Bioaccumulation of Brominated Flame Retardants

Angel Antelo Domínguez, Robin J. Law, Dorte Herzke, and Jacob de Boer

Abstract Brominated flame retardants (BFRs) account for the second largest market group of flame retardants currently in use. Since their detection in wildlife samples collected far from local sources, environmental concern about the use of BFRs has grown. Further research in biotic and abiotic matrices revealed the bioavailability of these chemicals in the terrestrial and aquatic ecosystems. Together with their persistency and potential long-range transport, bioaccumulation in wildlife and the potential for trophic magnification indicate serious risks for many organisms. In addition to the polybrominated diphenylethers, hexabromocyclododecane and tetrabromobisphenol A, other BFRs have entered the market in recent years. Not all BFRs show similar behaviour. Their structure and properties, and the metabolic processes taking place within the exposed organisms, are of great importance in determining their bioaccumulation profile.

Keywords Bioaccumulation, Bioavailability, Biomagnification, Brominated flame retardants, Trophic chain

Contents

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1 Introduction

In December 2006, a new European Union regulation (1907/2006; EC, 2006) stated the policy to be applied in the evaluation of potentially hazardous chemical substances. The principal aim of this new framework was to improve the existing legislation that regulates the chemicals industry in the EU, through a system of Registration, Evaluation and Authorization of Chemicals (REACH). The REACH regulation is based on the precautionary principle, which means that the lack of information about new chemicals or chemicals currently in use, and their possible toxicological effects, could not be a reason for the continued production and use of chemical substances. Information concerning their physicochemical and toxicological properties is therefore required before a substance is approved for sale [1]. The European Chemicals Agency (ECHA) plays an important role within the REACH framework. It coordinates the in-depth evaluation of high production volume chemicals (HPVCs) and toxic chemicals and runs a public database in which hazard information is provided. Important parameters are production, long-range atmospheric transport associated with particulate matter, persistency and bioaccumulation. Based on these criteria, several brominated flame retardants (BFRs) are of concern [2].

Flame retardants (FRs) are a group of structurally diverse chemicals that comprise more than 175 different types, divided into four major groups: inorganic, organophosphorous, nitrogen-containing and halogenated FRs. The main criteria for the usage of a compound as FR are stability during the lifetime of the product, compatibility with the polymer and fire-retarding properties. As a result, BFRs have been widely applied by the industry because they show a higher radical trapping efficiency, a lower decomposition temperature and more compatibility with plastics than most other FRs [3]. Of the FRs globally used, 39% are based on bromine, which is estimated at 200,000 tonnes of BFRs produced per year [4]. There are more than 75 different aliphatic, aromatic and cyclo-aliphatic compounds that have been developed for use as BFRs.

The main commercial BFRs currently in use are tetrabromobisphenol A (TBBP-A), hexabromocyclododecane (HBCD) and polybrominated diphenyl ethers (PBDEs), TBBP-A being the one with the highest production volume (130,000 tonnes per year [5]). For this reason, most of the studies regarding the occurrence of BFRs in the environment to date have involved PBDEs, TBBP-A and HBCD, while other

brominated compounds used for flame retardation have remained in the background. Similar to the polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), defined as persistent organic pollutants (POPs) within the Stockholm Convention, some PBDE congeners and HBCD appear to have persistent characteristics, and their bioaccumulation properties in aquatic and terrestrial organisms indicate the need for more strict control and regulation. In 2009, penta-mix and octa-mix BDEs were placed on the Stockholm Convention POPs list. Apart from the parent compounds, potential degradation products formed during usage or after release to the environment should also be taken into account. Decomposition of plastics may lead to the formation of bromophenols, bromotoluenes and aliphatic bromides, increasing the number of brominated compounds in the environment [6, 7]. Mono-, di- and tri-substituted bromoanilines have also been reported as intermediates in the formulation of FRs incorporated within plastic materials [8].

1.1 Characteristics of Selected BFRs

1.1.1 Tetrabromobisphenol A

TBBP-A is produced via bromination of bisphenol A in an organic solvent. It is mainly used as a reactive intermediate in the production of epoxy resins, but it is also transformed into derivatives such as dimethyl TBBP-A or *bis*-(2-hydroxyethyl ether) TBBP-A [3]. The presence of TBBP-A was not expected in the environment due to its covalent bond to the polymer, but it has been detected in sediments and organisms in the North Sea [9]. A rapid excretion of TBBP-A and metabolites from aquatic organisms and mammals was reported [10]. Although its presence in biota and sediments is generally low compared with the PBDEs and HBCD [11], its similarity in chemical structure to thyroxine (T4) is of special concern as it was demonstrated in in vitro studies to have the ability to interfere with thyroid hormone homeostasis [12]. TBBP-A is not readily biodegradable but can undergo primary biodegradation to form several products, including bisphenol-A. Photochemical degradation of TBBP-A may yield mono- or di-substituted bromophenols which could be bio-transformed into their corresponding bromoanisoles [13, 14]. Several studies indicate that TBBP-A can generate brominated dibenzo-*p*-dioxins and dibenzofurans although the scale of this production seems to be very low and to occur only under certain pyrolysis conditions [15]. In the human health risk assessment report (RAR), no health effects of concern were identified from the primary use of TBBP-A [2].

1.1.2 Polybrominated Diphenyl Ethers

Of the 209 theoretical congeners, only a subset of the possible brominated diphenyl ethers (BDEs) congeners is commonly found in the environment. Lower BDE congeners derived from the penta-mix and octa-mix commercial products are

the predominant BDEs in the aquatic environment, whereas the terrestrial ecosystem accumulates more of the higher brominated congeners, such as BDE209 [11, 16–18]. Due to the different size of the congener molecules and their degree of bromination, which implies variation in properties such as hydrophobicity and lipophilicity, individual BDE congeners show diverse behaviour in the environment.

Comprehensive risk assessments have been conducted within the European Union for the three commercial PBDE formulations, the penta-, octa- and deca-mix products. It was concluded that the technical mixtures penta- and octa-mixes should be banned and that additional data should be provided for the deca-mix [2]. The major components of penta-BDE are the BDE47 and BDE99, whereas the major component of the octa-BDE is the heptabrominated congener BDE183. The penta-BDE components have been widely found in sediments and at different levels in food webs. This demonstrates their ability to enter the ecosystem and, due to the higher rates of uptake and retention compared to elimination, their potential to bioaccumulate to the top of the food chain [19].

1.1.3 Deca-Brominated Diphenyl Ether

The Deca-brominated diphenyl ether (Deca-BDE) technical mixture is the commercial PBDE mixture with the highest production volume currently. Its major component, BDE209, has been found in different matrices, particularly sediments and some terrestrial biota, but to a lesser extent in aquatic organisms [3, 16]. There is a special concern regarding its potential for debromination which could yield lower brominated compounds with stronger bioaccumulation characteristics than the BDE209 itself. It has been shown in laboratory experiments that BDEs can be photochemically degraded by UV or sunlight in organic and aqueous solvents and in soil and sediments, resulting in the formation of less brominated BDEs. The degradation rates generally increase with an increasing degree of bromination [20–24]. However, it is unclear to what extent this degradation occurs in the natural environment as shielding effects may often limit the amount of UV light reaching the BDE molecules. Following advice from environmental agencies, industries in the USA will voluntary phase out the deca-BDE product within the next few years [5].

1.1.4 Hexabromocyclododecane

The commercial mixture of HBCD comprises mainly three diastereomers with the γ-HBCD as the dominant compound. Two other stereoisomers (δ, ε) have been detected at very low concentrations in the technical mixture [24]. All three diastereomers can occur as enantiomers. Although γ-HBCD is the predominant diastereomer in the technical mixture, the α-HBCD isomer is generally found to

dominate in biological samples, which suggests a possible selective metabolism of individual isomers or a diastereomer rearrangement [9, 25]. Thermal decomposition has been observed for HBCD at 170–190°C, with slower rates for α- and β-HBCD than for the γ-diastereomer [26].

HBCD has been detected in freshwater and marine biota. The high concentrations found in top predators such as marine mammals and birds of prey suggest a strong biomagnification potential [27, 28]. Its detection in bird eggs and porpoise blubber illustrates the potential of HBCD for maternal transfer [29]. HBCD has been reported to biodegrade in freshwater and wastewater through several dihaloelimination steps, resulting in 1,5,9-cyclododecatriene [30].

1.1.5 Decabromodiphenylethane

Decabromodiphenylethane (DBDPE) has been manufactured as an alternative to the deca-BDE formulation since the mid-1980s. Not much is known about this brominated compound as the main attention was focused on the aforementioned BFRs, but its similarity in structure to BDE 209 suggests a similar behaviour. Although there are few reports on the presence of DBDPE in the environment, it has already been detected in several matrices including sediments and fish, but at lower concentrations than BDE209 [31, 32]. DBDPE can be thermally degraded to bromotoluenes and photolytically debrominated to nona- and octa-BDE congeners [33].

