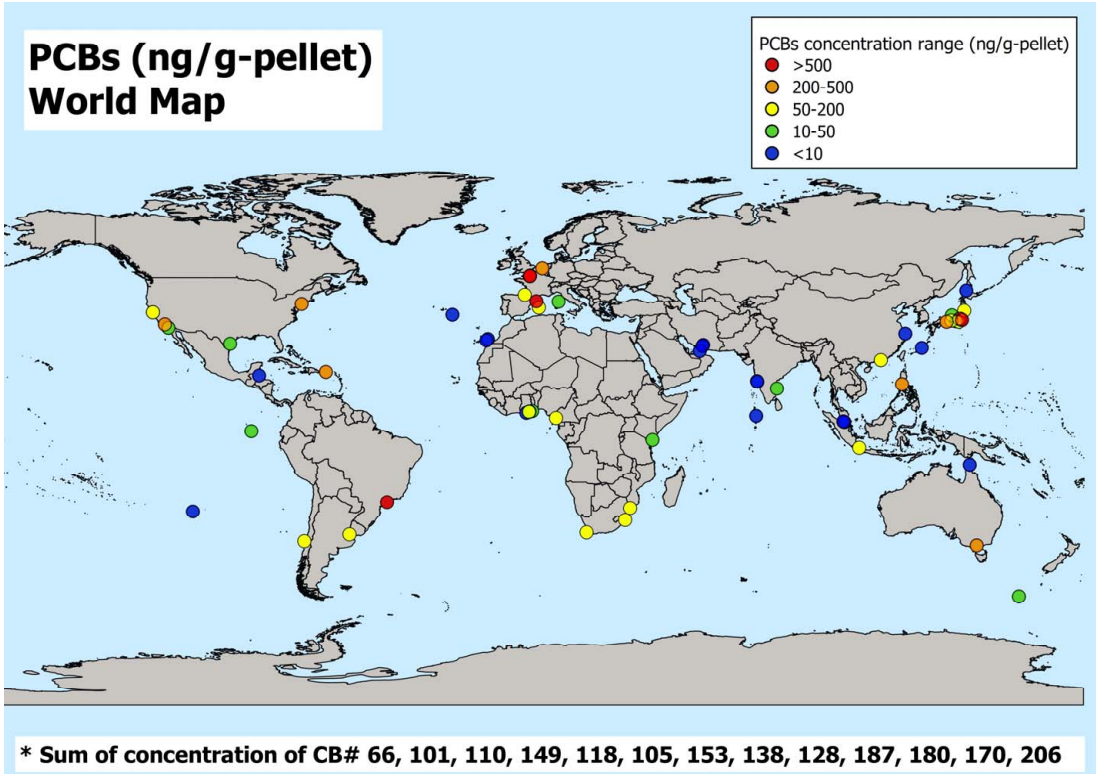

Fig. 5 Concentrations of Σ_{13}PCBs in beached plastic resin pellets. Σ_{13}PCBs: sum of concentrations of CB-66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, and 206

developed countries (Lundgren, 2012). Large amounts of old EEE are disposed of and transported to official (and unofficial) sites for disposal or recycling. Official sites have a large capacity to conduct appropriate processes, and the facilities and working environment are properly managed there. However, unofficial sites are unregulated and activities are not conducted under controlled conditions. At such sites, with small capacity and inefficient management (Tsydenova and Bengtsson, 2011), the release of PBDEs that have leached out from the EEE and e-waste into the surrounding environment is of great concern. Sometimes, EEE and e-waste are burned in the open (e.g., Fig. S4), and evaporated PBDEs could be deposited on the surrounding soil and transported to coastal waters in surface runoff.

