Emerging Brominated Flame Retardants in the Environment

Cynthia A. de Wit, Amelie Kierkegaard, Niklas Ricklund, and Ulla Sellström

Abstract A number of new brominated flame retardants (BFRs) are being found in the environment but the amount of data is still very small. The best studied emerging BFRs are 1,2-bis(2,4,6-tribromophenoxy)ethane and decabromodiphenyl ethane, with some data for hexabromobenzene, pentabromoethylbenzene, pentabromotoluene, tetrabromobisphenol A derivatives, bis(2-ethylhexyl) tetrabromophthalate, 2-ethylhexyltetrabromobenzoate, 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane, and 2,4,6-tribromophenol. Very little data are available for 2,4,6-tribromophenyl allyl ether, 2,3-dibromopropyl-2,4,6-tribromophenyl ether, hexachlorocyclopentadienyldibromocyclooctane, *tris*(2,3-dibromopropyl) isocyanurate, tetrabromophthalic anhydride, 1,2,5,6-tetrabromocyclooctane, and octabromo-1,3,3-trimethyl-1-phenylindane. Indoor air concentrations are generally higher than outdoor air concentrations, indicating emissions from flame-retarded products. Their presence in indoor air and dust indicates possible human exposure from this pathway, but there are little human data available to determine this. The presence of several of these BFRs in fish, birds, and mammals indicates that they are bioavailable and can be absorbed and bioaccumulated. Their presence in outdoor air and in the Arctic indicates that several are capable of long range atmospheric transport. More data on these new BFRs are needed in order to determine if they pose unacceptable risks to the environment and to human health.

Keywords 1,2,5,6-Tetrabromocyclooctane, 1,2-Bis(2,4,6-tribromophenoxy)ethane, 1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane, 2,3-Dibromopropyl-2,4,6-tribromophenyl ether, 2,4,6-Tribromophenol, 2,4,6-Tribromophenyl allyl ether, 2-Ethylhexyltetrabromobenzoate, Bis(2-ethylhexyl) tetrabromophthalate,

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C.A. de Wit (✉), A. Kierkegaard, N. Ricklund, and U. Sellström
Department of Applied Environmental Science (ITM) Stockholm University, 10691 Stockholm, Sweden
e-mail: Cynthia.de.wit@itm.su.se

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Decabromodiphenyl ethane, Hexabromobenzene, Hexachlorocyclopenta dienyl-dibromocyclooctane, Octabromo-1,3,3-trimethyl-1-phenylindane, Pentabromo-ethylbenzene, Pentabromotoluene, Tetrabromobisphenol A derivatives, Tetra bromophthalic anhydride, *Tris*(2,3-dibromopropyl) isocyanurate

Contents

Abbreviations

ATE	2,4,6-Tribromophenyl allyl ether
BFR	Brominated flame retardant
BTBPE	1,2-Bis(2,4,6-tribromophenoxy)ethane
DBDPE	Decabromodiphenyl ethane
DPTE	2,3-Dibromopropyl-2,4,6-tribromophenyl ether
HBBz	Hexabromobenzene
HBCD	Hexabromocyclododecane
HCDBCO	Hexachlorocyclopentadienyldibromocyclooctane
OBIND	Octabromo-1,3,3-trimethyl-1-phenylindane

PBDE	Polybrominated diphenyl ether
PBEB	Pentabromoethylbenzene
PBT	Pentabromotoluene
TBB	2-Ethylhexyltetrabromobenzoate
TBBPA	Tetrabromobisphenol A
TBBPA-DAE	Tetrabromobisphenol A bis(allyl ether)
TBBPA-DBPE	Tetrabromobisphenol A (2,3-dibromopropyl ether)
TBBPA-DHEE	Tetrabromobisphenol A dihydroxyethyl ether
TBC	*Tris*(2,3-dibromopropyl) isocyanurate
TBCO	1,2,5,6-Tetrabromocyclooctane
TBECH	1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane
TBP	2,4,6-Tribromophenol
TBPA	Tetrabromophthalic anhydride
TBPH	Bis(2-ethylhexyl) tetrabromophthalate

1 Introduction

At least 75 brominated compounds are listed as flame retardants [1] but analytical focus has been on only a few including polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), and tetrabromobisphenol A (TBBPA). Two of the PBDE technical products (PentaBDE, OctaBDE) are now being phased out or have been banned in North America and Europe. The remaining product (DecaBDE) is used more restrictively, and production, importation, and sales will be discontinued in the USA for all uses by the end of 2013 by the two major producers (Chemtura, Albemarle) and the largest US importer (ICL Industrial Products, Israel) [2–4]. Thus, other brominated flame retardants (BFRs) are finding increasing use as replacements for these BFRs. Some of these emerging BFRs are now being found in the environment, including in the Arctic, suggesting their potential for long range atmospheric transport [5]. This chapter is a review of the literature covering the environmental occurrence of a number of these less well-studied BFRs. Physico-chemical properties of these BFRs are given in Table 1 and their chemical structures are shown in Fig. 1.

2 1,2-Bis(2,4,6-tribromophenoxy)ethane

2.1 Background

1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE) is an additive flame retardant marketed as FF-680 (Great Lakes Chemical Corporation, Arkansas, USA, now a part of Chemtura). BTBPE has been produced since the mid-1970s and is now

Table 1 Physico-chemical properties of emerging brominated flame retardants

Chemical	Abbreviation	CAS number	Molecular weight	Log K_{ow}	Log K_{aw}[a]	Vapor pressure 25°C	References
1,2-Bis(2,4,6-tribromophenoxy)ethane	BTBPE	37853-59-1	687.64	7.88	−5.17	3.88E-10	[90][b]
Decabromodiphenyl ethane	DBDPE	84852-53-9	971.22	11.1	−6.29	6.0E-15	[90][b]
Hexabromobenzene	HBBz	87-82-1	551.49	5.85	−3.03	1.14E-04	[90][b]
				6.07		3.17E-04	[139]
						7.5E-04	[140]
Pentabromoethylbenzene	PBEB	85-22-3	500.65	6.40	−2.92	3.2E-04	[90][b]
Pentabromotoluene	PBT	87-83-2	486.62	5.872	−2.92	1.22E-03	[90][b]
Tetrabromobisphenol A diallyl ether	TBBPA-DAE	25327-89-3	624.00	8.539	−4.43	1.83E-08	[90][b]
Tetrabromobisphenol A 2,3-dibromopropyl ether	TBBPA-DBPE	21850-44-2	943.61	10.422	−8.01	1.60E-07	[90][b]
						8.5E-13	[72][c]
Tetrabromobisphenol A dihydroxyethyl ether	TBBPA-DHEE	4162-45-2	631.98	6.78		5.2E-12	[72][c]
Bis(2-ethylhexyl) tetrabromophthalate	TBPH	26040-51-7	706.14	10.08	−5.95	1.55E-11	[90][b]
				11.95	−4.91	2.28E-09	[136][c]
2-Ethylhexyltetrabromobenzoate	TBB	183658-27-7	549.92	8.75	−3.59	4.57E-06	[136][c]
1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane	TBECH	3322-93-8	427.8	5.24	−2.77	1.40E-02	[136][c]
2,4,6-Tribromophenol	TBP	118-79-6	330.8	4.33	−2.3	0.41	[90][b]
2,4,6-Tribromophenyl allyl ether	ATE	3278-89-5	370.86	4.97	−2.41	4.90E-02	[90][b]
				5.4			[90]
Hexachlorocyclopentadienyldibromocyclooctane	HCDBCO	51936-55-1	536	7.91	−3.14	1.43E-05	[136][c]
Tris(2,3-dibromopropyl) isocyanurate	TBC	52434-90-9	728.69	7.37	−16.31	1.57E-13	[136][c]
Tetrabromophthalic anhydride	TBPA	632-79-1	463.7	3.78	−9.04	1.27E-09	[90][b]
1,2,5,6-tetrabromocyclooctane	TBCO	3194-57-8	427.80	4.42[b]		3.59E-05[b]	
Octabromo-1,3,3,-trimethyl-1-phenylindane	OBIND	155613-93-7	867.52	11.38[d]		2.18E-15[a]	

Log K_{ow} – octanol water partition coefficient; Log K_{aw} – air–water partition coefficient

[a] Log K_{aw} or other values predicted using SPARC Online Calculator

[b] Physico-chemical properties calculated using SciFinder (ACD/Labs Software V9.04)

[c] Physico-chemical properties calculated using US EPA EPI Suite V3.20

[d] Physico-chemical properties calculated using ACD Chemscetch

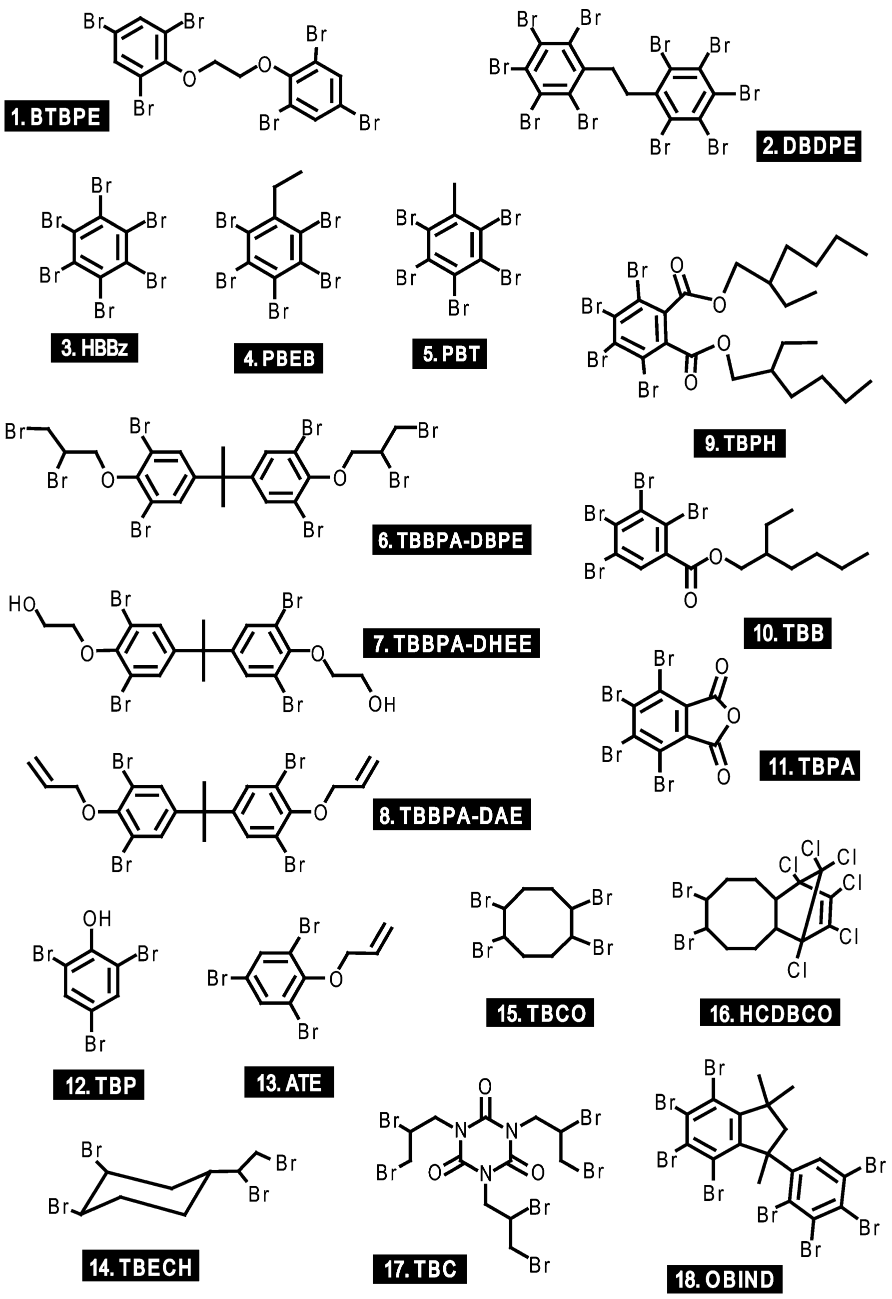

Fig. 1 1,2-bis(2,4,6-Tribromophenoxy)ethane (**1**), decabromodiphenyl ethane (**2**), Hexabromobenzene (**3**), Pentabromoethylbenzene (**4**), Pentabromotoluene (**5**), tetrabromobisphenol A (2,3-dibromopropyl ether) (**6**), tetrabromobisphenol A dihydroxyethyl ether (**7**), tetrabromobisphenol A bis(allyl ether) (**8**), bis(2-ethylhexyl) tetrabromophthalate (**9**), 2-ethylhexyltetrabromobenzoate