1.1.6 Polybrominated Biphenyls

Polybrominated biphenyls (PBBs) are a group of chemicals that were widely used in the past as fire retardants. The accidental introduction of the chemical into the food chain of Michigan in 1973 led to the quarantine of farms, the destruction of millions of animals and dairy products, and serious human health problems [34]. Nowadays, PBBs are controlled in Europe under the Restriction of Hazardous Substances Directive, which limits their use in electrical and electronic products to be sold within the EU [35].

2 Occurrence and Levels in Wildlife

A multitude of studies on PBDEs in wildlife has resulted in a large database of concentrations in all sorts of organisms. Although not exhaustive, an overview of the most important studies is given below.

2.1 Birds and Birds' Eggs

2.1.1 Aquatic Birds

Predatory birds are known to respond to relatively low levels of organohalogen compounds. The concentrations of these contaminants in birds may vary according to the species and the chemical compound involved [36]. Liver samples from cormorants [37, 38] and guillemot eggs from the Baltic Sea [39] showed higher concentrations of BDE47 and BDE99, compared to higher brominated congeners.

In eggs of eider ducks and greater black-backed gulls sampled from a contaminated Norwegian fjord, Haukås et al. [40] determined HBCD concentrations along a transect away from a known point source. Mean sum HBCD concentrations at the four locations in eider ducks declined from 140 ± 50 to 15 ± 5.0 μg kg^{-1} lipid weight. In the gulls, concentrations at all locations were similar, ca. 150 μg kg^{-1} lipid weight, possibly reflecting overlapping feeding areas.

Dauwe et al. reported PBDEs in eggs of Northern lapwing and Mediterranean gulls near the harbour of Antwerp (Belgium) [41]. Lapwing eggs had the highest median concentrations of BDEs (109 μg kg^{-1} lipid weight). Mediterranean gulls feed during breeding on ground-dwelling invertebrates on agricultural fields which differ from the marine food items in the rest of the year. Mediterranean gull eggs had the lowest median concentrations of Σ7PBDEs (25 μg kg^{-1} lipid weight). These birds are migratory and their wintering grounds may be less polluted with PBDEs than their breeding sites.

Verboven et al. reported Σ38BDE levels in plasma of 15 female and male glaucous gulls from Bjørnøya, Norway, collected in 2006 [42]. Female glaucous gulls showed a mean concentration of 7 μg kg^{-1} wet weight and males of 19.5 μg kg^{-1} wet weight. Verrault et al. [43] also reported data for Σ38PBDE in plasma from 42 glaucous gull collected in the same year. Similar sumPBDE levels (8.5 μg kg^{-1} wet weight for females and 19.6 μg kg^{-1} wet weight for males) were found in that study also.

BDEs were analysed in dead and dying glaucous gulls at Bjørnøya (Svalbard) by Sagerup et al. [44]. Σ11BDE concentrations were four to ten times higher in liver than in the brain, 13,000 μg kg^{-1} lipid weight and 1,800 μg kg^{-1} lipid weight, respectively. The brain concentration was 12% of the liver concentration for the tribrominated congener BDE28 and only 2% for the nona-brominated congener BDE207. The hepatic levels of ΣBDEs were 10–40 times higher in that previously reported in randomly sampled glaucous gulls from the Barents Sea area.

Ivory gull eggs from the Russian and Norwegian Arctic were investigated by Miljeteig et al. [45]. Thirty-five eggs were sampled from individual ivory gull nests within four colonies in Svalbard: Svenskøya (78° 47′ N, 26° 36′ E, in 2007, and in northwestern Russia in 2006), Nagurskoe (80° 48′ N, 47° 37′ E), Kluyv Cape (81° 39′ N, 62° 11′ E, in Franz Josef Land) and Domashny (79° 30′ N, 91° 05′ E, in Severnaya Zemlya). Σ7BDE concentrations in the eggs from Svalbard varied between 101 and 221 μg kg^{-1} lipid weight and were lower than those from the Russian locations

Nagurskoe and Kluyv Cape, which had concentrations of 302 and 287 μg kg^{-1} lipid weight, respectively. The Domashny colonies gave a median concentration of 51 μg kg^{-1} lipid weight, being the least contaminated. BDE47 was the dominant congener in all samples.

A population of lesser black-backed gulls was investigated by Bustnes et al. [46], determining Σ10BDE concentrations in whole blood samples. Breeding lesser black-backed gulls were caught during two distinct sampling periods from a colony on the coast of northern Norway. Only BDE47 could be detected in the samples, with a mean concentration of 1.9 μg kg^{-1} wet weight.

Herzke et al. analysed samples from two marine bird species, European shag and common eider sampled at a coastal site in Norway close to urban activity and at a remote site [47]. Six different PBDE congeners could be detected in the shag eggs. BDE 47 and 100 were the main contributors, with concentrations of 24 and 27 μg kg^{-1} lipid weight, respectively. A Σ6BDE concentration of 90 μg kg^{-1} lipid weight was found. The common eider eggs were less contaminated, with BDE47 as the dominant congener, followed by BDE99 and BDE100. The Σ6BDE concentrations were 5.5 μg kg^{-1} g lipid weight at the remote site and 48 μg kg^{-1} lipid weight at the urban site in 2004.

To assess whether the fluctuating wing asymmetry and hepatic concentrations of POPs are associated with European shag chicks, Jenssen et al. also determined BDEs [48]. Of eight BDE congeners determined, only BDE47 and BDE100 could be detected in livers of 21-day-old chicks from Sklinna, Norway. BDE47 concentrations varied from not detected to 3 μg kg^{-1} lipid weight, and BDE100 was detected in only one sample.

Guillemot eggs from North-Western Europe and the Baltic Sea were studied by Jörundsdóttir et al. [49]. Guillemot eggs were collected from Iceland (Vestmannaeyjar, 2002, 63° 24′ N, 20° 18′ W), from Sweden (Stora Karlsö, 2003, 57° 18′ N, 18° E), from the Faroe Islands (Sandøy, 2003, 61° 48′ N, 6° 48′ W) and from three locations in Norway (Sklinna, 65° 12′ N, 11° E, Hjelmsøya, 2005, 71° 6′ N, 24° 42′ E and Bjørnøya, 2005, 74° 24′ N, 19° E). In the North Atlantic, eggs from Iceland contain the highest concentrations of PBDEs. The Norwegian eggs contain the lowest amounts of PBDEs of all the egg samples analysed. Eggs from the Baltic Proper have up to an order of magnitude higher concentration of PBDEs than eggs from the North Atlantic. Σ4PBDE ranged from 51.6 μg kg^{-1} lipid weight in Iceland, 30.7 μg kg^{-1} lipid weight on the Farøe Islands, 12.4 μg kg^{-1} lipid weight in Norway and 147 μg kg^{-1} lipid weight in Sweden.

Hebert et al. [50] investigated the intra-specific differences in the food webs used by individual seabirds. Annual Herring gull egg collections (one egg from each of 10–13 nests) were made at Strachan Island (45° 02′ N, 74° 82′ W) in Lake St Lawrence from 1986 to 2005 (except in 1987). Concentrations of individual contaminants varied greatly between the least and most contaminated eggs. Concentration ranges for contaminants measured above detection limits in all samples were Σ29BDE (206–902 μg kg^{-1} wet weight).

In pooled samples of herring gull eggs from the Great Lakes, Gauthier et al. [51] studied temporal trends in BDE concentrations (particularly BDE209) over the

period 1982–2006. Concentrations of BDE209 in 2006 were 4.5–20 μg kg^{-1} wet weight. Octa- and nona-BDE concentrations doubled more slowly – doubling times of 3.0–11 and 2.4–5.3 years, respectively. The source of the octa- and nona-BDE congeners (e.g. BDE197 and BDE207) were the result of the debromination of BDE209, either metabolically by the herring gulls or before uptake via their diet. Congeners deriving mainly from the penta-mix and octa-mix formulations, in contrast, have shown rapid increases in concentration up to 2,000 and no trend subsequently. In an additional report, Gauthier et al. [49] described Σ7BDE levels from Herring gull egg pools collected in 2006 from seven colonies on the Laurentian Great Lakes (sum of BDE28, BDE47, BDE99, BDE100, BDE153, BDE154 and BDE183). The levels varied between 288 and 1,140 μg kg^{-1} wet weight (% lipid 7.7–10.7).

Custer et al. investigated archived great blue heron eggs collected from Indiana Dunes National Lakeshore, Indiana, USA in 1993 [52]. The ranking of PBDE congener concentrations by percent concentration (BDE47 > BDE99 > BDE100 > BDE153 > BDE154 > BDE28 > BDE183) was consistent with use of the penta-mix PBDE formulation. Total PBDE concentrations in great blue heron eggs from Indiana Dunes were elevated and probably reflect local contamination from urban and industrial inputs into Lake Michigan. PBDE concentrations were within the range of those associated with altered reproductive behaviour in other avian species and, based on trends in other Great Lakes birds, are probably higher today than in 1993.