Extremely high concentrations of Σ_6PBDEs were observed in Puerto Rico (17 ng/g) and Belize (26 ng/g). Puerto Rico is an unincorporated territory of USA in the Caribbean. The elevated levels of PBDEs in pellets collected from Península La Esperanza, Cataño, in Puerto Rico, might be associated with its location in San Juan Bay (Pérez-Alvelo et al., 2021). This semi-enclosed bay is located in a highly urbanized, commercialized, and industrialized zone that includes maritime cargo port facilities, cruise line terminals, and a nearby airport. Enclosed harbors where shipping and unloading operations occur are significantly contaminated by PBDEs (Zheng et al., 2004). We suspect pollution derived from industrial activities (stemming from its close association with USA) in the Bay area to be a source of the high concentrations of PBDEs. In addition, PBDEs derived from the use of imported consumer products (e.g., electronic and electrical equipment), mainly from USA, could be another pollution source. PBDEs could enter this harbor through improperly disposed-of PBDE-containing products from adjacent land-based sources, such as discharges from wastewater treatment plants, leachates from landfills, stormwater runoff, and riverine input. Belize also imports relatively large amounts of industrial equipment from USA. Shen et al. (2006) studied PBDEs (BDE-47, 99, 100, 153, and 154) in the air of North and Central America using a passive air sampler and reported that concentrations in Belize were the highest among all 40 locations, including those in mainland USA. The high concentration of PBDEs in pellets collected from Belize is consistent with the spatial pattern of atmospheric PBDEs.

The range of Σ_6PBDEs in Ghana (0.84–16 ng/g-pellet) was the same as or higher than that in Europe (<LOQ–8.8 ng/g-pellet). Σ_6PBDEs were significantly higher (13–16 ng/g-pellet) in Accra than in other areas sampled in Ghana (0.84–6.2 ng/g-pellet). Thus, the specific source of PBDEs is likely to be present in the capital city. In a previous study on PCBs in Accra (Hosoda et al., 2014), the e-waste scrapyard at Agbogbloshie was identified as the source of PCBs in the coastal zone there. Thus, the e-waste scrapyard in Accra is suspected to be an important source of PBDEs in pellets from the Accra coastal zone. The dismantling and dumping of e-waste could contribute to PBDE pollution there.

Pellets collected from the Philippines and Hong Kong exhibited moderate levels of PBDEs, i.e., 7.5 and 7.7 ng/g-pellet, respectively. These are similar to those found in Europe. The reason for these high concentrations could be e-waste. A similar trend was observed in the Asian Mussel Watch: higher concentrations of BDE-47 in mussels were reported from the Philippines (0.21–0.56 ng/g-dry, Ramu et al., 2007) and Hong

Kong (0.06–29.8, Liu et al., 2005; Ramu et al., 2007) than from other tropical Asian countries (0.002–0.108 ng/g-dry, Ramu et al., 2007) (Table S5). E-waste recycling plants (both official and unofficial) in Manila may be a major source of PBDEs in the Philippines. In addition, leachate from garbage dumping sites could be another important source. Landfill leachate in Manila exhibited higher concentrations of PBDEs among those in Asia (Kwan et al., 2013b). In Hong Kong, trading in e-waste is now banned. However, e-waste was imported and recycled in the unofficial e-waste sector in the past (Shinkuma and Nguyen Thi Minh, 2009) in Hong Kong. In another study, PBDEs were determined in soil samples collected from an e-waste dismantling workshop, an open burning site, and e-waste storage in the new territories of Hong Kong (Lopez et al., 2011). These findings suggest that e-waste activities cause PBDE pollution in those areas, which our results may reflect. In the background of these case studies, the global generation of e-waste was estimated to be 53.6 million t in 2019, up by 9.2 million t since 2014; it is projected to grow to 74.7 million t by 2030 (Forti et al., 2020). The fate of ~80% of e-waste is uncertain and the resulting environmental impact varies across regions (Forti et al., 2020). Thus, continuous PBDE monitoring through IPW must be performed in these regions.

CONCLUSIONS

High PBDE levels in pellets collected from USA, western Europe, and Japan reflect the legacy of the use of penta-BDE technical products. Elevated concentrations in some industrially developing countries can be attributed to the processing of e-waste. As the global generation of e-waste continues to increase, pollution potentially associated with it should be studied in more detail by testing sediment and air samples together with pellets. For the initial screening of areas potentially polluted by e-waste, IPW and the five-level categorization of PBDEs would provide a valuable benchmark.