being used as a replacement for OctaBDE [6]. It is marketed for use in high impact polystyrene (HIPS), thermoplastics, and thermoset resins. Great Lakes Chemical Corp./Chemtura is the only producer of BTBPE in the USA, and they produced 4,500–22,500 metric tons/year from 1986 to 1994, with a decline to 450–4,500 tons/year after 1998 [6]. No information is available on more recent US production volumes but it can be surmised that they will increase as a result of the ban on OctaBDE. BTBPE is produced and used in China, as well, but information on production and use volumes is not available [7]. It is listed as a low production volume (LPV) chemical in the EU [8]. Worldwide production/usage was estimated to be 16,710 tons in 2001 [9]. BTBPE was first identified in the environment in the 1970s in samples taken at or near the Great Lakes Chemical Corp./Chemtura production facility in El Dorado, Arkansas, USA [10–12].

2.2 *Outdoor Air and Tree Bark*

In 1977, BTBPE was identified in air particulate samples taken using high-volume samplers on the grounds of a production site in El Dorado, Arkansas [11, 12]. The concentrations found ranged from not detectable level to 183 ng/m^3 [11].

More recently, high-volume air samples were taken at a number of sites in the east-central USA within the Integrated Atmospheric Deposition Network (IADN). In a first sampling campaign covering the time period 2002–2004, sampling sites included Chicago (Illinois), Sleeping Bear Dunes National Lakeshore (Michigan), Bloomington (Indiana), Rohwer (Arkansas), and Cocodrie (Louisiana) [6, 13]. BTBPE was found predominantly on particulates with a concentration range of 0.03–70 pg/m^3, and a mean of 3.4 pg/m^3, more than 100 times lower concentrations than seen in particulates sampled on the production site. The highest BTBPE concentrations were found in samples from the Arkansas site, which is only 150 km west of the Chemtura production plant and the authors speculate that these higher concentrations may be due to production facility emissions. The next highest BTBPE concentrations were found in air particulates from Chicago (mean 1.6 pg/m^3, range 0.025–11 pg/m^3), reflecting possible urban sources. Concentrations were lower at the other sites (rural) and were lowest at the remote site at Sleeping Bear Dunes National Lakeshore (mean 0.16 pg/m^3, range 0.03–1.4 pg/m^3) [6, 13]. In a second sampling campaign in 2005–2006, sampling sites included Chicago (Illinois), Sleeping Bear Dunes National Lakeshore and Eagle Harbor (Michigan), Cleveland (Ohio), and Sturgeon Point (New York) [14]. Highest concentrations were found in the samples from the urban site of Chicago (mean 1.2 pg/m^3) and lowest concentrations at the remote site of Eagle Harbor (mean

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Fig. 1 (continued) (**10**), tetrabromophthalic anhydride (**11**), 2,4,6-tribromophenol (**12**), 2,4,6-tribromophenyl allyl ether (**13**), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (**14**), 1,2,5,6-tetrabromocyclooctane (**15**), Hexachlorocyclopentadienyldibromocyclooctane (**16**), *tris*(2,3-dibromopropyl) isocyanurate (**17**), octabromo-1,3,3-trimethyl-1-phenylindane (**18**)

0.5 pg/m^3). The BTBPE concentrations in both studies were similar to those for HBCD and some BDE congeners (BDE-47, -99, -209) in the same samples.

Other than the US, BTBPE has only been reported in air samples from Sweden and from Guangzhou City, in the Pearl River Delta (PRD) of southern China. Outdoor air samples from the city of Stockholm, Sweden, taken with a low volume sampler, had BTBPE concentrations below the limit of quantitation (3 pg/m^3) [15]. The PRD is a highly industrialized and urbanized area in China, with electronics and electrical equipment manufacturing and high usage of BFRs [16]. The mean BTBPE concentration in four high-volume air samples taken in Guangzhou City in 2007 was 30.7 pg/m^3 (range 3.8–67 pg/m^3) [7]. These higher BTBPE concentrations in Guangzhou City are similar to those seen in the air samples from Arkansas, USA, not far from a BTBPE production facility and indicate use of BTBPE in manufacturing facilities in the PRD. The concentrations of BTBPE were lower than those of the PBDEs.

In a sampling campaign of tree bark from 29 sites across North America in 2000–2001, BTBPE was detected in samples from only six of these sites, at concentrations of 0.68–24 ng/g lipid [17]. Sampling was done in rural residential areas away from roads. Interestingly, the samples with the highest BTBPE concentrations were from a site in Arkansas north of the Chemtura production facility (24 ng/g lipid), and several sites east, southeast, or northeast of this facility in the neighboring state of Mississippi (1.4, 1.5, and 1.9 ng/g lw). In another study, tree bark samples were collected in 2006 from 26 sites from the northeastern USA, and samples from 23 sites had BTBPE concentrations ranging from 0.40 to 17 ng/g lipid, with a mean of 3.2 ng/g lipid [18]. As there is only one production facility for BTBPE in the USA, located in the southcentral part of the country, the authors concluded that the presence of BTBPE on trees far from this source could only be explained by long range atmospheric transport and local use. BTBPE concentrations were lower than PBDE concentrations in both studies.

Qiu and Hites [18] also analyzed tree bark samples from Canada, Europe, and Asia. BTBPE was not detected in the sample from the Northwest Territories in Canada. Germany and Italy had BTBPE concentrations of 0.11 and 1.3 ng/g lipid, respectively. BTBPE concentrations were much higher in tree bark from South Korea (56 ng/g lipid), and three sites in China (3.1–38 ng/g lipid). The highest concentration in China was found in Shenzheng, which is located in the PRD. Thus, results from tree bark spatial studies support the results of air sampling studies, indicating that BTBPE is capable of long range atmospheric transport and that production and use facilities are emission sources.

2.3 Soil and Outdoor Dust

In the 1970s, BTBPE was identified but not quantified in soil samples taken near the Chemtura production facility in El Dorado, Arkansas, USA [12]. More recently, BTBPE was found in soil samples taken from two areas in southern China, one in the PRD and one near an electronics waste processing area in the agricultural area of Qingyuan City, north of the PRD [7]. The electronics waste area processes more than 1.7 million tons of e-waste per year imported to China from overseas. E-waste processing is done to recover metals using rudimentary methods in family workshops, including shredding, burning, and use of acids. Soil samples were collected from farmland near Guangzhou City, PRD, in 2007 and from the e-waste area in 2006. The mean BTBPE concentration was 0.05 ng/g dry weight (dw) (range 0.02–0.11 ng/g dw) for the PRD soils, but was much higher, 1.98 ng/g dw (range 0.07–6.2 ng/g dw) in the e-waste soils [7]. Outdoor dust samples collected from the ground surface near the e-waste workshops had a mean BTBPE concentration of 107 ng/g dw (range 14.6–232 ng/g dw), indicating that these workshops are probably a source of emissions to the nearby farmland. The concentrations of BTBPE were lower than those of PBDEs in the PRD samples, but were similar to PentaBDE concentrations at the e-waste site.

2.4 *Indoor Air and Dust*

BTBPE was included in analyses of indoor air at electronic recycling plants in Sweden [15, 19]. Sjödin et al. [15] found highest BTBPE concentrations in air samples taken near a shredder when BFR-containing plastics were shredded (140 and 150 ng/m^3). Lower concentrations were seen when shredding non-BFR-containing plastics (23 and 32 ng/m^3) and in the dismantling hall (mean 20 ng/m^3). These concentrations were in the same range as those of BDE-183 and -209, which were the predominant PBDEs found.

Petterson-Julander et al. [19] found similar BTBPE concentrations in personal air samples of electronic dismantlers at another electronics recycling plant (mean 22 ng/m^3). Personal air samples from other workers not directly exposed in the dismantling hall had lower BTBPE concentrations (mean 8.8 ng/m^3) and unexposed workers had the lowest concentration (0.8 ng/m^3). Again, concentrations of BTBPE were found to be in the same range as those of BDE-209 in all three groups. Expanding on this air sampling study, Julander et al. [20] used different types of air samplers to collect three different particle fractions (respirable, total, and inhalable dust) in air samples at this same electronics recycling plant. The highest BTBPE concentration ranged from 8.2 to 12.2 ng/m^3 in the inhalable fraction. BTBPE was also found in the total fraction (7.4–11.9 ng/m^3) with lowest concentrations in the respirable fraction (0.7–1.0 ng/m^3) [20]. Concentrations of BTBPE were somewhat higher than those of BDE-183, but much lower than those of BDE-209.

Sjödin et al. [15] also analyzed BTBPE in air samples from other indoor microenvironments (circuit board assembly, offices with computers, computer repair facilities, teaching halls). Concentrations were considerably lower and ranged from 41 pg/m^3 (circuit board assembly) to 3 pg/m^3 (teaching hall) and were similar to BDE-183 and -209 concentrations.

BTBPE was found in dust samples from five homes in Örebro, Sweden, with concentrations ranging from 2.5 to 8.2 ng/g dw, which were considerably lower than those of PBDEs [21]. Air samples were also analyzed, but BTBPE was not detected.

Researcher-collected dust samples were taken in 19 homes in Boston, Massachusetts, USA, in 2006, from the main living area, a bedroom, and also from the occupant's vacuum cleaner bag [22]. BTBPE concentrations ranged from 1.6 to 789 ng/g dw. Geometric mean BTBPE concentrations were 48.1 ng/g dw in the living area, 47.8 ng/g dw in the bedroom, and 17.7 ng/g dw in the vacuum cleaner dust [22]. BTBPE was not detected in the dust standard reference material (NIST SRM 2585) used. These concentrations were about ten times lower than HBCD concentrations found in the same samples. An additional 50 dust samples taken from vacuum cleaner bags between 2002 and 2007 from Boston houses also contained BTBPE [23]. BTBPE concentrations ranged from 1.4 to 950 ng/g dw with a geometric mean of 21 ng/g dw, which was eight times lower than the HBCD concentration and much lower than PBDE concentrations.

In the UK, Harrad et al. [24] collected dust samples from 30 homes, 18 offices, and 20 cars in 2006 and 2007. Average BTBPE concentrations were 120, 7.2, and 7.7 ng/g dw for homes, offices, and cars, respectively. The maximum concentration of 1,900 ng/g dw was also found in homes. BTBPE concentrations were generally lower than those of PBDEs. Estimated exposures via dust ingestion for adults and toddlers were as high as 13 and 69 ng/day, respectively, which were lower than those of tri-hexaBDEs.