Concentrations and time trends of PBDEs in aquatic bird eggs from San Francisco Bay, California, USA were investigated during the period 2000–2003 by She et al. [53]. Caspian and Forster's terns showed no change in Σ5PBDE concentration over time. Congener patterns in the two species from year to year are similar, with BDE47 dominating, followed by BDE99 > BDE100 > BDE153 > BDE154. The median ΣBDE concentrations in Caspian tern eggs were 2,410, 4,730, 3,720 and 2,880 μg kg^{-1} lipid weight, for 2000–2003, respectively. The median ΣBDE concentrations in Forster's tern eggs were 1,820, 4,380, 5,460 and 3,600 μg kg^{-1} lipid weight, for 2000–2003, respectively. The median Σ5BDE concentrations in least tern eggs collected in 2001 and 2002 were 5,060 and 5,170 μg kg^{-1} lipid weight, respectively. The median ΣBDE concentration in Clapper rail eggs collected in 2001 was 379 μg kg^{-1} lipid weight.

A spatial and temporal trend study of PBDEs carried out since the mid-1970s for herring gull eggs in the Great Lakes from North America showed higher concentrations of BDE47 followed by BDE99, BDE100, BDE153, BDE154, BDE28 and BDE183, in this bird species that feeds mainly on alewife and rainbow smelt [54].

Muscle tissue of herring gull was analysed by Wan et al. [55] to assess the trophodynamics of PBDEs in the marine food web of Bohai Bay, North China. BDE47 was the dominant congener, with a mean concentration of 1.6 μg kg^{-1} wet weight, followed by BDE100, BDE153 and BDE99 all with mean concentrations around 0.3 μg kg^{-1} wet weight. The reported mean Σ13BDE concentration was 3.3 μg kg^{-1} wet weight (33 μg kg^{-1} lipid weight), much lower than values reported for herring gulls from Europe and Canada.

Levels and pattern of PBDEs in eggs of Antarctic seabirds were investigated by Yogui and Sericano [56] (Fig. 1). Eggs of chinstrap penguin and South Polar skua were collected during the breeding season of 2004–2005, while eggs of gentoo penguin were collected in 2005–2006 at Admiralty Bay, King George Island. Σ29BDE levels ranged from 6.8 μg kg^{-1} lipid weight for Chinstrap penguin and 8.1 μg kg^{-1} lipid weight for Gentoo penguin, to 146 μg kg^{-1} lipid weight for South Polar skua. South Polar skuas occupy a higher trophic level than chinstrap penguins, since the nototheniid fish *P. antarcticum* that they eat is a zooplankton feeder that forages on krill. Gentoo penguins occupy an intermediate trophic position closer to that of chinstrap penguins. The level of BDEs in eggs of the three species is not exclusively explained by their diets during the breeding season. It is likely a result of several factors such as trophic level and type of prey items taken during both the breeding and non-breeding seasons. If BDE contamination was due to local sources only, gentoo eggs would be expected to exhibit intermediate concentrations significantly higher than those of chinstrap eggs. The higher contamination levels in South Polar skuas probably result from exposure during the non-breeding season when they migrate northward to the waters of the northern hemisphere.

Gao et al. [57] investigated BDEs, DBDPE and a PBB congener (BB153) in eggs of six species of wild aquatic birds. Egg samples ($n = 67$) were collected from the Yellow River Delta National Nature Reserve in China in May 2008. The sampled species included Saunders's gull, common tern, Kentish plover, black-winged stilt, oriental pratincole and common coot. With the exception of oriental pratincole,

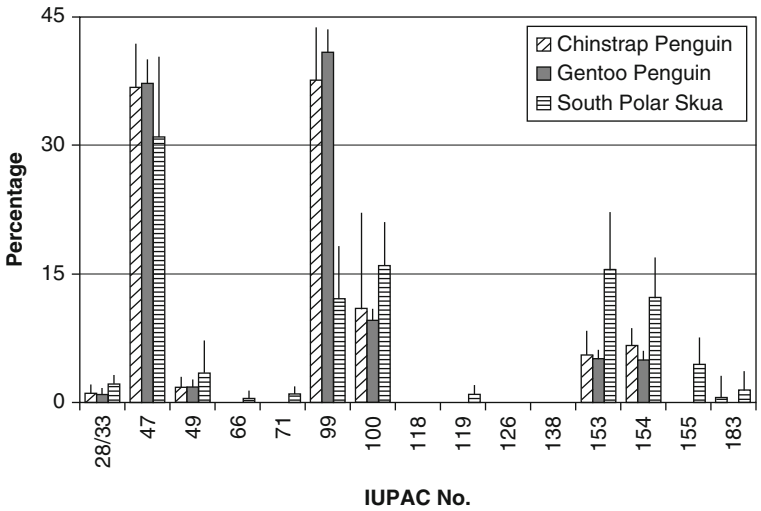


Fig. 1 Per cent distribution of BDE congeners in seabird eggs collected from nesting sites at King George Island, Antarctica. *Error bars* represent standard deviation [56]. Reprinted from Levels and pattern of polybrominated diphenyl ethers in eggs of Antarctic seabirds: endemic versus migratory species. Yogui GT, Sericano JL, Environ Pollut 157:975–980, 2009, with permission of Elsevier

BDE47 showed the highest abundance in all species of wild aquatic birds, comprising 34% of total BDE concentrations, followed by BDE99 and BDE153 in nearly equal proportions. The oriental pratinocole eggs were dominated by BDE209. Median concentrations of DBDPE and BB153 in all avian species were in the range of not detectable (ND) – 1.7 and ND – 0.7 μg kg^{-1} lipid weight, respectively.

Pectoral muscle samples of nine avian species, which were collected from the open sea and Japanese coastal and inland areas during 1994–2001, were analysed for BFR by Kunisue et al. [58]. BDEs were detected in all the avian samples. Among open sea birds, concentrations of BDEs in the black-footed albatross were the highest (60–210 μg kg^{-1} lipid weight), followed by the Laysan albatross (6.2–73 μg kg^{-1} lipid weight) and the northern fulmar (3.3–6.5 μg kg^{-1} lipid weight). As for Japanese coastal and inland birds, the goshawk accumulated the highest concentrations of Σ13BDEs (33,000 μg kg^{-1} lipid weight) > Steller's sea eagle (11,000 μg kg^{-1} lipid weight) > jungle crow (290–4,000 μg kg^{-1} lipid weight) ≈ golden eagle (270–2,300 μg kg^{-1} lipid weight) > common cormorant (230–820 μg kg^{-1} lipid weight) > black-tailed gull (220–530 μg kg^{-1} lipid weight). Small sample sizes for some species prevented any further inter-species comparison. In Japanese coastal and inland birds, relatively higher residue levels of BDE47 were found in fish-eating species, such as the Steller's sea eagle, black-tailed gull and common cormorant. On the other hand, in inland predators such as the goshawk and golden eagle, and jungle crow, a dedicated inland omnivore, BDE153 and higher brominated congeners were predominant, highlighting once more the contrast between uptake of BDEs in aquatic and terrestrial food chains (Fig. 2).

Luo et al. [19] investigated various waterbird species from an extensive e-waste recycling region in South China. Muscle samples from five bird species, including *Rallidae* (white-breasted waterhen, slaty-breasted rail, ruddy-breasted crake); *Ardeidae* (Chinese-pond heron) and *Scolopacidae* families (common snipe) were collected between 2005 and 2007 from Qingyuan County. The median Σ13BDE concentrations in five bird species ranged from 37 to 2,200 μg kg^{-1} lipid weight. BDE47, BDE99, BDE100, BDE153, BDE154 and BDE183 were detected in all the samples, and BDE28 and BDE209 were detected in less than 50% of the samples. The Chinese-pond heron was the most contaminated species, with a Σ13BDE concentration of 2,200 μg kg^{-1} lipid weight. BB153 was detected in 93% of the samples, at concentrations ranging from 1 to 2,800 μg kg^{-1} lipid weight.

PBDEs were measured in eggs of two Ardeid species, the little egret and black-crowned night heron from three port cities along the South China coast, Hong Kong, Xiamen and Quanzhou. ΣBDE levels were highest in Hong Kong, 480 μg kg^{-1} lipid weight, followed by Quanzhou, 220 μg kg^{-1} lipid weight and Xiamen, 40 μg kg^{-1} lipid weight [59].