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SUPPLEMENTARY MATERIAL

Fig. S1–1 to S1–10, Congener profiles of PBDEs in all the pellet samples. Gray bars: insignificant values (<LOQ); Fig. S2, Congener profiles of PBDEs in technical products. Data from La Guardia et al., 2006; Fig. S3, Relative compositions of PBDE congeners for 5 pools of pellets (tops) form Japan #7 (Fujimae) and Technical products (bottoms). Data for the technical products are from La Guardia et al., (2006); Fig. S4, Photos of incinerated e-waste in scrapyard at Agbogbloshie, Accra, Ghana (Sep. 14, 2015); Table S1, LOD of individual congeners of PBDEs in pellet (ng/g-pellet); Table S2, LOQ of individual congeners of PBDEs in pellet (ng/g-pellet); Table S3, Concentration of individual congeners of PBDEs in pellet (ng/g-pellet); Table S4, Concentration of individual congeners of PBDEs in virgin pellets (ng/g-pellet); Table S5, Concentrations of BDE-47 in mussel and related species reported in references.

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REFERENCES

Abbasi, G., Buser, A.M., Soehl, A., Murray, M.W., Diamond, M.L., 2015. Stocks and flows of PBDEs in products from use to waste in the U.S. and Canada from 1970 to 2020. *Environ. Sci. Technol.* 49, 1521–1528. doi: 10.1021/es504007v.

Alidoust, M., Yeo, G.B., Mizukawa, K., Takada, H., 2021. Monitoring of polycyclic aromatic hydrocarbons, hopanes, and polychlorinated biphenyls in the Persian Gulf in plastic resin pellets. *Mar. Pollut. Bull.* 165, 112052. doi: 10.1016/j.marpolbul.2021.112052.

Bao, L.-J., You, J., Zeng, E.Y., 2011. Sorption of PBDE in low-density polyethylene film: Implications for bioavailability of BDE-209. *Environ. Toxicol. Chem.* 30, 1731–1738. doi: 10.1002/etc.564.

Bayen, S., Thomas, G.O., Lee, H.K., Obbard, J.P., 2003. Occurrence of polychlorinated biphenyls and polybrominated diphenyl ethers in green mussels (Perna viridis) from Singapore, Southeast Asia. *Environ. Toxicol. Chem.* 22, 2432–2437. doi: 10.1897/02-452.

Bervoets, L., Voets, J., Chu, S., Covaci, A., Schepens, P., Blust, R., 2004. Comparison of accumulation of micropollutants between indigenous and transplanted zebra mussels (Dreissena polymorpha). *Environ. Toxicol. Chem.* 23, 1973–1983. doi: 10.1897/03-365.

Bodin, N., Abarnou, A., Fraisse, D., Defour, S., Loizeau, V., Le Guellec, A.M., Philippon, X., 2007. PCB, PCDD/F, and PBDE levels and profiles in crustaceans from the coastal waters of Brittany and Normandy (France). *Mar. Pollut. Bull.* 54, 657–668. doi: 10.1016/j.marpolbul.2007.01.018.

Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2002. Towards a global historical emission inventory for selected PCB congeners—a mass balance approach: 1. Global production and consumption. *Sci. Total Environ.* 290, 181–198. doi: 10.1016/S0048-9697(01)01075-0.

Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2007. Towards a global historical emission inventory for selected PCB congeners—A mass balance approach: 3. An update. *Sci. Total Environ.* 377, 296–307. doi: 10.1016/j.scitotenv.2007.02.026.