BTBPE was also detected in dust samples from 25 homes in the Czech Republic but no concentrations were reported [25].

2.5 Children's Toys

China is a major manufacturer of children's toys, particularly in the Guangdong Province in southern China [26]. Sixty-nine toys were purchased in Guangzhou City in southern China in 2007 and 2008 and analyzed for a range of BFRs. The materials included hard plastic, foam, rubber/soft plastic, and textile stuffed toys [26]. BTBPE was found in hard plastic toys with a median concentration of 101 ng/g, which was lower than PBDE concentrations. BTBPE was also detected in some rubber/soft plastic toys, but was not detected in foam or stuffed toys. The estimated exposure of children to BTBPE from mouthing toys was calculated to be 0.024–0.82 ng/kg body weight-day.

2.6 Sewage Sludge

Sewage sludge samples were collected from Guangzhou City, PRD, in southern China in 2007 and analyzed for BTBPE [7]. BTBPE concentrations ranged from 0.31 to 1.66 ng/g dw with a mean of 0.88 ng/g dw.

2.7 Water and Sediment

In a bioaccumulation study of various BFRs, BTBPE was quantified in the dissolved phase of freshwater sampled in 2004 from the south basin of Lake Winnipeg, Canada [27]. The mean BTBPE concentration was 1.96 pg/L, which was lower than BDE-47 and -99 concentrations, but comparable to concentrations of BDE-100, -153, and 154.

Besides finding BTBPE in air samples near a production site in Arkansas, Zweidinger et al. [10] also found detectable levels in sediments from streams near the plant. BTBPE concentrations ranged from not detectable level to 466 ng/g.

BTBPE concentrations in surficial sediment samples collected in 2002 from Lake Winnipeg, Canada were below detection limits [27], but were 7.2 and 6.7 ng/g dw in samples taken in 2004 from Lake Michigan [6] and Lake Ontario [28]. For Lake Michigan, BTBPE concentrations were lower than PBDE concentrations, but were similar to PBDE concentrations for Lake Ontario. In the studies from Lakes Michigan and Ontario, analysis of BTBPE in different levels of sediment cores also showed rapidly increasing temporal trends from the mid-1970s (Michigan) or early 1980s (Ontario) as shown in Fig. 2.

Surficial sediment samples were collected from the Dongjiang River in the PRD area of southern China in 2002 and 2006 and analyzed for BTBPE and a range of other BFRs [7]. The samples from 2002 had a mean BTBPE concentration of

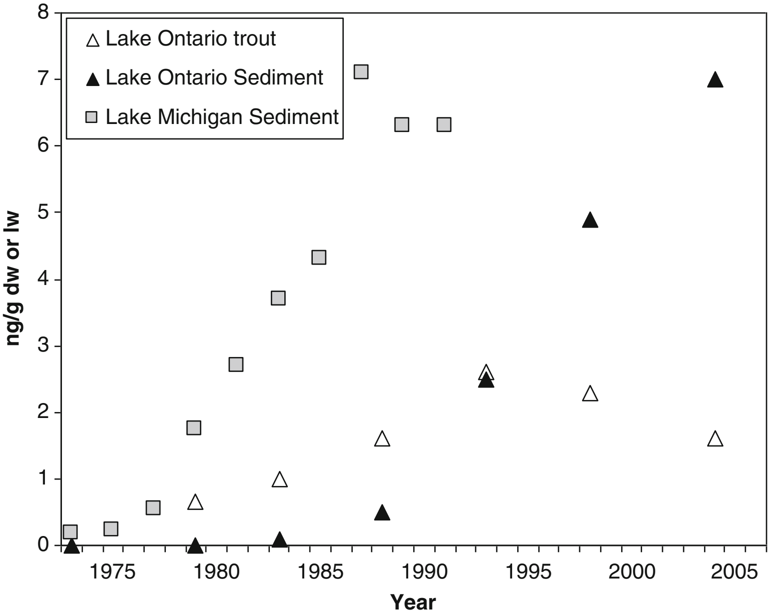

Fig. 2 Temporal trends of BTBPE in lake trout and sediment from Lake Ontario, and in sediment from Lake Michigan. Data from Ismail et al. [32], Hoh et al. [6], and Qiu et al. [28]

7.6 ng/g dw (range 0.27–21.9 ng/g dw), while the 2006 samples had a mean concentration of 1.3 ng/g dw (range 0.05–2.07 ng/g dw). The authors speculate that the lower BTBPE concentrations found in 2006, weighed together with results for a number of other BFRs in past or current use, may reflect changes in the use of different BFRs in the PRD area in recent years [7].

BTBPE was identified in sediments from two of four sites collected from the Western Scheldt along the coast of the Netherlands [29]. Concentrations at the two sites were 0.25 ng/g dw (Terneuzen) and 0.31 ng/g dw (Ouden Doel near the Belgian border). BTBPE was not detected in the suspended particulate matter collected from Terneuzen.

2.8 Invertebrates and Fish

Besides water and sediment, a food web study in Lake Winnipeg included samples of zooplankton, mussels (*Lampsilis radiata*) and six species of fish, including predatory fish such as burbot (*Lota lota*) and walleye (*Stizostedion vitreum*) [27]. Biota were collected between 2000 and 2002. Mean BTBPE concentrations were 0.37 ng/g lipid weight (lw) in zooplankton, 1.3 ng/g lw in mussels, and from 0.13 to 0.95 ng/g lw in the different fish species, which were much lower than HBCD and PBDEs concentrations. The trophic magnification factor of BTBPE for the entire food web was 1.0, which was generally lower than that of most PBDEs and HBCD [27, 30]. Biomagnification factors (BMFs) calculated on the basis of lipid weight BTBPE concentrations in various predator/prey relationships indicated that BTBPE may bioaccumulate within certain feeding relationships, particularly for walleye [27]. BMFs for walleye ranged from 0.4 to 2.5 depending on the prey. The propensity of BTBPE to biomagnify was confirmed in a laboratory feeding study in juvenile rainbow trout (*Oncorhynchus mykiss*) [31]. BTBPE was taken up from the gut with an assimilation efficiency of 27% over the 49 day feeding period, resulting in a BMF of 2.3.

BTBPE concentrations were determined in Lake Ontario lake trout (*Salvelinus namaycush*) sampled from 1979 to 2004 [32]. Concentrations were found to increase exponentially from 1979 to 1993, doubling every 6 years, and then to level off or possibly decrease (Fig. 2). Mean BTBPE concentration in the 2004 sample was 1.6 ng/g lw, which is higher than that seen in fish in the Lake Winnipeg study [27]. Lake trout PBDE and HBCD concentrations were considerably higher than BTBPE concentrations.

In a study near an e-waste processing area in southern China, a few individuals of three farmed fish species were collected (carp (*Cyprinus carpio*), bighead carp (*Aristichthys nobilis*), tilapia (*Tilapia*)) from a pond 2 km away from the workshops and BTBPE analyzed in liver and muscle samples [7]. BTBPE was detectable in four of five muscle samples (range <0.012–0.15 ng/g lw), but found in only two of five liver samples (range <0.012–0.041 ng/g lw). These concentrations were much lower than those found for PBDEs.

BTBPE concentrations in the marine flatfish sole (*Solea solea*) collected along the French coastline in 2003 and 2004 ranged from 0.12 to 2.2 ng/g lw, which were lower than the concentrations found for PBDEs [33]. The highest BTBPE concentration was found in sole from the Seine estuary.

2.9 Birds

BTBPE was detected in California peregrine falcon (*Falco peregrinus*) eggs collected in 1999–2007; however, no concentrations were reported [34].

Eggs of herring gulls (*Larus argentatus*) from several colonies on the North American Great Lakes have been analyzed for BTBPE to discern spatial [35] and temporal trends from 1982 to 2006 [36]. In the spatial trend study, BTBPE was found in all colonies and mean concentrations ranged from 0.04 to 0.70 ng/g ww, with highest concentrations found in colonies along Niagara River above Niagara Falls [35]. These concentrations were much lower than those of PBDEs. In the temporal trend study, BTBPE was detected primarily in eggs from the mid-1990s to 2006, with no discernible trends [36]. The mean concentrations in 2006 for seven colonies ranged from <0.06 to 0.20 ng/g ww.

In a study near an e-waste processing area in southern China, several specimens of watercock (*Gallicrex cinerea*) were collected and muscle, liver, and kidney tissues analyzed for BTBPE [7]. Higher concentrations were found in liver (0.27–1.0 ng/g lw) and kidney (0.12–0.89 ng/g lw) than in muscle tissues (0.07–0.39 ng/g lw). Concentrations of BTBPE were much lower than those of PBDEs.

In the marine environment, BTBPE has been found in northern fulmar eggs (*Fulmarus glacialis*) from the Faroe Islands [37] and in glaucous gull eggs and plasma (*Larus hyperboreus*) from the Norwegian Arctic [9]. Mean concentrations were 0.11 ng/g lw (range <0.02–0.17 ng/g lw) in fulmar eggs collected in 2003, which was much lower than tri-decaBDE concentrations [37]. For glaucous gull samples collected in 2006, BTBPE was detected in only 5% of male glaucous gull plasma samples, 0% of female plasma, and 29% of egg yolk samples [9]. Plasma concentrations ranged from <0.20 to 0.26 ng/g ww and <0.27 to 0.96 ng/g wet weight (ww) in egg yolk and were much lower than concentrations of HBCD and PBDEs.

2.10 Mammals

Tomy et al. [38] analyzed several BFRs including BTBPE in blubber from Canadian Arctic beluga (*Delphinapterus leucas*) collected during 2002–2005 from several sites. BTBPE was found in a few samples with concentrations ranging from 0.1 to 2.5 ng/g lw. These concentrations were similar to those found for HBCD but lower than those for PBDEs.

BTBPE was also found in 10% of ringed seal (*Phoca hispida*) blubber samples from five locations in the Canadian Arctic collected in 2006, with concentrations ranging between <0.01 and 0.29 ng/g lw [39]. These concentrations were lower than those found for PBDEs.

2.11 Humans

BTBPE was not detected in human serum samples from Swedish electronic recycling workers [40], nor in household residents [21], although it was detected in air or dust in these environments. A number of BFRs were screened for in 128 serum samples from Tianjin, China [41]. Although PBDEs were found, no BTBPE was detected in any of the samples. In laboratory experiments with orally dosed rats, BTBPE exhibited limited absorption and metabolism, with the majority of the compound excreted in feces, which could explain the lack of accumulation in humans [42, 43].

3 Decabromodiphenyl Ethane

3.1 Background

Decabromodiphenyl ethane (DBDPE) is marketed as an alternative for technical DecaBDE. The molecular structures of the two chemicals resemble each other and they have similar applications, i.e., as additive brominated flame retardants in a wide range of polymeric materials. According to one of the producers, DBDPE has high thermal stability and does not tend to leak from its host polymer (i.e., it has low “blooming” characteristics) and its use is therefore encouraged in systems where recycling is anticipated (http://www.albemarle.com, accessed March 2010).

DBDPE became available on the market in the mid-1980s [44]. It has been marketed under the trade names Saytex 8010 (Albemarle, Arkansas, USA) and Firemaster 2100 (Chemtura). It is also produced in China by Shouguang Guangda Chemical Co., Ltd. (Shouguang, Shandong Province, http://www.sggdchem.com, accessed March 2010) and Shou Guang Longfa Chemical Co., Ltd. (Qindao, Shandong Province, http://www.longfachem.com, accessed March 2010). One reason for the commercialisation of DBDPE was that it meets the demands of the German dioxin ordinance, which imposes limits for chlorinated and brominated dioxins and furans in commercial products [45]. In contrast to its predecessor, DecaBDE, DBDPE does not have an ether bridge in its molecular structure. This makes it less prone to produce dioxins and furans under pyrolysis conditions, [46].