PBDEs and HBCD in bird eggs from South Africa were analysed by Polder et al. [60]. During the period from November 2004 to March 2005, 43 unhatched eggs from eight different bird species were collected at five different localities in South Africa. BDEs were detected in eggs of all the studied species and in all locations. Highest concentrations of Σ8BDEs (61–396 μg kg^{-1} lipid weight) were measured

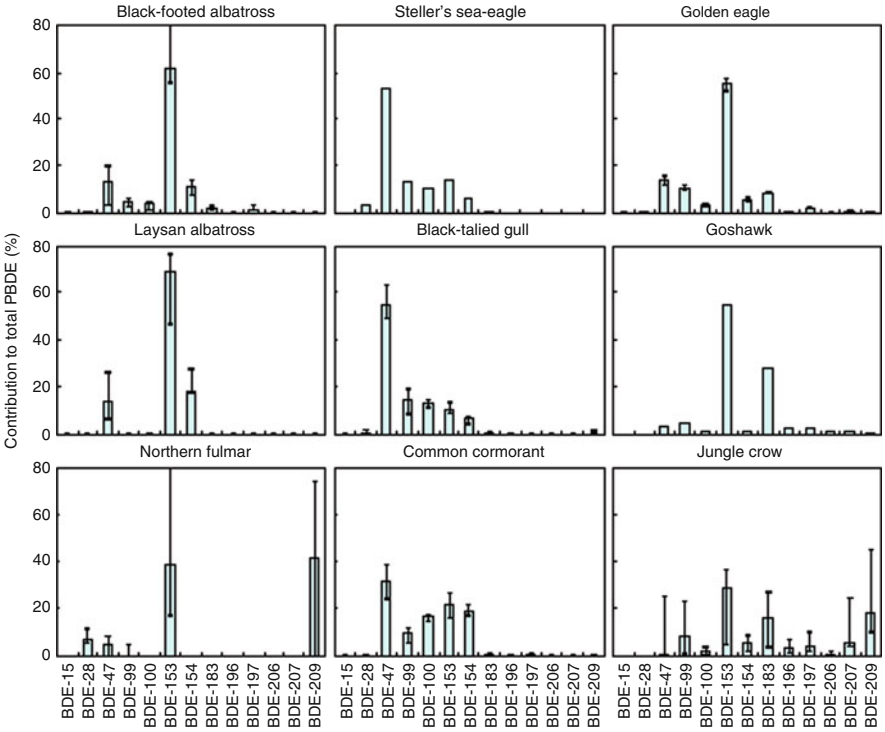


Fig. 2 Composition of PBDEs in avian species from Japan [58]. Reprinted from Spatial trends of polybrominated diphenyl ethers in avian species: utilization of stored samples in the Environmental Specimen Bank of Ehime University (es-Bank). Environ Pollut 154:272–282, 2008, with permission of Elsevier

in eggs of the African sacred ibis. The lowest ΣBDE concentrations were measured in eggs of cattle egrets (2.3 μg kg^{-1} lipid weight). Interestingly, only the little grebe, the white-fronted plover and the kelp gull showed a PBDE pattern dominated by BDE47. The profiles in the other bird species were dominated by either BDE154 (African darter and reed cormorant) or BDE183 (cattle egret, sacred ibis, crowned plover). HBCD was found in three species, at concentrations varying between 1.6 and 71 μg kg^{-1} lipid weight.

2.1.2 Terrestrial Birds

Whether BDEs can reduce the reproductive success of ospreys in Oregon and Washington, USA, was studied by Henny et al. who determined BDE concentrations in eggs [61]. Findings for the 89 osprey eggs collected between 2002 and 2006 indicate that the middle Willamette River eggs contained the highest geometric mean Σ12BDE concentrations and usually had the highest individual congener

concentrations. Eggs collected from the forested and sparsely populated headwater reservoirs of the Willamette River contained the lowest concentrations. ΣBDE concentrations in osprey eggs collected from the Columbia River in 2004 increased in a downstream pattern from 157 μg kg^{-1} wet weight to 403 μg kg^{-1} wet weight. BDE47 was the dominant congener in osprey eggs, followed by BDE100, BDE99, BDE154/BB153, BDE153 and BDE28. When the data including all of the ΣBDE concentrations <1,000 μg kg^{-1} (Willamette River in 2006 and Columbia River in 2007) were evaluated separately, the ten nests from the Willamette River in 2006 showed a negative relationship between productivity and ΣBDE concentrations ($Z = -2.4093$, $P = 0.008$). A negative relationship was also indicated for the 20 nests from the Columbia River in 2007 ($Z = -1.5809$, $P = 0.057$). McKernan et al. [62] suggested the lowest observable effect level may be as low as or 1,800 μg kg^{-1} wet weight of Σ12BDEs in eggs.

Time-trends and congener profiles of BDEs in Californian peregrine falcons were investigated by Park et al. [63] during the period 1986–2007. Over the past 22 years, BDE levels more than tripled in the eggs during each decade. For BDEs, eggs collected in large cities showed markedly different patterns to those in eggs from coastal locations: BDE209 and the higher brominated BDE congeners (hexa- to nona-brominated) were the dominant congeners in eggs from cities, while BDE47 and BDE99 were dominant in coastal eggs. In many of the birds that yielded multiple eggs over time, BDE patterns changed over time: the high proportions of BDE209 and higher brominated BDEs (short half-lives) in young birds contrasted with increasingly higher proportions of BDE153 (long half-life) and other lower brominated PBDEs as the birds aged (Fig. 3). These data are consistent with metabolic debromination of BDE209 to the lower brominated BDE congeners, with accumulation over time of BDE153. Diet (prey birds) may explain the urban BDE congener pattern, as the patterns in urban pigeons and peregrines were similar, with high proportions of BDE209 and the higher brominated BDEs. In summary, these data indicate that BDE209 is taken up by wildlife (particularly in urban locations) and undergoes metabolic debromination to the lower brominated BDE congeners.

An additional study on peregrine falcons focused on urban and rural trends in the Northeastern USA [64]. A total of 23 peregrine falcon eggs were obtained between 1993 and 2002 from 13 nests, encompassing 11 locations in the Chesapeake Bay region, USA. The maximum Σ11BDE concentration in an individual egg, from an urban highway bridge site, was 354 μg kg^{-1}. This egg also exhibited the highest BDE209 burden (48.2 μg kg^{-1}). The congeners BDE153, BDE99 and BDE100 constituted 26.0%, 24.8% and 13.1%, respectively, of ΣBDEs. BDE47 constituted only 4.4% of Σ11BDEs in the eggs in this study. The median BDE209 concentration was 6.3 μg kg^{-1}. The sum of the octa- to nona-brominated congeners (BDE196, BDE197, BDE206, BDE207 and BDE208) contributed, on average, 14% of Σ11BDEs, exceeding the contribution from BDE209 (5.9%). Median BDE209 concentrations were significantly correlated ($p < 0.01$, Spearman $R = 0.690$) with the human population density of the area surrounding the nest. ΣBDE concentrations were not correlated with human population density.

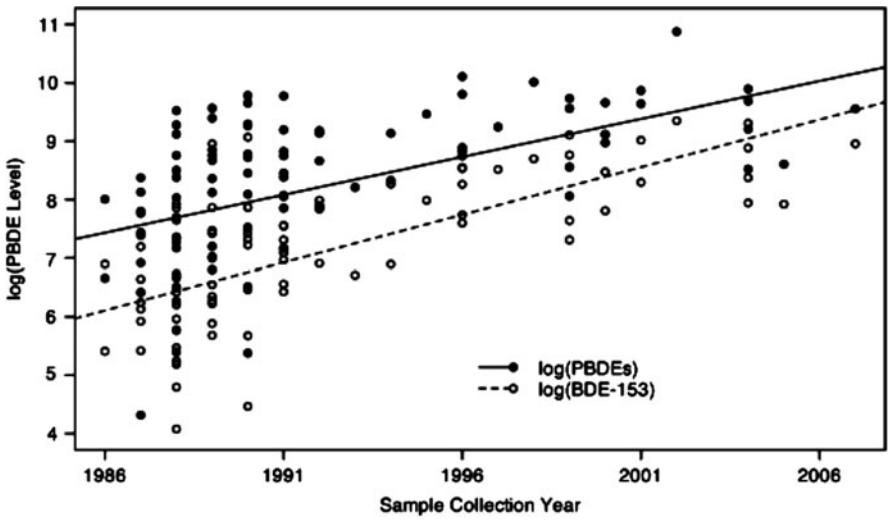


Fig. 3 Temporal changes in the log (natural logarithm) of levels (μg kg^{-1} lipid weight) of ΣBDEs and BDE153 in peregrine falcon eggs from California ($n = 90$) [63]. Reprinted (and adapted) from Time-trends and congener profiles of PBDEs and PCBs in California Peregrine Falcons (*Falco peregrinus*). Park, J.S., Holden, A., Chu, V., Kim, M., Rhee, A., Patel, P., Shi, Y.T., Linthicum, J., Walton, B.J., McKeown, K., Jewell, N.P., Hooper, K., Environmental Science and Technology 43, 8744–8751. 2009, Copyright American Chemical Society

BDEs in Peregrine Falcon Eggs from the Northeastern USA were studied by Chen et al. [65]. Eggs were collected from 1996 to 2006, excluding 1997 and 1998. Σ31BDE concentrations ranged from 74.5 to 6,610 μg kg^{-1} wet weight, with a median of 440 μg kg^{-1} wet weight, showing clearly higher levels than in eggs collected from the west coast, in California. These levels were generally also higher than those observed in European peregrine eggs, but comparable to those seen in North American seabird eggs. Congener patterns were dominated by BDE153, followed by BDE99, BDE183, BDE209, BDE197, BDE207, BDE154, BDE100 and BDE196, with lower contributions from BDE47, BDE208, BDE203, BDE201, BDE206, BDE202, BDE138 and BDE119, similar to eggs from California. Urban and rural falcon eggs contained similar total BDE concentrations but different congener profiles. Urban eggs exhibited higher BDE209 concentrations and greater percentages of other highly brominated congeners. BDE209 was detectable in all eggs, at concentrations ranging from 1.4 to 420 μg kg^{-1} wet weight. Five octa- and three nona-brominated congeners were also frequently detected, some likely derived from the biodegradation of BDE209. Temporal analyses indicated no significant changes in concentrations of total BDEs, or of most individual congeners during the study period. An exception was BDE209, which exhibited a significant increase, with a doubling time of 5 years.