Camacho, M., Herrera, A., Gómez, M., Acosta-Dacal, A., Martínez, I., Henríquez-Hernández, L.A., Luzardo, O.P., 2019. Organic pollutants in marine plastic debris from Canary Island beaches. *Sci. Total Environ.* 662, 22–31. doi: 10.1016/j.scitotenv.2018.12.422.

de Boer, J., Wester, P.G., van der Horst, A., Leonards, P.E.G., 2003. Polybrominated diphenyl ethers in influents, suspended particulate matter, sediments, sewage treatment plant and effluents, and biota from the Netherlands. *Environ. Pollut.* 122, 63–74. doi: 10.1016/S0269-7491(02)00280-4.

de Wit, C.A., 2002. An overview of brominated flame retardants in the environment. *Chemosphere* 46, 583–624. doi: 10.1016/S0045-6535(01)00225-9.

Eriksson, J., Green, N., Marsh, G., Bergman, Å., 2004. Photochemical decomposition of 15 polybrominated diphenyl ether congeners in methanol/water. *Environ. Sci. Technol.* 38, 3119–3125. doi: 10.1021/es049830t.

Eriksson, P., Jakobsson, E., Fredriksson, A., 2001. Brominated flame retardants: A novel class of developmental neurotoxicants in our environment? *Environ. Health Perspect.* 109, 903–908. doi: 10.1289/ehp.01109903.

Fang, L., Huang, J., Yu, G., Wang, L., 2008. Photochemical degradation of six polybrominated diphenyl ether congeners under ultraviolet irradiation in hexane. *Chemosphere* 71, 258–267. doi: 10.1016/j.chemosphere.2007.09.041.

Forti, V., Baldé, C.P., Kuehr, R., Bel, G., 2020. The Global E-waste Monitor 2020: Quantities, flows, and the circular economy potential. ISBN Digital: 978-92-808-9114-0, http://ewastemonitor.info/ (accessed 2 Nov. 2020)

Frouin, H., Lebeuf, M., Hammill, M., Masson, S., Fournier, M., 2010. Effects of individual polybrominated diphenyl ether (PBDE) congeners on harbor seal immune cells in vitro. *Mar. Pollut. Bull.* 60, 291–298. doi: 10.1016/j.marpolbul.2009.09.006.

Hirai, H., Takada, H., Ogata, Y., Yamashita, R., Mizukawa, K., Saha, M., Kwan, C., Moore, C., Gray, H., Laursen, D., Zettler, E.R., Farrington, J.W., Reddy, C.M., Peacock, E.E., Ward, M.W., 2011. Organic micropollutants in marine plastics debris from the open ocean and remote and urban beaches. *Mar. Pollut. Bull.* 62, 1683–1692. doi: 10.1016/j.marpolbul.2011.06.004.

Hosoda, J., Ofosu-Anim, J., Sabi, E.B., Akita, L.G., Onwona-Agyeman, S., Yamashita, R., Takada, H., 2014. Monitoring of organic micropollutants in Ghana by combination of pellet watch with sediment analysis: E-waste as a source of PCBs. *Mar. Pollut. Bull.* 86, 575–581. doi: 10.1016/j.marpolbul.2014.06.008.

Jaward, F.M., Meijer, S.N., Steinnes, E., Thomas, G.O., Jones, K.C., 2004. Further studies on the latitudinal and temporal trends of persistent organic pollutants in Norwegian and U.K. background air. *Environ. Sci. Technol.* 38, 2523–2530. doi: 10.1021/es035292t.

Johansson, I., Héas-Moisan, K., Guiot, N., Munschy, C., Tronczyński, J., 2006. Polybrominated diphenyl ethers (PBDEs) in mussels from selected French coastal sites: 1981–2003. *Chemosphere* 64, 296–305. doi: 10.1016/j.chemosphere.2005.12.014.

Kajiwara, N., Noma, Y., Takigami, H., 2008. Photolysis studies of technical decabromodiphenyl ether (DecaBDE) and ethane (DeBDethane) in plastics under natural sunlight. *Environ. Sci. Technol.* 42, 4404–4409. doi: 10.1021/es800060j.

Karapanagioti, H.K., Endo, S., Ogata, Y., Takada, H., 2011. Diffuse pollution by persistent organic pollutants as measured in plastic pellets sampled from various beaches in Greece. *Mar. Pollut. Bull.* 62, 312–317. doi: 10.1016/j.marpolbul.2010.10.009.