Information about production and sales are scarce. DBDPE is considered an LPV chemical in the EU [8]. In 2001, the imports to Europe of Saytex 8010 were estimated to be a few thousand metric tons mainly to Germany [45]. In 2007 and 2008 two major expansions of the production of Saytex 8010 were completed according to one of the producers [47]. Shi et al. [7] reported that in China, in 2006, DBDPE was the second most highly used BFR after DecaBDE. The estimated domestic production volumes of DecaBDE and DBDPE were 20,000 and 12,000 metric tons, respectively. The annual DBDPE consumption in China has a yearly increase of 80% [48]. In Japan, the use of DBDPE increased continuously from 1993 to 2000 whereas the consumption of DecaBDE decreased over the same period. During 1997–1998, the annual consumption of DBDPE surpassed that of DecaBDE [49].

3.2 Outdoor Air and Tree Bark

DBDPE has been found in the particulate phase of air samples taken during the years 2005–2006 in the area of the Great Lakes in North America [14]. The mean levels at the five sampling sites ranged from 1.0 to 22 pg/m^3. The highest levels of DBDPE were found in Cleveland where a rough correlation to BDE-209 levels was observed, suggesting similar sources. For several PBDE congeners, levels fluctuated over time (i.e., levels increased during warm summer months) and were dependent on population density, but no such patterns were observed for DBDPE. A part of the explanation was likely the low number of detections and low levels of DBDPE.

Higher concentrations of DBDPE were measured in air samples (gas + particulates) collected in 2007 from the PRD, south China, with concentrations ranging from 400 to 3600 pg/m^3 [7]. These concentrations were higher than those found for PBDEs including BDE-209.

The presence of DBDPE in tree bark from North America has been reported in two studies [17, 18]. In the study of Zhu and Hites [17], levels up to 100 ng/g lw were found in tree bark collected during 2000–2001, but the detection frequency among the samples was low (~7%). In this study, a manufacturing plant (in Arkansas) was suggested as a point source. In the study of Qiu and Hites [18], an average concentration of 8.5 ng/g lw was reported in samples collected in the northeastern US in 2006. There were no strong point sources of DBDPE influencing the levels in their data set. In the same study, average levels in tree bark samples from a few sites in other parts of the world were presented. DBDPE was not detected in samples from Canada, Germany, and Italy, but found at concentrations of 34 ng/g in South Korea, and up to 1,000 ng/g in China. In both studies, atmospheric deposition was believed to be the source of the DBDPE contamination.

3.3 Soil and Outdoor Dust

In Southern China, Shi et al. [7] found DBDPE along with other BFRs in soil from farmland situated in the highly industrialized PRD. Levels of DBDPE ranged from

18 to 36 ng/g dw. In this study, samples were also collected from an e-waste processing area, where DBDPE levels in dust and soil ranged between <2.5–140 ng/g dw and <2.5–4.6 ng/g dw, respectively. DBDPE had a higher relative abundance compared to the other BFRs analyzed in the samples from the PRD compared to the e-waste area. As an explanation, the PRD was suggested to be exposed to emissions that reflect more recent usage of BFRs in China. Conversely, the e-waste area may rather reveal previously used BFRs, e.g., lower brominated BDEs, which have limited usage during recent years.

3.4 Indoor Air and Dust

The occurrence of DBDPE has been studied in indoor environments in a handful of studies. In a Swedish dismantling facility for electronic equipment, Kierkegaard et al. [46] identified DBDPE in an air sample at a concentration of 0.7 ng/m^3. Petterson-Julander et al. [19] found geometric mean air concentrations ranging from 0.01 to 0.06 ng/m^3 in personal air samples from dismantlers and unexposed workers. Julander et al. [20] reported the presence of DBDPE in different particle size fractions of air samples from another Swedish electronic dismantling factory. DBDPE was found in all of the three different size fractions of dust that were collected with concentrations ranging from <0.02 to 0.79 ng/m^3. These concentrations were lower than those of PBDEs and BTBPE.

DBDPE was analyzed in air and dust from five Swedish households [21]. DBDPE was present in one air sample and four dust samples. The concentration in air was 23 pg/m^3, which was close to the detection limit, while the levels in dust were higher, from 21 to 120 ng/g dw. The dust DBDPE concentrations were in a similar range as BDE-47 and -99 concentrations, but somewhat lower than BDE-209 concentration. Together they comprised 85% of the total BFR levels.

In the UK, Harrad et al. [24] analyzed BFRs including DBDPE in dust from homes, offices, and cars. The average concentrations of DBDPE in these environments were 270, 170, and 400 ng/g dw, respectively. The DBDPE levels, as well as octa- to decaBDE levels, did not differ between the studied microenvironments, whereas the levels of tri-hexaBDEs were significantly higher in cars compared to homes. Estimated exposure via ingestion of dust for adults and toddlers (up to 44 and 190 ng/day, respectively) suggests that DBDPE intake is similar to that of tri-hexaBDEs.

In the USA, DBDPE was found in household dust from 19 homes in the Boston area collected from the main living area, the bedroom, and from the home vacuum cleaner bag [22]. The geometric means of DBDPE concentrations in the three different compartments were 138, 153, and 39.4 ng/g dw, respectively, but there was a large variation, ranging from <10 to 11,070 ng/g dw. Comparison with previous analysis of PBDEs in the same samples revealed a correlation between levels of BDE-209 and DBDPE; therefore, similar sources were suggested.

In Japan, DBDPE was recently detected in nearly all samples of indoor dust from a hotel, at levels up to 210 ng/g dw [50]. Levels were one or two orders of magnitude lower than those of PBDEs and HBCDs.

Positive identification of DBDPE in indoor dust has also been reported from the Czech Republic [25] and from the Netherlands [51].

3.5 Children's Toys

In a Chinese study of BFRs in children's toys, DBDPE was the second most prevalent BFR after decaBDE with a detection frequency of 40–90% in the different types of toys [26]. Compared to foam, rubber/soft plastic and stuffed toys, the hard plastic toys generally contained the highest levels of individual BFRs, with a median level of DBDPE at 5,540 ng/g. The estimated exposure of children to DBDPE from mouthing these toys was calculated to be 1.3–15 ng/kg body weight-day.

3.6 Sewage Water and Sludge

In a screening study of sewage sludge from 50 Swedish wastewater treatment plants (WWTPs), DBDPE was detected in 25 of the samples, with estimated concentrations up to 100 ng/g dw [46]. DBDPE was also positively identified in sludge from Spain at concentrations ranging from 0.2 to 90 ng/g dw [52, 53] and Canada with concentrations ranging from 5.6 to 32 ng/g dw [54].

Recently, an international survey of DBDPE in sewage sludge was performed [55]. Samples of sewage sludge from 11 different countries were analyzed for DBDPE and BDE-209. DBDPE was present in sludge from all countries and levels ranged from <0.58 to 220 ng/g dw. Diffuse leakage from the technosphere was suggested to be the primary source of DBDPE to the sludge, as suggested for other BFRs [56]. The concentration ratio of DBDPE to BDE-209 was calculated to estimate the relative usage of the two BFRs in the different countries. The ratio ranged from 0.0018 to 0.83 and was high in and around Germany, where imports of DBDPE are known to be high [45]. The high ratios found are indicative of a shift in consumption from DecaBDE to DBDPE. Lower ratios, possibly indicating lower DBDPE usage, were found in the USA and UK, which have traditionally been high consumers of the DecaBDE mixture.

A mass balance study of a WWTP in Sweden showed that DBDPE was delivered to the plant at the rate of 8.5 μg/day per person [57]. DBDPE was efficiently transferred from the sewage influent to the digested sludge, generating a mean level of 81 ng/g dw, while only a small fraction of the influent mass flow was emitted via the effluent water (<1%). There was no evidence for losses by anaerobic degradation. The behavior of DBDPE in the WWTP did not differ from that of BDE-209, for which mass flows were approximately one order of magnitude higher.

3.7 Landfills

DBDPE was analyzed in samples of leachate water and solid compost from five landfill sites in Spain [58]. DBDPE was found at three of these sites and levels in leachate and compost samples ranged from 1.2 to 35 ng/L and from 100 to 320 ng/g dw, respectively. Compared to the levels of BDE-209, the DBDPE concentrations were high in the compost samples, resulting in a DBDPE/BDE-209 ratio of 0.7–21.

3.8 Water and Sediment

The presence of DBDPE in the environment was initially identified in sediment from the Western Scheldt estuary in the Netherlands with DBDPE levels of 24 ng/g dw [46]. This is an industrialized area highly contaminated by decaBDE. Later, sediments from another two locations in the same area were analyzed, reporting DBDPE levels between 0.65 and 10 ng/g dw [29, 51]. The levels of BDE-209 were between one and two orders of magnitude higher.

Water and sediment from Lake Winnipeg were analyzed for DBDPE but concentrations were below the detection levels [27].

Recently, DBDPE was analyzed in sediments from isolated lakes and in a marine transect in Sweden [59]. Results from the analysis of the lake sediments showed that DBDPE was present in all of the 11 sampled lakes, at levels from 0.23 to 11 ng/g dw. The results indicate that the environmental contamination of DBDPE is widespread, and that long range transport and deposition may be important for the transport of DBDPE to remote areas. The marine sediment transect was from the city of Stockholm out through its archipelago [59]. The influence of local urban sources on DBDPE levels in the sediment decreased exponentially along the transect, starting at 10 ng/g dw. This was approximately only one order of magnitude lower than that measured in sludge from an adjacent WWTP [57]. In the transect, DBDPE levels dropped to half of their initial values within 14 km. Levels thereafter reached a low baseline, which was suggested to originate from atmospheric deposition.

DBDPE levels were reported in a study of 15 Chinese surficial river sediment samples and two sediment cores [48]. The samples were taken in the Dongjiang River, one of the main tributaries of the PRD area in Southern China. DBDPE was present in the surficial sediments at levels ranging from 19 to 430 ng/g dw. These levels exceeded the sum of tri- to heptaBDE concentrations (range 0.7–7.6 ng/g dw), but were lower compared to the sum of octa- to decaBDE concentrations (range 30–5,700 ng/g dw). The sediment cores showed that the levels of DBDPE as well as those of TBBPA and tri- to heptaBDEs are increasing in the sediment layers, while the levels of octa- to nonaBDEs are decreasing, possibly reflecting a shift in usage from the DecaBDE formulation to DBDPE.

Shi et al. [7] compared DBDPE concentrations in river sediment from the same sites in the PRD in China between the years 2002 and 2006. The levels of DBDPE were clearly higher in the samples from 2006.

3.9 Invertebrates and Fish

In a study of a freshwater food web in Lake Winnipeg in Canada, zooplankton, mussels, and six species of fish, including predatory fish such as burbot and walleye were analyzed for DBDPE [27]. No detectable levels of DBDPE were found in zooplankton or mussels. However, the mean concentrations in the fish ranged from below the limit of detection to 1 ng/g lw. Lipid adjusted BMFs for 5 out of 13 possible predators to prey interactions were reported, and ranged from 0.2 to 9.2. BMFs above 1 were mainly found for the predatory species, burbot and walleye. For all 13 predator to prey interactions, the BMFs for BDE-209 were in the range of 0.1–34. Furthermore, the trophic magnification factor (TMF) obtained for DBDPE was 2.7, which was similar to that for BDE-209, i.e., 3.6 [30]. Both these TMFs were higher than those obtained for BDE-47, -99, -100, and BTBPE (1.5, 0.7, 1.6, and 1.0, respectively).