Adult American kestrels exposed to environmentally relevant levels of the PBDE mixture DE-71 were investigated by Fernie et al. in two studies [66, 67].

Captive American kestrels were exposed via their diet to environmentally relevant concentrations of DE-71 and to HBCD. This exposure resulted in delayed egg laying and smaller eggs being laid, caused thinner eggshells and differential weight loss during embryonic development, and reduced fertility and reproductive success. The thickness of the eggshell declined as the concentrations of all measured BDE congeners (except BDE183 and BDE209) and of α-HBCD increased; increasing concentrations of BDE153, BDE154, BDE28 and BDE17 delayed egg laying, reduced eggshell mass (and ΣBDEs) and reduced fledging success (BDE153 and BDE154 only). As uptake of DE-71 continued following pairing, the timing of the courtship behaviours shown by the treated birds differed markedly from that of the control birds. Exposure to low and high levels of DE-71 changed the appropriate timing of the birds' copulatory behaviour, nest box inspections, pair-bonding behaviours and food consumption patterns. Perhaps, most critically, as the birds were continuously exposed to DE-71 during the courtship period, the treatment birds failed to copulate, participate in pair-bonding sexual behaviours and investigate their nest boxes, neither at appropriate times nor as frequently as the control birds.

The enantiomer-specific accumulation of HBCD in eggs of predatory birds was investigated by Janák et al. [68]. Eggs of peregrine falcon, white-tailed sea eagle, guillemot and common tern sampled in Sweden were analysed. Only the α-HBCD diastereomer was found in the eggs of peregrine falcon and white-tailed sea eagle and it was the predominant diastereomer in terns and guillemots. Clear differences in the enantiomer fraction (EFα) were found between the different species analysed, indicating species-specific stereoselective mechanisms for uptake and metabolism of the enantiomers of α-HBCD. Sum HBCD levels varied between 80 and 3,100 μg kg^{-1} lipid weight.

BDE congener patterns, HBCD and BB153 in eggs of peregrine falcons breeding in Sweden were investigated by Johansson et al. [69]. Geometric mean concentrations of Σ13BDEs, HBCD and the hexabrominated biphenyl (BB153) were 3,100, 140 and 81 μg kg^{-1} lipid weight for the southern population; 2,500, 110 and 84 μg kg^{-1} lipid weight for the northern population; and 47, not detected, and 8 μg kg^{-1} lipid weight for the captive population. The BDE congener pattern was dominated by BDE153, BDE99 and BDE100. The average brood size for individual females from the southern population decreased with increasing concentrations of Σ13BDE in the eggs (log-linear regression $p < 0.01$).

Sonne et al. described summed BDE concentrations in plasma of raptor chicks sampled in Northern Norway. Σ8BDE concentrations varied between 2.8, 7.3 and 2.0 ng ml^{-1} for golden eagle, goshawk and white-tailed sea eagle, respectively [70].

Concentrations of BDEs in common magpie feathers were determined by Jaspers et al. [71] while assessing regional differences in contamination. BDE47 and BDE99 could be detected in all samples collected at a rural and an urban location in Flanders, Belgium. BDE47 had a higher contribution in feathers from the urban area ($p < 0.05$), while BDE99 was the most prominent congener in feathers from the rural areas (0.3 μg kg^{-1} dry weight and 0.11 μg kg^{-1} dry weight for BDE47 and 0.17 and 0.19 for BDE99, respectively, in urban and rural locations). The analysis

of preen gland samples of the same species showed Σ6BDE levels of 13 μg kg^{-1} lipid weight (3.2 and 4.8 μg kg^{-1} lipid weight for BDE47 and BDE99, respectively), indicating that the preen gland might be an important elimination route for BDEs in birds.

Three studies by Van den Steen et al. focused on the use of great tit and starlings to monitor BFRs and their effects [72–74]. Eggs from 22 locations were sampled across Europe. The concentrations of Σ7BDE ranged from 4.0 ± 0.7 to 136 ± 19 μg kg^{-1} lipid weight. Σ7BDE concentrations differed significantly among the sampling locations (one-way ANOVA: $F_{21,129} = 16.67$, $p < 0.001$). Σ7BDE concentrations were significantly higher in the urban sampling locations than in the rural and remote locations (urban > rural > remote). Eggs from the rural sampling locations showed significantly higher Σ7BDE levels compared to the eggs from remote sampling locations. Eggs from the urban sampling locations showed significantly higher concentrations compared to the remote locations but not compared to the rural locations. Second, eight complete first clutches with known laying order were collected in 2006 from two sites near Antwerp (Belgium). Σ7BDE concentrations decreased in relation to the laying order from 68 ± 10 to 53 ± 11 μg kg^{-1} lipid weight, but this was not statistically significant. Mean ΣBDE concentrations were significantly lower in eggs of replacement clutches compared to first clutches. And finally, in an exposure study with PBDEs in female European starlings, toxicokinetics and reproductive effects were investigated. Female European starlings were exposed to a pentabromodiphenyl ether mixture through subcutaneous implants, and levels and profiles of BDEs together with reproductive effects were examined. Σ7BDE levels increased significantly in the serum of the exposed females from 218 ± 43 to 23,400 ± 2,035 pg ml^{-1}. ΣBDE concentrations in the eggs of the exposed group ranged from 130 ± 12 to 220 ± 37 μg kg^{-1} wet weight. The profile in serum after egg laying was very similar to that observed in eggs. There were no detectable levels of OH-BDEs in either serum or eggs. Fewer females of the exposed group initiated egg laying compared to the control group, although the difference was not significant. In addition, egg weight and volume were significantly higher in the exposed group. These results suggest that, at the investigated exposure levels (150 μg ΣPBDEs per bird), PBDEs may have a negative effect on reproductive performance.

Covaci et al. [75] studied BDEs and HBCD in the eggs of free-range chickens from Belgium sampled in 2006–2007, thereby addressing both environmental and food concerns simultaneously. Concentrations of both BFRs were relatively low and comparable to those seen elsewhere. Σ6BDE concentrations ranged from not detected up to 32 μg kg^{-1} lipid weight; those of HBCD from not detected up to 62 μg kg^{-1} lipid weight with a lower detection frequency. When present, BDE209 was the major congener (45% of Σ6BDE), otherwise BDE47 and BDE99 predominated. Soil seemed to be the major, but not the sole, source of the BFRs in hens' eggs.

The BDE congener profile observed in sparrow hawks, buzzards and blackbirds from Switzerland was dominated by BDE47, BDE99, BDE100 and BDE153, which was found to be in agreement with previous studies in birds of prey from Australia and Flanders [76–78].

A study in terrestrial birds of prey from China showed the presence of BDE209 in almost 80% of the samples, which confirms the bioaccumulation ability of this congener [79]. Starling muscle tissue [74] and peregrine falcon eggs [80] from terrestrial ecosystems showed higher concentrations of BDEs 153, 154, 100, 99, 183 and 209 compared to BDE47. Similar patterns were found in eggs from a study comparing peregrine falcons feeding from species belonging to terrestrial and aquatic food chains, but the hypothesis that higher brominated congeners would be present to the greatest extent in the terrestrial food chain was not supported [28].

2.2 Fish and Shellfish

In 11 species of fish from the River Scheldt in Belgium, Roosens et al. [81] reported concentrations of BDEs and HBCD. The sum of tri- to hepta-BDE congeners (2,270 ± 2,260 μg kg^{-1} lipid weight; range 660–11,500 μg kg^{-1} lipid weight) and total HBCDs (4,500 ± 3,000 μg kg^{-1} lipid weight; range 390–12,100 μg kg^{-1} lipid weight) were 10-fold higher than those usually reported for freshwater systems, indicating local point sources. Eels showed a considerable decrease in levels of both BDEs and HBCD from 2000 to 2006.

In Zebra mussels from Lake Maggiore in Italy, Binelli et al. [82] reported Σ14BDE concentrations from 40 to 447 μg kg^{-1} lipid weight, similar to those found in environments polluted by deposition or atmospheric transport. The congener profile showed BDE47 > BDE99 > BDE100 > BDE209, closely resembling patterns observed in freshwater ecosystems worldwide.

In shore crabs sampled from a contaminated Norwegian fjord, Haukås et al. [33] determined HBCD concentrations along a transect away from a known point source. Mean ΣHBCD concentrations at the four locations declined from 300 ± 220 to 26 ± 6.8 μg kg^{-1} lipid weight. In lugworms and mussels, concentrations declined from 7,000 ± 2,000 μg kg^{-1} lipid weight to not detected and 1,400 ± 110 μg kg^{-1} lipid weight to not detected, respectively.

In three species of deepwater fish (caught at >1,000 m depth in 2006) off the west coast of Scotland, Russell et al. [83] reported Σ17BDE concentrations from 12 to 51 μg kg^{-1} lipid weight. In wild and rope-grown mussels from Scottish coastal waters taken since 1999, Σ9BDE concentrations were not detected to 3.7 μg kg^{-1} wet weight, with the highest concentration in Aberdeen in summer 2008 [84]. Σ17BDE concentrations in flatfish muscle from 11 locations around Scotland were up to 1.7 μg kg^{-1} wet weight, while in muscle of brown trout from freshwater lochs the maximum concentration was 1.2 μg kg^{-1} wet weight [85]. In the same study, Σ17BDE concentrations of 4.1–536 μg kg^{-1} wet weight were recorded in the livers of fish from the former sewage sludge disposal site at Garroch Head in the Firth of Clyde.