Kim, M., Guerra, P., Theocharides, M., Barclay, K., Smyth, S.A., Alaee, M., 2013. Parameters affecting the occurrence and removal of polybrominated diphenyl ethers in twenty Canadian wastewater treatment plants. *Water Res.* 47, 2213–2221. doi: 10.1016/j.watres.2013.01.031.

Kunisue, T., Takayanagi, N., Isobe, T., Takahashi, S., Nakatsu, S., Tsubota, T., Okumoto, K., Bushisue, S., Shindo, K., Tanabe, S., 2008. Regional trend and tissue distribution of brominated flame retardants and persistent organochlorines in raccoon dogs (Nyctereutes procyonoides) from Japan. *Environ. Sci. Technol.* 42, 685–691. doi: 10.1021/es071565z.

Kwan, C.S., Takada, H., Mizukawa, K., Torii, M., Koike, T., Yamashita, R., Rinawati, Saha, M., Santiago, E.C., 2013a. PBDEs in leachates from municipal solid waste dumping sites in tropical Asian countries: Phase distribution and debromination. *Environ. Sci. Pollut. Res.* 20, 4188–4204. doi: 10.1007/s11356-012-1365-3.

Kwan, C.S., Takada, H., Mizukawa, K., Saha, M., Rinawati, Santiago, E.C., 2013b. Sedimentary PBDEs in urban areas of tropical Asian countries. *Mar. Pollut. Bull.* 76, 95–105. doi: 10.1016/j.marpolbul.2013.09.023.

La Guardia, M.J., Hale, R.C., Harvey, E., 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.* 40, 6247–6254. doi: 10.1021/es060630m.

La Guardia, M.J., Hale, R.C., Harvey, E., 2007. Evidence of debromination of decabromodiphenyl ether (BDE-209) in biota from a wastewater receiving stream. *Environ. Sci. Technol.* 41, 6663–6670. doi: 10.1021/es070728g.

Li, Y., Chang, Q., Luo, Z., Zhang, J., Liu, Y., Duan, H., Li, J., 2020. Transfer of POP-BFRs within e-waste plastics in recycling streams in China. *Sci. Total Environ.* 717, 135003. doi: 10.1016/j.scitotenv.2019.135003.

Li, B., Danon-Schaffer, M.N., Li, L.Y., Ikonomou, M.G., Grace, J.R., 2012. Occurrence of PFCs and PBDEs in landfill leachates from across Canada. *Water, Air, Soil Pollut.* 223, 3365–3372. doi: 10.1007/s11270-012-1115-7.

Liu, Y., Zheng, G.J., Yu, H., Martin, M., Richardson, B.J., Lam, M.H.W., Lam, P.K.S., 2005. Polybrominated diphenyl ethers (PBDEs) in sediments and mussel tissues from Hong Kong marine waters. *Mar. Pollut. Bull.* 50, 1173–1184. doi: 10.1016/j.marpolbul.2005.04.025.

Lopez, B.N., Man, Y.B., Zhao, Y.G., Zheng, J.S., Leung, A.O.W., Yao, J., Wong, M.H., 2011. Major pollutants in soils of abandoned agricultural land contaminated by e-waste activities in Hong Kong. *Arch. Environ. Contam. Toxicol.* 61, 101–114. doi: 10.1007/s00244-010-9590-6.

Lundgren, K., 2012. The global impact of e-waste Addressing the challenge. International Labour Organization, Geneva.

Luo, Y., Luo, X.-J., Lin, Z., Chen, S.-J., Liu, J., Mai, B.-X., Yang, Z.-Y., 2009. Polybrominated diphenyl ethers in road and farmland soils from an e-waste recycling region in Southern China: Concentrations, source profiles, and potential dispersion and deposition. *Sci. Total Environ.* 407, 1105–1113. doi: 10.1016/j.scitotenv.2008.10.044.