In another study of the Great Lakes, Lake Ontario lake trout collected between the years 1979 and 2004 were analyzed for different BFRs. DBDPE was below the detection limit in all samples [60].

Likewise, no DBDPE was detected (<3.8 ng/g lw) in liver and muscle samples of farmed fish (carp, bighead carp, tilapia) collected near an e-waste processing area in southern China [7].

In a study by Munschy et al. [33], various BFRs including DBDPE were analyzed in pooled muscle samples from the marine species, common sole. Sampling was performed in 2003 and 2004, at three sites representing nursery zones in coastal areas of France (English Channel and Biscay Bay). DBDPE was detected in all of the six samples, at levels in the range of 0.18–3.9 ng/g lw, with higher levels in the samples from 2004 compared to those from 2003. This pattern between years was also observed for hexabromobenzene (HBBz), while no pattern was observed for the other BFRs, namely tri-hexaBDEs, BDE-209, BTBPE, and BB-153.

3.10 Birds

There are a few recent studies where the presence of DBDPE in avian species has been reported. In North America, Gauthier et al. [36] analyzed DBDPE in herring gull eggs collected between the years 1982 and 2006 from seven sites around the

Great Lakes. The detection frequency among the samples was ~13% (10–13 eggs per pooled sample). DBDPE was only detected in samples from 1996 and later, but neither temporal trends nor spatial trends were possible to discern. At some sites, the DBDPE concentrations exceeded BDE-209 concentrations, with levels up to 288 ng/g ww.

Gao et al. [61] analyzed DBDPE in eggs from wild and captive birds (terrestrial and aquatic) in a nature reserve area in Northern China. The area is highly influenced by industrial discharges. Among the species studied, the highest level of 2.4 ng/g lw was found in the terrestrial ring-necked pheasant (*Phasanius colchicus*). Samples from the other birds contained levels in the range from not detectable level to 2.2 ng/g lw.

Tissue samples from three watercocks from near an e-waste recycling area in South China were analyzed for DBDPE [7]. DBDPE levels were in the range of 9.6–124 ng/g lw. Higher levels were found in liver and kidney compared to muscle. BDE-209 levels exceeded those of DBDPE by a factor of at least two in all samples.

In a study from the PRD in South China, 29 water birds of five different species were collected and muscle samples were analyzed for different persistent halogenated compounds [62]. DBDPE was present in all samples except one, at levels from 4 to 800 ng/g lw. The upper range is higher than what was found by Shi et al. [7] in watercock. In the birds analyzed by Luo et al. [62], the concentration of BDE-209 was approximately one order of magnitude higher. The authors suggest that leaching from local sources was responsible for the DBDPE contamination of the birds.

3.11 Mammals

Hu et al. [63] reported findings of DBDPE in various tissue samples (liver, kidney, brain, muscle) from captive giant (*Ailuropoda melanoleuca*) and red panda (*Ailurus fulgens*) (eight individuals of each species) from China, at levels from below the detection limit to 40.9 ng/g lw. In one gonad sample, the level was as high as 863 ng/g lw.

Blubber samples of ringed seal from five locations in the Canadian Arctic (collected in 2006), contained no detectable DBDPE [39].

3.12 Humans

In a recent study from China, 128 human serum samples were analyzed for PBDEs and non-PBDEs including DBDPE [41]. Although BDE-209 was present at levels up to 1,770 ng/g lw, DBDPE levels were below detectable levels (<15 ng/5–10 mL blood) in all samples. DBDPE was also below the detection limit (<1.03 ng/g lw) in plasma samples from residents of five homes in Örebro, Sweden [21].

4 Hexabromobenzene

4.1 Background

HBBz is an additive flame retardant, historically used in plastics, textiles, and woods [64], but also in paper and electric manufactured goods [65]. Information on producers and production volumes are scarce. Gauthier et al. [35] state that it is classified as an LPV chemical (1,000–5,000 tons) and that a large historical source of this compound in the USA was Velsicol Chemical Corporation, St. Louis, Missouri (now a part of Chemtura), which was shut down in the 1980s. In Japan, production of HBBz was 270 tons in 1983 [64]. Although the total consumption of BFRs in Japan increased between 1994 and 2001, the consumption of HBBz lay constant at about 350 tons/year [49]. In China, 600 tons of HBBz per year are produced at Shou Guang Longfa Chemical Co. Ltd. (Qindao, Shandong Province, http://www.longfachem.com, accessed March 2010). HBBz is marketed by the Japanese Nippoh Chemicals Corp. as FR-B and is also marketed by Dayang Chemicals in China.

Apart from being commercially produced, there are other possible sources for HBBz to the environment. HBBz was found to be the major product from pyrolysis of Octa- and DecaBDE technical products [66]. Polymeric BFRs could be possible sources of volatile brominated compounds even at low thermal stress. HBBz and other volatile brominated organics were released from a pentabromobenzyl acrylate oligomer (FR-1025, ICL Industrial Products, formerly Dead Sea Bromine Group, Israel) at room temperature [67]. The release rate increased as temperature increased (up to 100°C), suggesting that compounding of thermoplastics (done at higher temperatures) could lead to the release to the environment, although fugacity modeling indicated that concentrations found in outdoor air were better explained by its use as a flame retardant. The maximum temperature of 100°C in the study is well below the melting point for the polymer suggesting that the volatiles emitted were present in the polymer, either as unreacted monomers or as impurities.

4.2 Abiotic Samples

HBBz was detected at low levels (0.02–0.09 pg/m^3) in four outdoor air samples collected at a rural/suburban location in Canada in 2005 [67]. A low concentration of HBBz (0.48 ng/g dw) was also found in a sample of outdoor dust (from atmospheric deposition) in Germany [68].

The HBBz concentrations in indoor air in Tokyo, Japan, ranged from <470 to 710 pg/m^3 in houses and <470–950 pg/m^3 in office buildings [69]. In outdoor air sampled in connection with the indoor samples, no HBBz was found. HBBz was also detected in laboratory air (500 pg/m^3) and in migration samples from the floor (0.5 μg/m^2/h) [69].

HBBz was occasionally detected in dust samples from 25 Czech households but no concentration data were reported [25].

HBBz was detected but not analyzed quantitatively in four samples of scrap raw materials from an aluminum recycling plant in Finland [70].

None of the 126 water samples from multiple sites in Japan collected in 1989 and analyzed by the Environmental Agency of Japan had HBBz levels above the limit of quantitation (<50 ng/L) [49].

In sediment samples collected in 1982 and analyzed by the Environmental Agency of Japan, HBBz was detected in 3 out of 126 samples (range <0.9–4.3 ng/g dw) [49]. River sediment samples from Japan, collected during 1981–1983, contained HBBz at 6–60 ng/g dw and estuary sediments had lower concentrations (~0.5–6 ng/g dw) [65].

4.3 Biota

HBBz was not detected (<5 ng/g ww) in any of the 126 fish samples collected in 1982 and analyzed by the Environmental Agency of Japan [49]. No information on collection sites was given.

Six pooled samples of juvenile common sole from three nursery zones along the French Atlantic coast, collected in 2003 and 2004 were analyzed for a number of BFRs. HBBz was detected in all samples with a concentration range of 0.03–4.3 ng/g lw [33].

Nyholm conducted two studies where zebrafish (*Danio rerio*) were fed a mixture of BFRs, including HBBz, during 42 days. The first study was on maternal transfer to eggs [71]), and the second on male fish to study uptake, elimination, and possible biotransformation ([72]. HBBz levels were below (or just above) the limit of quantitation in both studies but a possible metabolite, TeBBz, was detected. It was concluded that the presence of TeBBz in eggs was due to maternal transfer from the female zebrafish rather than metabolism in the eggs [71]. The TeBBz levels increased in male zebrafish during the exposure period but it appeared to be rapidly eliminated when the fish were fed untreated food [72].

A subset of peregrine falcon eggs from California, previously analyzed for PBDEs, were analyzed for new BFRs. The eggs were collected during 1999–2007 and selected because of their high PBDE levels and/or were from the most recent years. According to the authors, HBBz was detected in most of the 19 eggs analyzed although at much lower levels than the PBDEs [34]. No concentration data were given.

Egg pools from seven colonies of herring gulls from the Laurentian Great Lakes of North America collected between 1982 and 2006 were analyzed for a number of BFRs to study spatial and temporal trends [35, 36]. HBBz was present in all samples (range 0.10–3.9 ng/g ww), although at much lower levels than the PBDEs (<0.2% of sumBDE). No temporal trends of HBBz were detected over the 25 year study period [36]. Comparable levels in eggs from across the Great Lakes suggest low-level, common origins of exposure to HBBz, possibly via atmospheric transport.

The detection frequency of HBBz in male and female plasma and egg yolk samples of glaucous gulls collected in 2006 from the Norwegian Arctic was high [9]. The HBBz levels were the second highest of the non-BDE BFRs analyzed (after α-HBCD). The frequency of HBBz detections were higher in male (47%) compared to female (13%) plasma. The concentrations ranged from below the limit of quantitation to 0.15 ng/g ww in male, and 0.1 ng/g ww in female plasma. All egg yolk samples had detectable levels of HBBz with a mean of 1.1 ng/g ww (range 0.4–2.6 ng/g ww).

Low levels of HBBz were found in samples of polar bear adipose tissue collected from East Greenland, but no quantitative information was given [73].

4.4 Humans

While HBBz was detected in three samples of human adipose tissue from Japan (~0.5–1.8 ng/g lw) [64], no detectable levels were found in a screening study of 37 human adipose tissue samples from Finland [74]. In the Japanese study, the possible metabolites of HBBz, Te- and PeBBz, were also detected, with TeBBz constituting about 60–80% of the sumBBz [64].

Higher concentrations of HBBz were detected in mother's milk and placenta in Denmark than in Finland [75]. Mean concentration in Danish milk was 0.050 ng/g lw (range 0.005–0.50 ng/g lw, 77% detections) and 0.037 ng/g lw in Finnish milk (range 0.012–0.120 ng/g lw, 48% detections). The Danish placenta samples had higher concentrations of HBBz (mean 0.880 ng/g lw, range 0.071–10 ng/g lw) than the Finnish (mean 0.120 ng/g lw, range 0.008–0.940), but the frequency of detection was lower, 18 and 30%, respectively. PeBBz was also detected in the samples, although at lower levels and frequencies than HBBz.

HBBz was detected in 26 out of 128 human blood serum samples from a typical industrial metropolis in North China [41]. The median concentration was 0.27 ng/g lw (mean 0.46 ng/g lw, range 0.11–1.5 ng/g ww).

5 Pentabromoethylbenzene

5.1 Background

The main applications of pentabromoethylbenzene (PBEB), used as an additive BFR, have been in thermoset polyester resins, circuit boards, textiles, adhesives, wire and cable coatings, and polyurethane foam [6, 76]. PBEB was produced by Dead Sea Bromine Group Ltd (now ICL Industrial Products) under the trade name FR-105 mainly in the 1970s and 1980s in the US [6]. After 1986, no US production or import volumes have been reported. In the EU, PBEB is classified as an LPV chemical [8], while in the OSPAR list of chemicals with rankings of persistence, liability to bioaccumulate, and toxicity it is marked as a chemical with no current production [77].

An additional identified source of PBEB emissions was from polymeric BFRs [67]. PBEB was released from the polymer at room temperature and the emissions increased several orders of magnitude when the polymer was exposed to thermal stress, a situation that normally occurs during compounding of thermoplastic polyesters. The prevalent concentrations of PBEB in air from the Great Lakes could, however, not be explained by the release from polymeric BFRs but are more likely to derive from the use of PBEB as an additive.