Harrad et al. [86] determined HBCD and TBBP-A in fish collected in 2008 from nine English lakes. Concentrations ranged from 14 to 290 μg kg^{-1} lipid weight and <0.3–1.7 μg kg^{-1} lipid weight, respectively.

In three fish species from the southern Baltic Sea, Szlinder-Richert et al. [87] recorded mean Σ7BDE concentrations of 1.2 (herring), 1.6 (sprat) and 2.5 (salmon) μg kg^{-1} wet weight. BDE47 predominated in all samples, and BDE concentrations in herring were similar to those observed in herring from the northern Baltic Sea but lower than in those from the Belgian North Sea. In salmon, BDE concentrations were similar to those in samples from the northern and northeastern Baltic Sea but similar to those found in fish from the central part.

Samples of marine and freshwater mussels from different locations showed a similar pattern of BDEs congeners, with predominance of the lower brominated ones (BDE47 and BDE99) [88]. In a study on common frogs from Scandinavia, more than 90% of the liver samples revealed the presence of BDE47, and less than 50% that of BDE99 [89].

In four species of Antarctic fish, Borghesi et al. [90] reported ΣBDE concentrations from 0.09 to 0.44 μg kg^{-1} wet weight. In tuna from the Mediterranean Sea, concentrations were 15 μg kg^{-1} wet weight, 100–1,000× higher. Lower brominated congeners prevailed in Antarctic species while, in tuna, tetra- and penta-BDE congeners dominated, consistent with the major source to the Antarctic being long-range atmospheric transport. In swordfish from the Mediterranean, Corsolini et al. [91] reported Σ19BDE concentrations of 2.2 ± 3.3 μg kg^{-1} wet weight in liver and 0.6 ± 0.6 μg kg^{-1} wet weight in muscle tissue.

In two fish species, two crab species and three bivalve species from Tokyo Bay, Japan, Σ20BDE concentrations were 97 and 192, 92 and 97, and 17–66 μg kg^{-1} lipid weight, [92]. Hong et al. [93] determined BDEs in mussels from two locations in France and South Korea. Mean Σ13BDE concentrations were 13 μg kg^{-1} dry weight in Masan Bay, South Korea, and 0.9 μg kg^{-1} dry weight in Thau lagoon, France. The authors suggested that these data indicated a growing pollution problem in Asia, and in South Korea in particular.

Twelve species of deep-sea fishes collected in 2005 off the coast of Japan were analysed for BDEs and HBCD [94]. The fish were caught at depths from 410 to 900 m, and so remote from land-based sources. The concern of the authors was that the deep-sea might act as an ultimate sink for such compounds. Σ14BDE concentrations ranged from 1.3 to 53 μg kg^{-1} lipid weight, and HBCD from <0.05 to 110 μg kg^{-1} lipid weight. A significant positive correlation was found between $\delta^{15}N$ and lipid-normalized concentrations of BDEs showing their high biomagnification potential for food web uptake, though this was not the case for HBCD.

Bivalves (mussels and oysters) in coastal waters from Japan (22 locations) were sampled and analysed for BDEs and HBCD [95]. HBCD and Σ14BDE concentrations ranged from 12 to 5,200 μg kg^{-1} lipid weight and 3.1–86 μg kg^{-1} lipid weight, respectively. The authors noted that HBCD concentrations were among the highest levels reported from Asia and Europe. Estimated uptake levels for human consumers from oysters and mussels as seafood for HBCD and

Σ14BDEs were 0.45–34 ngkg^{-1} body weight and 0.58–6.8 ngkg^{-1} body weight, respectively.

To determine the potential input sources of PBDEs to fish farms in south China, Zhang et al. [96] sampled seven environmental matrices in 2006–2007. Tri- to deca-BDE congeners were detected in all samples, at mean Σ46BDE concentrations (including BDE209) of 5.7 ± 3.6 ngl^{-1} in pond water, 15 ± 11 μg kg^{-1} dry weight in pond sediments, 12 ± 3.8 μg kg^{-1} dry weight in bank soil, 21 ± 20 μg kg^{-1} lipid weight in fish and 93 ± 62 μg kg^{-1} lipid weight in fish feed. BDE209 was the dominant congener in all samples other than fish, where BDE47 predominated. As in other studies, fish feed (in this case, along with pond water) was the dominant source of BDEs in farmed fish.

Fish and invertebrates collected from the Pearl River Delta (PRD) region in China during 2005–2007 were analysed for BDEs [97]. Σ7BDE concentrations ranged from 6.2 to 208 μg kg^{-1} lipid weight, a decrease relative to those seen in 2004. In two species of fish and in winkles from the vicinity of a local source from e-waste recycling, Zhang et al. [96] reported ΣHBCD concentrations of 377 and 1,790, and 186 μg kg^{-1} lipid weight, respectively. Gao et al. [57] determined BDEs in 16 species of aquatic biota, including fish, crab and shrimp, from the lower Yangtze River in East China sampled in 2004–2007. Σ12BDE concentrations were 3.5–604 μg kg^{-1} lipid weight (mean 44 μg kg^{-1} lipid weight), low to average on a global scale.

Jin et al. [98] determined BDEs in five species of shellfish sampled in 2006 from Laizhou Bay, China. Σ11BDE concentrations (including BDE209) in the shellfish ranged from 230 to 720 μg kg^{-1} lipid weight.

Σ23BDE concentrations were determined in seafood from China as part of a market study [99]. In fatty fish, concentrations ranged from 0.04 to 0.91 μg kg^{-1} wet weight, and in shellfish, from 0.02 to 0.35 μg kg^{-1} wet weight. Van Leeuwen et al. [100] determined BDEs and HBCD in farmed fish and shrimp from Southeast Asia, Europe and South America. Concentrations were generally very low. Carnivorous species contained high concentrations than omnivorous species. In another diet study, Miyake et al. [101] determined BDEs in seafood samples from two cities in China, Guangzhou and Zhoushan. Guangzhou is one of the largest cities in China and has experienced rapid economic growth since 1979. Zhoushan is a coastal city and port less influenced by industry and not opened for economic development until 1988. Mean Σ10BDE concentrations in the two cities were: fish, 46 and 6.7 μg kg^{-1} lipid weight; crab, 11 and 3.0 μg kg^{-1} lipid weight; cephalopods, 9.2 and 8.3 μg kg^{-1} lipid weight; shrimp, 28 and 7.4 μg kg^{-1} lipid weight; bivalves, 14 and 11 μg kg^{-1} lipid weight; respectively.

Li et al. [102] determined BDEs in ten species of fish and shellfish from Yuandang Lagoon, Xiamen Island, China. Σ8BDE concentrations ranged from 0.3 to 1.3 μg kg^{-1} lipid weight and were higher in crabs and clams than in fish, probably because benthic organisms are in closer contact with contaminated sediments. BDE congener patterns also differed: fish contained mainly lower brominated BDEs with BDE209 not detected, while higher brominated BDE congeners (including BDE209) were observed in crabs and clams.

Shaw et al. [103] determined BDEs in seven species of teleost fish comprising the major prey items of harbour seals in the NW Atlantic. Σ16BDE concentrations in whole fish samples (as eaten by seals) ranged from 18 to 94 μg kg^{-1} lipid weight (62 ± 34 μg kg^{-1} lipid weight); total HBCD concentrations from 2.4 to 38 μg kg^{-1} lipid weight (17 ± 10 μg kg^{-1} lipid weight). Σ16BDE concentrations were ca. 100-fold higher than the levels in fish.

In muscle tissue of wild Chinook salmon from Chile, Montory et al. [104] reported Σ14BDE concentrations between 0.3 and 1.05 μg kg^{-1} wet weight, similar to levels reported for the northern hemisphere. Sloan et al. [105] reported Σ10BDE concentrations in juvenile Chinook salmon from the Columbia River and Estuary and Puget Sound, NW USA. The mean Σ10BDE concentrations in fish from the various urban and nonurban sites sampled ranged from 0.35 to 2.8 μg kg^{-1} lipid weight. Levels of PBDEs in hatchery fish were significantly lower than those in the wild fish.

Concentrations of TBBP-A and HBCD were determined in sharks (bull shark and Atlantic sharpnose shark) from US waters by Johnson-Restrepo et al. [106]. The highest concentrations of TBBP-A and HBCD were found in bull shark, 36 and 413 μg kg^{-1} lipid weight, respectively.

In lake trout from Lake Ontario, Canada, sampled between 1979 and 2004, Σ6BDE concentrations (BDE28–BDE154) increased significantly from 1979 until the mid-1990s, then levelled off or decreased to 2004 [107]. In contrast, concentrations of BDE209 increased by a factor of 4 between 1998 and 2004. Concentrations of total HBCD showed some decline and pentabromoethyl benzene (PBEB) showed no consistent trend over the period studied; 1,2-*bis*(2,4,6,tribromophenoxy)ethane (BTBPE) showed a rising trend until ca. 1993 and then concentrations decreased to 2004.