Magalhães, C.A., Taniguchi, S., Cascaes, M.J., Montone, R.C., 2012. PCBs, PBDEs, and organochlorine pesticides in crabs Hepatus pudibundus and Callinectes danae from Santos Bay, State of São Paulo, Brazil. *Mar. Pollut. Bull.* 64, 662–667. doi: 10.1016/j.marpolbul.2011.12.020.

Magalhães, C.A., Taniguchi, S., Lourenço, R.A., Montone, R.C., 2017. Organochlorine pesticides, PCBs, and PBDEs in liver and muscle tissues of Paralonchurus brasiliensis,

Trichiurus lepturus and Cathorops spixii in Santos Bay and surrounding area, São Paulo, Brazil. *Reg. Stud. Mar. Sci.* 16, 42–48. doi: 10.1016/j.rsma.2017.08.010.

Malarvannan, G., Kunisue, T., Isobe, T., Sudaryanto, A., Takahashi, S., Prudente, M., Subramanian, A., Tanabe, S., 2009. Organohalogen compounds in human breast milk from mothers living in Payatas and Malate, the Philippines: Levels, accumulation kinetics and infant health risk. *Environ. Pollut.* 157, 1924–1932. doi: 10.1016/j.envpol.2009.01.010.

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., Kaminuma, T., 2001. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environ. Sci. Technol.* 35, 318–324. doi: 10.1021/es0010498.

McDonald, T.A., 2002. A perspective on the potential health risks of PBDEs. *Chemosphere* 46, 745–755. doi: 10.1016/S0045-6535(01)00239-9.

Melymuk, L., Robson, M., Csiszar, S.A., Helm, P.A., Kaltenecker, G., Backus, S., Bradley, L., Gilbert, B., Blanchard, P., Jantunen, L., Diamond, M.L., 2014. From the City to the Lake: Loadings of PCBs, PBDEs, PAHs and PCMs from Toronto to Lake Ontario. *Environ. Sci. Technol.* 48, 3732–3741. doi: 10.1021/es403209z.

Mizukawa, K., Takada, H., Ito, M., Geok, Y.B., Hosoda, J., Yamashita, R., Saha, M., Suzuki, S., Miguez, C., Frias, J., Antunes, J.C., Sobral, P., Santos, I., Micaelo, C., Ferreira, A.M., 2013a. Monitoring of a wide range of organic micropollutants on the Portuguese coast using plastic resin pellets. *Mar. Pollut. Bull.* 70, 296–302. doi: 10.1016/j.marpolbul.2013.02.008.

Mizukawa, K., Takada, H., Takeuchi, I., Ikemoto, T., Omori, K., Tsuchiya, K., 2009. Bioconcentration and biomagnification of polybrominated diphenyl ethers (PBDEs) through a lower-trophic-level coastal marine food web. *Mar. Pollut. Bull.* 58, 1217–1224. doi: 10.1016/j.marpolbul.2009.03.008.

Mizukawa, K., Yamada, T., Hirai, Y., Takada, H., 2021. Environmental factors in debromination activity of polybrominated diphenyl ethers by hepatic microsomes of freshwater fish. *Environ. Sci. Pollut. Res.* 28, 326–335. doi: 10.1007/s11356-020-10431-w.

Mizukawa, K., Yamada, T., Matsuo, H., Takeuchi, I., Tsuchiya, K., Takada, H., 2013b. Biomagnification and debromination of polybrominated diphenyl ethers in a coastal ecosystem in Tokyo Bay. *Sci. Total Environ.* 449, 401–409. doi: 10.1016/j.scitotenv.2013.01.092.

Ogata, Y., Takada, H., Mizukawa, K., Hirai, H., Iwasa, S., Endo, S., Mato, Y., Saha, M., Okuda, K., Nakashima, A., Murakami, M., Zurcher, N., Booyatumanondo, R., Zakaria, M.P., Dung, L.Q., Gordon, M., Miguez, C., Suzuki, S., Moore, C., Karapanagioti, H.K., Weerts, S., McClurg, T., Burres, E., Smith, W., Valkenburg, M.V., Lang, J.S., Lang, R.C., Laursen, D., Danner, B., Stewardson, N., Thompson, R.C., 2009. International Pellet Watch: Global monitoring of persistent organic pollutants (POPs) in coastal waters. 1. Initial phase data on PCBs, DDTs, and HCHs. *Mar. Pollut. Bull.* 58, 1437–1446. doi: 10.1016/j.marpolbul.2009.06.014.