5.2 Abiotic Samples

Hoh et al. [6] found comparably high levels, 520 pg/m^3, of PBEB in air samples from Chicago in the summer of 2003. The concentrations exceeded that of the tri-decaBDEs, by almost one order of magnitude. The samples also contained a number of other early eluting brominated compounds identified as tetrabromochloroethylbenzene and tentatively congeners of tetrabromoethylbenzene. These compounds were also present in the analytical PBEB standard (98% purity) purchased for quantification which made the authors suggest them to be byproducts formed during synthesis and/or environmental debromination products. Both PBEB and its impurities were detectable but below the detection limit in other sampling sites studied during the same period as well as in Chicago air samples collected previously [6]. PBEB was also reported in air samples collected near Oxford in the south of England at a concentration of 30 pg/m^3, which exceeded the concentrations of ΣPBDEs [78]. Only one of four air samples from Egbert, 70 km north of Toronto, Canada contained PBEB [67]. The level was low (0.1 pg/m^3), and together with pentabromotoluene (PBT) and HBBz, the concentrations comprised only 1.5% of the BDE-47 concentration in the sample. PBEB was also occasionally present in dust collected in Czech households (no levels reported) [25].

Scrap samples of raw material from an aluminum recycling plant (filter dust, cyclone dust, and light fluff from an electronic crusher and a car shredder) contained PBEB but no concentrations were reported [70].

Although PBEB was detected in air samples, neither PBEB nor any of its proposed lower brominated byproducts were found in a sediment core taken in Lake Michigan [6].

5.3 Biota

A number of non-PBDE flame retardants were analyzed in archived Lake Ontario lake trout whole-body homogenates collected between 1974 and 2004 [32]. The

PBEB concentrations in the lake trout ranged from 17 to 320 ng/g lw, and showed no significant trend over the sampling period. The authors conclude that the lack of a decreasing trend after this period may support more recent emissions.

The dietary absorption efficiency of PBEB in rainbow trout after a single dose was 26% and the half-life was calculated to be 38 days [79].

Two studies report the presence of PBEB in avian species. PBEB was detected in herring gull eggs from six colonies from the North American Great Lakes and was present in all samples at concentrations up to 1.4 ng/g ww (7.6% lipid) [35]. Low levels of PBEB (up to 0.23 ng/g ww) were detected in egg yolk from glaucous gulls collected in the Norwegian Arctic [9]. The levels were about 15 times lower than in pooled herring gulls eggs reported by Gauthier et al. [35]. PBEB was detected in all yolk samples ($n = 31$) but represented only 0.04% of the sum of the 18 brominated substances. In contrast to PBT, PBEB was not identified in glaucous gull plasma samples. Still, its presence and detection frequency in yolk indicate that PBEB undergoes long range transport and that it is maternally transferred to eggs.

5.4 Humans

PBEB was included but not detected in a survey of BFRs in 128 serum samples from office cleaners, university students, and policemen from an industrial region in North China [41].

6 Pentabromotoluene

6.1 Background

PBT is an additive flame retardant used in unsaturated polyesters, polyethylene, polypropylenes, polystyrenes, textiles, and rubbers [76]. The production volume is categorized as moderate (1,000–5,000 tons/year). Commercial trade names are Flammex 5-BT from Berk Ltd. (U.K.) [80] and FR-105 from Ameribrom, a subsidiary of the Dead Sea Bromine Group (ICL Industrial Products) and Chemtura [35]. PBT is listed as an LPV chemical in the EU [8]. In China, 600 tons of PBT per year are produced at Shou Guang Longfa Chemical Co. Ltd. (Qindao, Shandong Province, http://www.longfachem.com, accessed March 2010).

Like HBBz and PBEB, PBT may be released from polymeric BFRs when exposed to thermal stress [67]. The rate at which PBT was released from the polymeric BFRs exceeded that of PBEB and HBBz. Furthermore, PBT may be formed from thermal decomposition of DBDPE. Cleavage of the aliphatic bridge and the evolution of PBT constituted the major pathway for the decomposition of

DBDPE treated polystyrene while the decomposition of BDE-209 resulted in ring closure forming brominated dibenzofurans [81]. Both pathways included partially debrominated homologues.

6.2 Abiotic Samples

Low levels of PBT (<0.01–0.02 pg/m^3) were detected in one of four air samples collected at the sampling station of Egbert, 70 km north of Toronto, Canada [67].

PBT was occasionally detected in dust from 26 Czech households [25].

The presence of PBT and its lower brominated homologues (di- and triBT) was positively confirmed in water from the Western Scheldt area in the Netherlands [82]. Generally the levels of the dibrominated toluenes exceeded PBT, which was quantified to be 2.4 ng/L in one of the four samples (<0.1 ng/L in the remaining samples).

A number of brominated and mixed brominated and chlorinated toluenes including PBT were detected in surface sediment samples from the Rivers Havel and Spree close to Berlin, Germany [83]. The concentrations for PBT ranged from <1 to 25 ng/g dw. Lower levels were measured in sediment and suspended particulate matter from the Western Scheldt area in the Netherlands [29]. PBT concentrations were in the range of 0.01–0.33 ng/g dw.

PBT was identified already in 1975 in sewage sludge from Sweden [80]. The levels ranged from 8,000 to ~180,000 ng/g dw, tentatively quantified versus the technical product. The sludge also contained two isomers of tetrabromotoluene, isomers that also were present in the technical product Flammex 5BT. Low levels of PBT (<100 ng/g) were found in soil amended with sludge and in barley.

6.3 Biota

Liver and muscle samples from perch and pike possibly exposed to PBT via effluents from a WWTP had PBT levels below the detection limit (<30 ng/g ww) [80]. The absorption efficiency of PBT was determined to be 18–28% after a single oral dose of a mixture of brominated and chlorinated chemicals and the half-life was 13–23 days in rainbow trout [79] and up to 83 days in Atlantic salmon [84]. PBT was among the non-PBDE BFRs detected in pooled herring gull eggs from the Great Lakes in North America [35]. The levels were the lowest of the non-PBDEs measured (0.004–0.02 ng/g ww) comprising less than 0.05% of the sum of BDE-47, -99, and -100.

PBT was detected in both egg yolk and plasma from glaucous gulls captured in the Norwegian Arctic [9]. The levels reported were <0.04–0.15 ng/g ww in plasma and <0.02–0.12 ng/g ww in egg yolk.

6.4 Humans

PBT was included in a screening study of Finnish human adipose tissue but was not detected in any of the samples [74].

7 Tetrabromobisphenol A Derivatives

7.1 Background

Tetrabromobisphenol A diallyl ether (TBBPA-DAE) is used as a reactive flame retardant in polystyrene foams but also as an additive flame retardant in expanded polystyrene and polystyrene foams. It is produced by Chemtura under the trade name BE-51 (http://www.chemtura.com, accessed March 2010). The US production volume in 2006 was <230 metric tons [85] and it is listed as an LPV chemical in the EU [8]. Tetrabromobisphenol A 2,3-dibromopropyl ether (TBBPA-DBPE) is used as an additive flame retardant in polyolefin resins and polystyrene [86]. It is produced under the trade names PE-68 (Chemtura) and FR-720 (ICL Industrial Products) [72]. US production in 2006 was <4,500 metric tons [85] and it is listed as an LPV chemical in the EU [8]. JiangSu HaoHua Fine Chemical Co., Ltd (Jiangsu Province) in China produces 3,000 metric tons/year (http://www.huadingchem.com, accessed March 2010). Weidong International Group, Ltd. (Weifang, Shandong Province, China) also produces TBBPA-DBPE (http://www.oceanchemical.en.ecplaza.net, accessed March 2010). Tetrabromobisphenol A dihydroxyethyl ether (TBBPA-DHEE) is used as an additive flame retardant in engineering polymers and coatings [87]. It is produced by Chemtura under the trade names BA-50P and BA-50 and has previously been produced by Teijin Chemicals Ltd. (Japan) under the trade name Fireguard 3600. The data base is inadequate for an evaluation or to support its use commercially [87]. No information on production volumes is available for TBBPA-DHEE for the US but it is listed as an LPV chemical in the EU [8].

TBBPA-DAE and TBBPA-DBPE are neutral compounds, DAE being very resistant towards hydrolysis and DBPE being rapidly dehydrohalogenated [88]. TBBPA-DHEE is a dihydroxylated compound, most probably not affected by environmentally relevant pH because of a likely high pK_a ($\sim$15), [89]. The TBBPA family is very hydrophobic and, considering environmental partitioning, its members would preferably adsorb to solids [89]. If present in the atmosphere, TBBPA-DBPE and TBBPA-DAE will, because of their low volatility, be attached to particles and hence their atmospheric transport behavior will be determined by particle transport [90]. Their molecular size is much larger and volatility much lower than that of substances typically believed to have the potential to become Arctic contaminants, but were included in a list of substances potentially relevant for further investigation and monitoring because of their type of usage, both being additive BFRs [90]. They are considered LPV compounds with low potential for long range atmospheric transport and low bioaccumulative potential as is generally the case with compounds having molecular weights close to or above 700 Da. Their overall persistence is probably high (estimated to >500 days [90]), because of their association with particles. They may have similar transport mechanisms in the environment as BDE-209 [91] and thus a likelihood of becoming global pollutants.

7.2 Abiotic Samples

Findings of these chemicals in environmental samples are scarce. TBBPA-DBPE was indicated qualitatively in indoor dust from Swedish homes [92]. It was also detected in outdoor dust (atmospheric deposition) collected from a metal surface near the artificial stream and pond system in Berlin-Marienfelde in Germany [68] at a higher concentration (1,300 ng/g dw) than BDE-209 (730 ng/g dw).

TBBPA-DBPE was below the detection limit in German sediment (<10 ng/g) and sewage sludge (<22 ng/g) [93] but was detected in sediment (<1.5–2,300 ng/g dw), outdoor air (130–1,240 pg/m^3), sewage sludge (240–8,900 ng/g dw), and soil (17–60 ng/g dw) from the PRD, in southern China, known for its electronic and electrical manufacturing [7]. The levels in sediments from 2006 were higher than in those taken in 2002 from the same sites. In outdoor dust and soil samples from an e-waste recycling area north of the PRD, the TBBPA-DBPE concentrations were below detection limits. The e-waste is to a large extent imported from abroad. The authors interpreted the different patterns of TBBPA-DBPE for the two areas as indication of different uses. The e-waste site is affected more by usage of older, now discontinued BFRs while the PRD samples reflect the introduction of replacement BFRs.

7.3 Biota

TBBPA-DAE was detected in 5 out of 30 Lake Ontario lake trout samples (0.2–1.7 ng/g ww) collected between 1997 and 2004 [60]. TBBPA-DBPE was analyzed for in watercock and three farmed fish species near an e-waste recycling area in southern China, but levels were below the detection limit [7].

Nyholm et al. [71, 72] conducted two studies where zebrafish were fed a mixture of BFRs, including TBBPA-DHEE and TBBPA-DBPE for 42 days. In the first study of maternal transfer to eggs, TBBPA-DHEE was not detected but TBBPA-DBPE was absorbed by the fish and transferred to the eggs (egg/fish ratio of >1 on lipid weight basis) [71]. In the second study on male fish, TBBPA-DHEE levels were not quantified because of low recovery but TBBPA-DBPE was found to be taken up and eliminated rapidly [72].

In rats, TBBPA-DBPE was absorbed poorly, but the small amounts that were taken up accumulated in the liver were metabolized slowly and eliminated via feces [94].