Blocksom et al. [108] determined BDEs in whole fish from three major US rivers (upper Mississippi, Missouri and Ohio) in 2004–2005 with the aim of estimating human and wildlife exposure risks from fish consumption. Σ6BDE concentrations were highest in fish in the Missouri and Ohio rivers (>1,000 μg kg^{-1} lipid weight) with BDE47 dominating. Concentrations were positively correlated to fish size, lipid content, trophic guild and proximity to urban areas.

The Hawaiian Islands are located in the middle of the Pacific Ocean and are geographically isolated. PBDEs have been determined in the muscle tissue of wild tilapia from the vicinity of Honolulu and Waikiki [109]. Σ8BDE concentrations at three sampling sites were 567 ± 54, 232 ± 18 and 686 ± 79 μg kg^{-1} lipid weight. Although few industries have been developed in the islands, these PBDE concentrations are still relatively high. BDE183 and BDE209 were not detected in these samples.

Losada et al. [110] determined BDEs in six species of marine fish, one species of crab and squid from Sydney Harbour, Australia. Mean Σ10BDE concentrations ranged from 6.4 μg kg^{-1} lipid weight in squid to 115 μg kg^{-1} lipid weight in flounder. Blue swimmer crab and squid had lower concentrations than the fish species. BDE47 was the dominant congener; BDE183 was not detected and BDE209 was not determined.

Elevated levels of BDEs in farmed compared to those observed in wild salmon have previously been ascribed to the levels in their feed, usually derived from fish meal and oil [111]. Berntssen et al. [112] have assessed the impact of replacing these with novel alternative feeds based on ingredients of plant origin with a minor inclusion of krill. In their study, the use of the alternative feed reduced Σ10BDE levels by approximately two-thirds. In an earlier study, in Atlantic salmon fed on fish oil, rapeseed oil or a 1:1 mixture of the two oils, mean Σ7BDE concentrations were 2.2, 1.1 and 1.7 μg kg^{-1} wet weight, respectively, indicating a lower level of contamination in the oil of vegetable origin.

Maternal transfer was also observed for all BFRs detected in female zebra fish and for the metabolites. The egg/fish concentration ratios were significantly above 1 for several compounds. Generally, high egg/fish ratios were observed for BFRs with high log K_{ow} values. These compounds seemed to be more efficiently transferred to eggs [113].

2.3 Marine Mammals

The detection of BDE congeners in sperm whale tissues, feeding offshore and in deep water, and the particularly high concentrations found in dolphins and seals highlighted the ubiquity and bioavailability of these chemicals in the marine ecosystem [114]. A wide range of marine mammals has been investigated since with a similar BDE congener pattern [114–124] (Fig. 4). A large number of harbour porpoises from England and Wales were analysed for 14 tri- to hepta-BDEs, and the major congeners detected were BDE47, BDE99 and BDE100. Porpoise foetuses were also analysed and BDEs were also detected, demonstrating transplacental transfer from mother to offspring [125]. Three BDE congeners were analysed in 11 stranded harbour seals from San Francisco Bay between 1989 and 1998, showing that the contribution of BDE47 to the sum of the congener concentrations ranged between 62% and 94% [126]. Long-finned pilot whales from the Faroe Island showed higher BDE concentrations in juvenile animals, which were ascribed to lactational transfer [127]. A study out of BDEs in blubber samples from Baikal seals detected a gender difference for the concentrations of BDEs and HBCD. The transfer of these contaminants from mother to pup during gestation and lactation was suggested as the cause of this difference [128].

Liver samples from ten species of cetaceans stranded 1994–2006 in Southeast Brazil were analysed for BDEs [130]. Σ9BDE concentrations were 3–5,960 μg kg^{-1} lipid weight, similar to those observed in Northern Hemisphere dolphins. A positive correlation was observed between Σ9BDE concentrations and year of stranding, indicating rising concentrations.

Von der Recke and Vetter [131] studied PBBs in blubber of seals and harbour porpoises (as well as in fish) originating from the North Sea, the Baltic Sea, and the coastal waters of Iceland and North America. Hexa-BB congeners dominated, followed by penta-BBs and hepta-BBs, while octa-BBs were detected only

Species	Location	BDE	Reference
Grey seal	Baltic Sea	730 419	[115] [116]
Ringed seal	Svalbard Canadian Arctic	51 26–50*	[115] [117]
Harbour seal	North Sea San Francisco Bay	600–6,000 67–7,140	[114] [126]
Caspian seal	Azerbayan	BDE47: 15 (ww)	[125]
Bottlenose dolphin	Gulf of Mexico	8,000	[118]
Striped dolphin	Mediterranean Sea	726–8,130	[120]
Indo-Pacific humpback dolphin	India	10–12*	[128]
Spinner dolphin	Philippines	2,600–5,400*	[129]
Harbour porpoise	Br. Columbia England & Wales Pacific	350–2,300* 440–7,670* 860–3,160*	[140] [121] [129]
Beluga	Canadian Arctic	81–160*	[117]
Long-finned pilot whale	Faroe Islands	843–3,160*	[127]
Minke whale	Netherlands	870	[114]
Melon headed whale	Queensland Japan	36 (ww) 190–510	[125] [133]
Killer whale	UK Shiretoko	490–2,000, max. 16,200* (ww) 170–540*	[123] [122]

Fig. 4 Overview of concentrations of PBDEs in marine mammals and sample location around the world. Concentrations given in ng g^{-1} lipid weight unless otherwise stated. ΣBDE = sum of BDEs 47, 99 and 100. * More congeners included

occasionally and nona-BBs and BB209 not at all. The hexa-BB pattern in samples from Iceland was a mixture of those seen in samples from North America and continental Europe. BB153 dominated, and BB155 and BB154 were also prominent. The patterns of some congeners indicated degradation of more highly

brominated products. Concentrations of individual BB congeners or of the sum of those congeners determined were not reported.

Tanabe [132] summarized a number of studies using archived marine mammal tissue samples from a specimen bank. In recent years, HBCD concentrations seemed to exceed those of ΣBDEs in samples from Japan, presumably reflecting a change in usage following controls. ΣBDE levels peaked in the 1990s (as for sediments above) and then stabilized. In finless porpoises from the South China Sea, ΣBDE levels were much higher than those of HBCD both in past and recent years, implying a lower consumption of HBCD than of PBDEs in China.

Kajiwara et al. [133] determined BDEs in blubber of melon-headed whales from Japan sampled in 1982–2006. In 2006, Σ10BDE concentrations were 190–510 μg kg^{-1} lipid weight, as against 7.5–30 μg kg^{-1} lipid weight in 1982. Maternal transfer was estimated to be 85% of the mother's body burden. In striped dolphins (1978–2003), Isobe et al. [134] determined BDEs and HBCD in blubber of striped dolphins from Japan 1978–2003. Σ11BDE concentrations ranged from 13 to 850 μg kg^{-1} lipid weight, and HBCD concentrations from 10 to 940 μg kg^{-1} lipid weight. In both instances, the highest concentrations were seen in 2003, suggesting growing consumption in recent years.

In muscle-blubber biopsy samples from 21 Galapagos sea lions collected from the Galapagos Islands (1,000 km off the coast of Ecuador) in 2005, Alava et al. [135] determined BDEs. Only traces of BDEs were detected in one male pup.

Schiavone et al. [136] studied BDEs in Antarctic fur seals collected on the Antarctic Peninsula in 2004. The mean Σ9BDE concentration was 11 μg kg^{-1} lipid weight – in fact, only BDE47 and BDE66 were above the limit of detection.

Peck et al. [137] determined HBCD in blubber and liver of Atlantic white-sided dolphins that stranded on the east coast of the USA during 1993–2004. α-HBCD concentrations in blubber and liver ranged from 19 to 380 μg kg^{-1} lipid weight and 2.9 to 140 μg kg^{-1} lipid weight, respectively. These were lower than HBCD concentrations in cetaceans from Western Europe, and than concentrations of BDEs reported earlier in a subset of the same animals. Concentrations of TBBP-A and HBCD were determined in blubber of bottlenose dolphins from US waters by Johnson-Restrepo et al. [100]. The mean concentrations of TBBP-A and HBCD were 86 and 413 μg kg^{-1} lipid weight, respectively. In the Hawaiian Islands, Ylitalo et al. [138] determined BDEs in false killer whales from Hawaii. Σ10BDE concentrations ranged from not detected to 2,900 μg kg^{-1} wet weight, with adult females having lower concentrations than adult males and juveniles. Meng et al. [139] studied BDEs in Cliformia sea lion, harbour seal and Northern elephant seal from California. Σ14BDE concentrations were 0.06–236, 0.32–7.2 and 0.04–2.0 μg kg^{-1} lipid weight, respectively. Ikonomou and Addison [140] measured BDE concentrations in the blubber of five mother–pup pairs of grey seals from Nova Scotia sampled in 1995, and of 20 harbour seals from British Columbia sampled in 1991–1992. Σ10BDE concentrations in maternal grey seals averaged 112 ± 55 μg kg^{-1} lipid weight and were over twice the concentrations measured in their pups. Lower brominated congeners transferred more efficiently than hepta-BDEs and larger congeners. Σ10BDE concentrations in harbour seals

from the Strait of Georgia were 319 ± 132 μg kg^{-1} lipid weight, while those in harbour seals from the more remote Quatsino Sound were 28 ± 12 μg kg^{-1} lipid weight. In a study in central west Greenland, Vorkamp et al. [141] determined BDEs in archived samples of ringed seal blubber over the period 1982–2006. Median Σ11BDE concentrations ranged from 2.2 to 8.5 μg kg^{-1} lipid weight. Levels were lower than those observed previously in seals from east Greenland in a similar time trend study [142].