Oros, D.R., Hoover, D., Rodigari, F., Crane, D., Sericano, J., 2005. Levels and Distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and Bivalves from the San Francisco Estuary. *Environ. Sci. Technol.* 39, 33–41. doi: 10.1021/es048905q.

Pérez-Alvelo, K.M., Llegus, E.M., Forestier-Babilonia, J.M., Elías-Arroyo, C.V., Pagán-Malavé, K.N., Bird-Rivera, G.J., Rodríguez-Sierra, C.J., 2021. Microplastic pollution on sandy beaches of Puerto Rico. *Mar. Pollut. Bull.* 164, 112010. doi: 10.1016/j.marpolbul.2021.112010.

Pozo, K., Urbina, W., Gómez, V., Torres, M., Nuñez, D., Přibylová, P., Audy, O., Clarke, B., Arias, A., Tombesi, N., Guida, Y., Klánová, J., 2020. Persistent organic pollutants sorbed in plastic resin pellet—"Nurdles" from coastal areas of Central Chile. *Mar. Pollut. Bull.* 151, 110786. doi: 10.1016/j.marpolbul.2019.110786.

Ramu, K., Kajiwara, N., Sudaryanto, A., Isobe, T., Takahashi, S., Subramanian, A., Ueno, D., Zheng, G.J., Lam, P.K.S., Takada, H., Zakaria, M.P., Viet, P.H., Prudente, M., Tana, T.S., Tanabe, S., 2007. Asian mussel watch program: Contamination status of polybrominated diphenyl ethers and organochlorines in coastal waters of Asian countries. *Environ. Sci. Technol.* 41, 4580–4586. doi: 10.1021/es070380p.

Shen, L., Wania, F., Lei, Y.D., Teixeira, C., Muir, D.C.G., Xiao, H., 2006. Polychlorinated biphenyls and polybrominated diphenyl ethers in the North American atmosphere. *Environ. Pollut.* 144, 434–444. doi: 10.1016/j.envpol.2005.12.054.

Shinkuma, T., Nguyen Thi Minh, H., 2009. The flow of E-waste material in the Asian region and a reconsideration of international trade policies on E-waste. *Environ. Impact Assess. Rev.* 29, 25–31. doi: 10.1016/j.eiar.2008.04.004.

Söderström, G., Sellström, U., de Wit, C.A., Tysklind, M., 2004. Photolytic debromination of decabromodiphenyl ether (BDE 209). *Environ. Sci. Technol.* 38, 127–132. doi: 10.1021/es034682c.

Takada, H., 2006. Call for pellets! International Pellet Watch Global Monitoring of POPs using beached plastic resin pellets. *Mar. Pollut. Bull.* 52, 1547–1548. doi: 10.1016/j.marpolbul.2006.10.010.

Takada, H., Yamashita, R., 2016. Chapter 7.2: Pollution status of persistent organic pollutants, In: Large Marine Ecosystems: Status and Trends, pp. 165–176, United Nations Environment Programme, Nairobi.

Taniguchi, S., Colabuono, F.I., Dias, P.S., Oliveira, R., Fisner, M., Turra, A., Izar, G.M., Abessa, D.M.S., Saha, M., Hosoda, J., Yamashita, R., Takada, H., Lourenço, R.A., Magalhães, C.A., Bícego, M.C., Montone, R.C., 2016. Spatial variability in persistent organic pollutants and polycyclic aromatic hydrocarbons found in beach-stranded pellets along the coast of the state of São Paulo, southeastern Brazil. *Mar. Pollut. Bull.* 106, 87–94. doi: 10.1016/j.marpolbul.2016.03.024.