8 Bis(2-ethylhexyl) Tetrabromophthalate and 2-Ethylhexyltetrabromobenzoate

8.1 *Background*

Bis(2-ethylhexyl) tetrabromophthalate (TBPH) is used as a plasticizer in polyvinylchloride (PVC) plastic and neoprene rubber [86] as well as in wire and cable insulation, film and sheeting, carpet backing, coated fabrics, wall coverings, and adhesives (http://www.chemtura.com, accessed March 2010). TBPH is also used, together with 2-ethylhexyltetrabromobenzoate (TBB), in the additive flame retardant product Firemaster 550, produced since 2003 by Chemtura as a replacement for PentaBDE in polyurethane foam applications [22]. The approximate ratio of TBB to TBPH in Firemaster 550 is 4:1 by mass [22]. Davis and Stapleton [95] also report that TBB and TBPH are found in the fire retardant BZ-54, and TBPH is present in a mixture called DP-45, both produced by Chemtura. US production volumes of TBPH were 450–4,500 metric tons/year from 1990 to 2006 [85, 96]. No production information after 2006 is available for TBPH. There is no production information available for TBB. In laboratory photodegradation experiments, TBB and TBPH have both been shown to undergo sequential reductive debromination, possibly down to nonbrominated degradation products [95]. For TBPH, this could lead to the formation of bis(2-ethylhexyl)-phthalate (DEHP), a plasticizer which is currently restricted or banned for specific uses in many countries.

8.2 *Abiotic Samples*

TBPH was recently found in dust samples from 19 homes in Boston, Massachusetts, USA, at concentrations ranging from 1.5 to 10,630 ng/g dw [22]. The highest geometric mean concentrations were found in researcher-collected dust from the main living area (234 ng/g dw), followed by the bedroom (105 ng/g dw) and vacuum cleaner dust (65.8 ng/g dw). In the same study, Stapleton et al. [22] found TBB concentrations ranging from <6.6 to 15,030 ng/g dw, with highest geometric mean concentrations in dust from the main living area (322 ng/g dw), followed by the home vacuum cleaner bag (91.1 ng/g dw) and the bedroom (90.4 ng/g dw). These concentrations were similar or somewhat lower than that found for HBCD in the same samples. The ratio of TBB/TBPH in dust ranged from 0.05 to 50, indicating different sources or fate in indoor environments.

Stapleton et al. [22] also found TBPH, but not TBB in the standard reference material dust (NIST SRM 2585).

In an additional 50 house dust samples collected from vacuum cleaner bags from homes in Boston, TBPH was found in 60% and TBB in 44% of the samples [23]. Geometric mean TBPH and TBB concentrations were 650 ng/g dw (range <300–47,110 ng/g dw) and 840 ng/g dw (range <450–75,000 ng/g dw), respectively.

In a screening study of foam from 26 pieces of furniture bought in the USA between 2003 and 2009, TBB and TBPH were both detected in one sample at 4.2% by weight [23].

TBPH and TBB have been detected in sewage sludge from two wastewater treatment plants in San Francisco, California, US [97–99]. Concentrations for TBB ranged from 40 to 1,412 ng/g dw and for TBPH, 57–515 ng/g dw and were in the same range as or higher than concentrations of HBCD and BDE-209.

8.3 Biota

A commercial dietary cod liver oil supplement using Norwegian cod liver oil, was analyzed for a large number of organohalogen compounds [100]. Among these, TBB and TBPH were identified. However, they were also detected in the blank samples after clean up using gel permeation chromatography (GPC), and the authors concluded that the clean up step contaminated the cod liver oil extract. They compared the cod liver oil extract and blank with the Firemaster 550 technical product and concluded that this was the source of both chemicals, but could not explain how the contamination occurred.

Blubber samples from stranded Indo-Pacific humpback dolphins (*Sousa chinensis*) and finless porpoises (*Neophocaena phocaenoides*) were analyzed for TBB and TBPH [101]. Samples were collected from Hong Kong, south China during 2002–2008. Mean TBB concentrations were 5.6 ng/g lw in the porpoises but below the detection limit (<0.04 ng/g lw) in the dolphins. Mean TBPH concentrations were 342 ng/g lw in the porpoises and 0.51 ng/g lw in the dolphins, with TBB: TBPH ratios ranging from 0.0003 to 3. These concentrations were much lower than those found for PBDEs in the same samples. However, TBPH concentrations in the porpoises were higher than HBCD concentrations [101].

9 1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane

9.1 Background

Commercial 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH) is marketed by Albemarle as Saytex BCL-462 and contains equal amounts of the two diastereomers, α- and β-TBECH [36, 102]. It is an additive flame retardant used in expandable polystyrene beads for house insulation, extruded polystyrene, for adhesives in fabric, electrical cable coatings, high impact plastic in appliances, and some construction materials [86] (http://www.albemarle.com, accessed March 2010). U.S. production volumes were 4.5–230 metric tons/year from 1986 to 2002 [96]. No production information is available after this time point. TBECH undergoes some thermal rearrangement to γ– and δ-TBECH at temperatures above 120°C, which could be expected to occur at the high temperatures used to incorporate it into products [103]. Muir and Howard [104] reviewed screening and categorization studies of chemicals in commerce with high predicted bioconcentration potential, low biodegradation rates, and long range atmospheric transport potential. TBECH was one of the 30 chemicals included in their list.

9.2 Sediment

In a screening of a broad range of chemicals, TBECH was identified in one sediment sample collected in 1996 from the dry channel near a discharge pipe of the Frutarom VCM/PVC plant near Haifa, Israel [105]. No quantitative data were given however.

9.3 Biota

In two laboratory studies, zebrafish were fed a diet containing 11 BFRs including TBECH for 42 days [71, 72]. In the study of maternal transfer from female fish to eggs, TBECH was found in both, indicating that TBECH is absorbed and can be transferred to the eggs [71]. The second study on male fish showed a high uptake efficiency from the gut (>60%), but rapid elimination, with a half-life of less than 2 days [72]. However, after the 2-week elimination period, the fish still had detectable levels of TBECH as well as HBCD and several PBDEs, indicating that TBECH has bioaccumulation potential.

ΣTBECH (sum of α- and β-TBECH isomers) was analyzed in herring gull eggs collected from seven colonies on the Great Lakes between 1982 and 2006 [36]. TBECH was found in eggs from all seven colonies with mean ΣTBECH for 2006 ranging from 0.11 to 0.54 ng/g ww. The highest concentration was found in eggs from Channel-Shelter Island, Lake Huron. ΣTBECH was also found in eggs from all years studied at each site, but no temporal trends were discernible. However, the isomer pattern did differ between sites and years, with the β-TBECH isomer being predominant [36].

In support of the predictions of Muir and Howard [104], Tomy et al. [103] identified and quantified TBECH in Canadian Arctic beluga (*Delphinapterus leucas*). Beluga blubber samples from males were obtained from four Arctic sites in 2003, 2005, and 2006 and analyzed on a diastereomer basis. Only the β-TBECH isomer was found, at concentrations of 1.1–9.3 ng/g lw. These concentrations were in the same range as of HBCD, but about ten times lower than that of PBDEs.

10 2,4,6-Tribromophenol

10.1 Background

The commercial 2,4,6-tribromophenol (TBP) product is produced by Chemtura under the trade name PH-73FF and by ICL Industrial Products under the trade name FR-613. It is used as a reactive flame retardant, an antifungal agent (e.g., wood treatment), and as a chemical intermediate (http://www.chemtura.com, http://www.icl-group.com, accessed March 2010). U.S. production was 4,500 to <23,000 metric tons in 2006 and it is considered a high production volume chemical (HPV) in the EU [8]. Japanese production in 2001 was 3,600 metric tons [49]. In China, TBP is produced by Weidong International Group, Ltd. (Weifang, Shandong, http://www.oceanchemical.en.ecplaza.net, accessed March 2010). 2,4,6-TBP is also produced naturally by marine algae [106–108] and polychaetes [109]. It may also be formed metabolically from some PBDEs [110] and is a by-product in commercial BTBPE productions [111]. Thus there are multiple sources of TBP that may explain its presence in various environmental compartments. On reading the literature, its presence in the marine environment, i.e., water [112], sediments [113], invertebrates [114], and fish [115, 116] seems to be the result of its presence as a natural product. Its presence on vegetation collected near sawmills is probably related to its use as a fungicide on wood products [117]. TBP has also been found in marine birds and polar bears [116] at low concentrations, with possible origins speculated to be from metabolism of hydroxy-PBDEs and methoxy-PBDEs. These compounds in turn may be present largely as a result of natural production from marine organisms [118–120].

10.2 Abiotic Samples

Perhaps the best evidence of TBP presence due to its use as a flame retardant or as a by-product in other BFRs is from the indoor environment. Takigami et al. [121] found that indoor air concentrations inside two Japanese homes were much higher (range 220–690 pg/m^3) than air concentrations outside the homes (49 and 73 pg/m^3). The authors also found high bromine contents in various electronic equipment as well as some textiles in the homes indicating that TBP and other BFRs were released from flame-retarded materials in the homes. TBP air concentrations were higher than those of HBCD, TBBPA, BDE-209, and ΣPBDEs. Dust samples from the two homes had TBP concentrations of 15 and 30 ng/g, which were lower than concentrations for HBCD, TBBPA, BDE-209, and ΣPBDEs.

In a study of BFRs, TBP was found in air samples from 18 houses and 14 offices in Tokyo, Japan in 2002 [69]. TBP air concentrations ranged from not detectable level to 6,800 pg/m^3. For outdoor air, TBP concentrations were below the detection limit.

Indoor air (passive sampling) and dust were sampled in 2006 for BFRs from various rooms of a Japanese hotel in Osaka [50]. Unfortunately, data are only given for the sum of four tribromophenols, including TBP, and these ranged from 1.6 to 380 ng/g in dust and 12 and 70 ng/g in air sample (no air volumes were reported).

House dust from 19 houses and 14 offices collected from Japan in 2005 were analyzed for TBP [111]. TBP was a major phenolic component with higher concentrations in offices (median 90 ng/g, range 27–620 ng/g) than in houses (median 34 ng/g, range 16–130 ng/g).

TBP has been found in sewage sludge in a study of 22 wastewater treatment plants in Sweden [122]. Concentrations ranged from not detectable level to 0.9 ng/g ww, which were lower than those of PBDEs and TBBPA. TBP was also found in 16% of leachate samples from 38 municipal solid waste landfill sites in Japan, with a mean concentration of 21 ng/L (range <3–430 ng/L) [123].

10.3 Biota

Nyholm et al. [71, 72] conducted two studies where zebrafish were fed a mixture of BFRs, including TBP for 42 days. In the study of maternal transfer, TBP was found in both the female fish and the eggs [71]. In the second study, TBP was found to have a relatively high uptake rate (45%) but was eliminated rapidly in the male fish [72].

10.4 Humans

TBP was identified but not quantified in human plasma samples from Sweden [124]. Thomsen et al. [125] included TBP in a study of BFRs in plasma from three different occupational groups from Norway. Mean TBP concentrations were 24 ng/g lw (range 4.7–81 ng/g lw) in electronics dismantlers, 31 ng/g lw (range 8.7–65 ng/g lw) in circuit board producers, and 11 ng/g lw (range 0.17–28 ng/g lw) in laboratory personnel (nonexposed). No statistically significant difference was found between the three groups and diet was indicated to be the main exposure route for TBP. The TBP concentrations were higher than tri-heptaBDE and TBBPA concentrations.