Thiel, M., Hong, S, Jambeck, J.R., Gatta-Rosemary, M., Honorato-Zimmer, D., Kiessling, T., Knickmeier, K., Kruse, K., 2017. Marine litter–bringing together citizen scientists from around the world, In: Cigliano, J.A., Ballard, H.L. (eds.), Citizen Science for Coastal and Marine Conservation (1st ed.), Chapter 6, pp. 104–129, Taylor & Francis, London.

Tsydenova, O., Bengtsson, M., 2011. Chemical hazards associated with treatment of waste electrical and electronic equipment. *Waste Manag.* 31, 45–58. doi: 10.1016/j.wasman.2010.08.014.

Ueno, D., Isobe, T., Ramu, K., Tanabe, S., Alaee, M., Marvin, C., Inoue, K., Someya, T., Miyajima, T., Kodama, H., Nakata, H., 2010. Spatial distribution of hexabromocyclododecanes

(HBCDs), polybrominated diphenyl ethers (PBDEs), and organochlorines in bivalves from Japanese coastal waters. *Chemosphere* 78, 1213–1219. doi: 10.1016/j.chemosphere.2009.12.058.

UNEP, 2010. Technical review of the implications of recycling commercial Penta and Octabromodiphenyl ethers. Stockholm Convention document for 6th POP Reviewing Committee meeting. The United Nations Environment Programme, Nairobi. http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC.6-INF-6.English.pdf (accessed 29 Dec. 2020)

UNEP, 2017. Stockholm Convention on Persistent Organic Pollutants (POPs) Texts and Annexes. The United Nations Environment Programme, Nairobi. http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-COP-CONVTEXT-2017.English.pdf (accessed 28 Dec. 2020)

Vojta, Š., Bečanová, J., Melymuk, L., Komprdová, K., Kohoutek, J., Kukučka, P., Klánová, J., 2017. Screening for halogenated flame retardants in European consumer products, building materials and wastes. *Chemosphere* 168, 457–466. doi: 10.1016/j.chemosphere.2016.11.032.

Wurl, O., Lam, P.K.S., Obbard, J.P., 2006. Occurrence and distribution of polybrominated diphenyl ethers (PBDEs) in the dissolved and suspended phases of the sea-surface microlayer and seawater in Hong Kong, China. *Chemosphere* 65, 1660–1666. doi: 10.1016/j.chemosphere.2006.02.024.

Yeo, B.G., Takada, H., Hosoda, J., Kondo, A., Yamashita, R., Saha, M., Maes, T., 2017. Polycyclic aromatic hydrocarbons (PAHs) and hopanes in plastic resin pellets as markers of oil pollution via International Pellet Watch monitoring. *Arch. Environ. Contam. Toxicol.* 73, 196–206. doi: 10.1007/s00244-017-0423-8.

Yeo, B.G., Takada, H., Taylor, H., Ito, M., Hosoda, J., Allinson, M., Connell, S., Greaves, L., McGrath, J., 2015. POPs monitoring in Australia and New Zealand using plastic resin pellets, and International Pellet Watch as a tool for education and raising public awareness on plastic debris and POPs. *Mar. Pollut. Bull.* 101, 137–145. doi: 10.1016/j.marpolbul.2015.11.006.

Zettler, E.R., Takada, H., Monteleone, B., Mallos, N., Eriksen, M., Amaral-Zettler, L.A., 2017. Incorporating citizen science to study plastics in the environment. *Anal. Methods* 9, 1392–1403. doi: 10.1039/C6AY02716D.

Zheng, G.J., Martin, M., Richardson, B.J., Yu, H., Liu, Y., Zhou, C., Li, J., Hu, G., Lam, M.H.W., Lam, P.K.S., 2004. Concentrations of polybrominated diphenyl ethers (PBDEs) in Pearl River Delta sediments. *Mar. Pollut. Bull.* 49, 520–524. doi: 10.1016/j.marpolbul.2004.06.026.

Zhu, L.Y., Hites, R.A., 2003. Determination of polybrominated diphenyl ethers in environmental standard reference materials. *Anal. Chem.* 75, 6696–6700. doi: 10.1021/ac034643j.