Thomsen et al. [126] also studied temporal and age trends of BFRs in human plasma from Norway, including TBP. The mean TBP concentration in plasma samples from 1999 was 0.3 ng/g lw and no temporal trends were seen from 1977 to 1999, unlike the tri-hexaBDEs which increased with time. There was also no clear age trend, unlike the mean for tri-hexaBDE concentration where the highest concentrations were found in the 0–4 year-old group. For TBP, highest concentrations were found in the 25–59 year-old women (26 ng/g lw) and in the 4–14 year-old group (14 ng/g lw).

In a study of BFRs in Canadian Inuit from Nunavik, Quebec, plasma samples were found to contain a geometric mean TBP concentration of 58 ng/L or approximately 9.4 ng/g lw [127]. These concentrations were somewhat higher than those of BDE-47 and -153 and in the same range as those found in Norway. TBP concentrations were not explained by dietary intake measures (marine based diet, western diet) and were not correlated to PBDE concentrations, ruling out their presence as metabolites of these. The authors concluded that, at present, there is no clear explanation for TBP exposure routes in this population.

In the US (Indiana), Qiu et al. [110] found mean TBP concentrations of 5.6 ng/g lw in fetal plasma and 0.8 ng/g lw in maternal plasma. TBP concentrations were lower than the sum of the concentrations of tri-hexaBDEs.

In the only study of human breast milk, Ohta et al. [128] found TBP to be present but only as a minor portion of the total tribromophenol content.

11 2,4,6-Tribromophenyl Allyl Ether and 2,3-Dibromopropyl-2,4,6-tribromophenyl Ether

11.1 Background

2,4,6-Tribromophenyl allyl ether (ATE) is marketed by Chemtura as PHE-65 and recommended as a reactive [90, 129] and an additive FR for expanded polystyrene and foamed polystyrene (http://www.chemtura.com, accessed March 2010). It may also be used as a synergist for aromatic bromine containing FRs in applications where maximum process temperatures do not exceed 150°C. ATE can also be formed from anaerobic degradation of 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE, CAS 35109-60-5) and is probably also formed metabolically [130]. ATE is listed as an LPV chemical in the EU [8]. The US production volume of ATE in 2006 was <227 metric tons [85].

In a screening exercise, ATE was one of 120 chemicals identified to be structurally similar to known Arctic contaminants and/or have partitioning properties that suggest that they are potential Arctic contaminants [131]. ATE was defined as a multihopper compound with partitioning properties that make it exceptionally susceptible to becoming an Arctic contaminant [90].

2,3-Dibromopropyl-2,4,6-tribromophenyl ether (DPTE) was manufactured by Chemische Fabrik Kalk in Germany under the trade name Bromkal 73-5PE until the mid-1980s but seems to no longer be a commercial product [132].

11.2 Sewage Sludge

ATE was detected in 15 of 18 municipal sewage sludge samples in Germany from ten different plants (<5–91 ng/g dw) (Weisser, 1992 cited in [90]. DPTE was also detected in 12 of the samples (<25–600 ng/g dw). The mean ATE/DPTE ratio was 0.17.

11.3 Biota

DPTE has been detected in fish from the north Pacific and the south Atlantic as summarized in Vetter et al. [132]. ATE was screened for but not detected in Great Lakes herring gull eggs [36].

ATE was detected in blubber (5.4–9.1 ng/g ww) and brain (3.1–10 ng/g ww) samples of harp seals (*Phoca groenlandica*) from the Barents and Greenland Seas [130]. DPTE was the predominant organobromine compound in these samples (blubber 322–470 ng/g ww, brain 130–340 ng/g ww). 2-Bromoallyl-2,4,6-tribromophenyl ether (BATE) was also present in the samples at about the same concentrations as ATE. The ATE/DPTE and BATE/DPTE ratios were 0.018 and 0.015 respectively in blubber and 0.030 and 0.019 respectively in brain. The general co-occurrence of ATE and BATE indicates that the source for ATE in these samples was from the biotransformation of DPTE. In brain, as opposed to blubber extracts, PBDEs were virtually absent, indicating that ATE, DPTE, and BATE penetrate the blood–brain barrier to a much higher degree [130].

12 Hexachlorocyclopentadienyldibromocyclooctane

12.1 Background

There is very little information on this chemical in the open literature. No information has been found on producers or production volumes. Hexachlorocyclopentadienyldibromocyclooctane (HCDBCO) is marketed by Wellington Laboratories as a reference standard. It has been reported to be used as a flame retardant in “styrenic polymers” [76]. Structurally it belongs to a group of halogenated norbornane flame retardants, which is a subgroup of alicyclic halogenated flame retardants. HCDBCO is unusual as it contains both chlorine and bromine atoms. According to Riddell et al. [133] it was first described as a BFR agent in a US patent in 1975. HCDBCO exists as a pair of enantiomers. No information is available on production volumes in the US or in the EU.

12.2 Indoor Air and Dust

The only environmental findings of HCDBCO seem to be from the indoor environment, i.e., in residential indoor air and dust collected during 2002–2003 in Ottawa, Canada. In 44 out of 55 indoor air samples, the HCDBCO levels were above the detection limits [134]. The median HCDBCO air concentration (66 pg/m^3) was higher than that found for the major PBDEs (BDE-47 (66 pg/m^3), and BDE-99 (15 pg/m^3)), and the maximum HCDBCO concentration (3,000 pg/m^3), was almost twice the maximum BDE-47 concentration. The median HCDBCO concentration in dust was 2.0 ng/g and this was lower than the median concentrations of major PBDEs (BDE-99 (430 ng/g) and BDE-209 (630 ng/g)). The maximum measured HCDBCO concentration in dust (93,000 ng/g) was however higher than both BDE-99 (60,000 ng/g) and BDE-209 (10,000 ng/g) concentrations [134]. Air and dust levels did not correlate.

12.3 Fish and Mammals

There are a few reports where HCDBCO was analyzed for in environmental samples but not detected. All 50 blubber samples from marine mammals (Hong Kong, China) had concentrations below the detection limit (0.04 ng/g lw), [101]. Likewise, HCDBCO levels in all 22 fish samples from Great Lakes were below the limit of quantitation (0.39 ng/g, probably fw) [135].

13 *Tris*(2,3-dibromopropyl) Isocyanurate

13.1 Background

Structurally *tris*(2,3-dibromopropyl) isocyanurate (TBC) belongs to the group of heterocyclic flame retardants with a triazine ring. It is used as an additive flame retardant in a variety of polymeric materials, e.g., glass fiber reinforced plastics and polyurethane and is also used widely in polyolefin, PVC, polyphenyl alkenes, ABS, unsaturated polyester, synthetic rubber, and fiber (reference to a document in Chinese in [136]). It is added at about 5–10% w/w. The production in China began in the mid-1980s, and was ~500 metric tons/year in 1996 [136]. It is marketed by a number of Chinese companies under several trade names. It is considered an LPV chemical in the EU [8].

13.2 Environmental Levels

TBC has been detected in the vicinity of a manufacturing plant in southern China. Ruan et al. [136] sampled river water and surface sediment upstream and downstream (several sites) from the factory, and soil and earthworms upwind and downwind (predominant wind direction) at several sites. The concentrations ranged from 2.3 to 160 ng/L in river water, 85–6,000 ng/g dw in surface sediment, 20–670 ng/g dw in soil, and 9.8–79 ng/g dw in earthworms, with a trend of decreasing concentrations with distance from the factory. It was assumed that soil concentrations could be the result of dust deposition and river water irrigation. TBC concentrations in common carp sampled 6 km downstream from the outlet were 12–650 ng/g dw. The distribution was uneven in carp tissues and organs, indicating accumulation in the fat-rich organs such as brain and adipose [136].

14 Tetrabromophthalic Anhydride

14.1 Background

Tetrabromophthalic anhydride (TBPA) is used as a reactive BFR in unsaturated or saturated polyesters, polyols, esters, and imides (http://www.albemarle.com, accessed March 2010), and is marketed as PHT4 by Chemtura and Saytex RB-49 by Albemarle. Its derivatives have been used as FRs in applications as diverse as rigid polyurethane polyols, wire coatings, and wool (http://www.chemtura.com, accessed March 2010). The US production volume in 2006 was 4,500 to <23,000 tons [85]. In Europe TBPA is registered as an LPV chemical [8].

14.2 Environmental Levels

TBPA was detected in cod liver oil samples, most probably because of blank problems (GPC) and thermal degradation of TBB and TBPH in the GC–MS system [100]. It was not detected in Dutch sediments and suspended particulate matter [29]. TBPA is on the list of chemicals predicted to become Arctic contaminants because of its structural similarity to known Arctic contaminants [131].

15 1,2,5,6-Tetrabromocyclooctane

15.1 Background

1,2,5,6-Tetrabromocyclooctane (TBCO) is an additive flame retardant marketed by Albemarle Corporation under the trade name Saytex BCL-48 [36]. No information is available on production volumes in the US or in the EU. TBCO can exist as two diastereomers that can easily interconvert thermally [137]. TBCO meets the EU criteria as a potential aquatic hazardous substance and a very persistent and bioaccumulative substance [129], and is on the Canadian nondomestic substances list with as much as 10 metric tons/year being currently imported into Canada [137].

15.2 Birds

TBCO was detected in herring gull eggs from the Great Lakes, in North America, but was not quantifiable [36].

16 Octabromo-1,3,3-trimethyl-1-phenylindane

16.1 Background

There is no information on octabromo-1,3,3-trimethyl-1-phenylindane (OBIND) production volumes. It has previously been manufactured by Dead Sea Bromine Group (now ICL Industrial Products) as FR-1808.

16.2 Environmental Levels

OBIND was found to be present as a contaminant in the feed additive choline chloride at 0.140–0.700 ng/g [138]. OBIND was occasionally detected in dust samples from Czech households but no concentration data were reported [25]. Leonards et al. [51] found maximum OBIND concentrations of 1 ng/g dw in sediments from two locations in the Western Scheldt.

OBIND was screened for and detected in herring gull eggs from the Great Lakes, North America, but was not quantifiable [36].

17 Other

Lopez et al. [29] quantified pentabromocyclohexane, 2,3,5,6-tetrabromo-*p*-xylene, and tetrabromo-*o*-chlorotoluene in sediments and suspended particulate material from several sites in the Western Scheldt of the Netherlands.

18 Conclusions

The database on the environmental occurrence of emerging BFRs is small. The best studied emerging BFRs are BTBPE and DBDPE, with some data for HBBz, PBEB, PBT, TBBPA derivatives, TBB, TBPH, TBECH, and TBP, and much less available for ATE, TBPA, TBCO, TBC, HCDBCO, and OBIND. There are many other BFRs on the market but we found no environmental data on these. For those that have been studied, the findings show that they are present in many environmental compartments including biota. Indoor air concentrations are generally higher than outdoor air concentrations, and where measured, they are even higher in occupational settings. Many are found in indoor air and dust, indicating possible human exposure from this pathway, but there are little human data available for evaluating the extent of exposure to most of these BFRs. The presence of several of these compounds in fish, birds, and mammals indicates that they are bioavailable, can be absorbed, and accumulated and in some cases, bioaccumulation and biomagnification may occur. Their presence in outdoor air and in the Arctic indicates that several are capable of long range atmospheric transport. Higher concentrations are seen in samples near BFR production facilities or manufacturing facilities using BFRs, making these point sources to the environment. Many of the emerging BFRs are showing similar environmental behavior as older BFRs, such as the PBDEs, that have recently been banned or restricted. As many of these emerging BFRs are being used as replacements for PBDEs, and the use of flame retardants is increasing because of more stringent fire regulations, there is a risk that the emerging BFRs will also become environmental problems. More data are therefore needed in order to determine if any of these emerging BFRs poses a threat to the environment or to human health.

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