Lam et al. [143] looked at concentrations of HBCD and BDEs in Indo-Pacific humpback dolphins and finless porpoises from Hong Kong, during 2002–2007 and 2003–2008, respectively. The concentrations of ΣHBCD and Σ14BDE were 4.1–519 and 103–51,100 μg kg^{-1} lipid weight, respectively. A significant increasing trend in HBCD concentrations was seen in dolphins from 1997 to 2007, with an estimated annual rate of increase of 9%. No trend was observed for BDEs. This may reflect increasing use of HBCD in response to controls on the PBDE products. Three "novel" BFRs compounds were studied: hexachlorocyclopentadienyldibromocyclooctane (HCDBCO) was not detected; while 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and *bis*(2-ethylhexyl)-tetrabromophthalate (TBPH) were detected at maximum concentrations of 70 and 3,860 μg kg^{-1} lipid weight, respectively. Levels of HBCD and TBPH were comparable in porpoise samples.

In ringed seals from East Greenland, Letcher et al. [144] determined BDEs, BBs and HBCD and their metabolites. Mean Σ13BDE concentrations were 149 ± 87 μg kg^{-1} lipid weight, and the mean concentration of BB101 was 0.25 ± 0.12 μg kg^{-1} lipid weight. The mean α-HBCD concentration was 19 ± 2 μg kg^{-1} lipid weight.

Houde et al. [145] determined BDEs and their hydroxylated analogues in plasma of bottlenose dolphins from the east coast of the USA. Significantly lower Σ12BDE concentrations were found in animals from Florida than in those from South Carolina (5.5 ± 4.6 μg kg^{-1} wet weight and 30 ± 40 μg kg^{-1} wet weight, respectively). Similarly, Σ16OH-BDE were 1.15 ± 0.7 and 0.6 ± 0.4 μg kg^{-1} wet weight in South Carolina and Florida, respectively. A significant proportion might be a consequence of naturally produced MeO- and OH-BDEs. In Europe, Weijs et al. [146] determined BDEs and OH-BDEs in serum of captive harbour seals and harbour porpoises from 2006 to 2008. Median Σ6BDE concentrations were 130 $pgml^{-1}$ in seals and 1,300 $pgml^{-1}$ in porpoises. OH-BDEs were not detected in either species.

Fair et al. [147] reported concentrations of BDEs in bottlenose dolphins sampled in 2003–2005 from two estuarine areas in the southeastern USA, Charleston in South Carolina and the Indian River Lagoon in Florida. Σ13BDE concentrations ranged from 295 to 22,800 and 196 to 3,790 μg kg^{-1} lipid weight, respectively. Concentrations in bottlenose dolphins from Charleston were among the highest recorded in marine mammals in the world to date.

Montie et al. [148] studied BDEs and OH-BDEs in cerebrospinal fluid and cerebellum grey matter of short-beaked common dolphins and Atlantic white-sided dolphins from the east coast of the USA. In cerebrospinal fluid, Σ33BDE concentrations were 0.3 and 0.9 μg kg^{-1} wet weight in female common dolphins,

0.7 and 1.6 μg kg^{-1} wet weight in male white-sided dolphins and 13 ± 16 μg kg^{-1} wet weight in female white-sided dolphins. Concentrations of HO-BDEs were very low, maximum 0.3 μg kg^{-1} wet weight. In grey matter of white-sided dolphins, concentrations of Σ14OH-BDEs were 4.2–8.9 μg kg^{-1} wet weight.

2.4 Turtles

Few data are available for turtles, but Swarthout et al. [149] reported Σ27BDE concentrations in blood samples from two species of turtles (Kemp's ridley and green sea turtles) sampled in the Gulf of Mexico in 2001–2002. BDEs were detected in all 58 turtles analysed, and BDE47, BDE99, BDE100, BDE153 and BDE154 were the dominant congeners (deriving from the penta-mix PBDE product). Summed concentrations ranged from 0.0002 to 0.0015 μg kg^{-1} wet weight.

2.5 Terrestrial Animals

Verreault et al. [150] determined BDEs in adipose tissue from captive sledge dogs in Greenland. Σ36BDE concentrations were 42 ± 0.7 μg kg^{-1} wet weight in an exposed group (fed on minke whale blubber) compared to 2.1 ± 0.4 μg kg^{-1} wet weight in a control group fed on pork fat.

Concentrations of higher brominated BDE congeners in terrestrial animals have been found to be relatively high, which indicates their bioaccumulation capacity in these animals. Higher brominated BDE congeners were also bioaccumulated in the meat and body fat of cows [151]. BDE 209 was found to be the most abundant congener in studies on the terrestrial top predators red fox and grizzly bears. Grizzly bears consuming salmon had a congener profile dominated by the lower brominated BDEs [17, 18].

These variations in the pattern of the BDEs congeners depending on the ecosystem emphasize the importance of the bioavailability of the BFRs and their potential degradation.

3 Bioaccumulation and Bioavailability

Bioavailability and bioaccumulation are intrinsically connected with each other and directly related to the interaction of chemical substances with the abiotic and biotic environment. The bioavailability of chemical contaminants in the environment depends on several factors including structure and physicochemical properties of a compound, its main sources of production, its ability to be transported to different environments and the nature of the medium in which these chemicals are found.

There are different emission routes through which a contaminant can reach the environment. This may be during production, product formulation, application, its lifetime usage and its disposal after the end of their in-service life. Once released into the environment, they can be adsorbed to particulate matter depending on their water solubility and binding affinity to particles. Consequently, they may be transported through the aquatic environment or travel far from the emission source while attached to dust particles with a high spatial mobility.

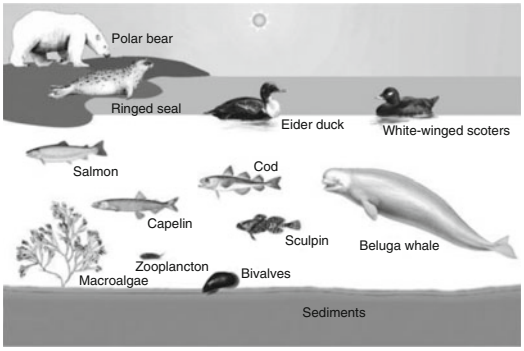
The bioconcentration factor (BCF) is defined as the accumulation of a compound through the respiratory system or dermal contact after exposure to the medium, measured in laboratory tests. It results in a higher concentration of the substance within an organism than in its surrounding environmental medium, such as water or air. This factor is correlated to the water solubility of a chemical and its vaporization rate, referring to the maximum solute concentration possible at equilibrium, and the octanol–water partition coefficient (K_{ow}), referring to the ratio of the concentration of a chemical in *n*-octanol and in water at equilibrium at a specific temperature and pressure [152]. The quantification of process rates and partition coefficients of organic pollutants in air, water, soil and biota is an important step in defining the level of organic contaminants in environmental systems and their potential impact on environmental quality.

A specific way of determining the bioconcentration of a substance is by calculating the biota-soil accumulation factor (BSAF), which relates the concentration of the chemical in the organism on a lipid weight basis to its concentration in the surrounding soil on an organic carbon basis.

The bioaccumulation factor (BAF) is defined as the ratio between the concentration of a compound in an organism and the concentration in the surrounding environment at steady state after exposure from any source. The level to which a substance is bioaccumulated depends on the rate and mode of uptake, through inhalation (respiratory system: lungs or gills) or ingestion along with food, through contact with the epidermis (skin), and the elimination rate. It is also important to consider the possible transformation of the substance by metabolic processes, the lipid content of the organism and other environmental factors. BCF and BAF are often determined as the ratio between the concentration of a compound (on a lipid weight basis) in an organism and its concentration in the surrounding water.

As a general rule, the more hydrophobic (lipophilic) a substance, the higher the expected BAF will be in organisms. Lipophilic substances are less likely to be diluted or excreted in urine, and so can accumulate in fatty tissues. However, it has been shown that an increasing degree of halogenation with a related increase in the molecular size and K_{ow} lowers the absorption efficiency of a halogenated compound in fish [153]. It has been argued that this reduced dietary absorption of large super hydrophobic substances (such as BDE209) was due to the physically restricting size of the molecule which hinders its passage through the membrane via the gills or the gut [154].

As a consequence of the persistence and bioaccumulation potential of chemicals, and due to the interaction between the different trophic levels in a selected ecosystem, a chemical may biomagnify in a food web. When a chemical is bioaccumulated



ORGANISM	δ15N (‰)	TROPHIC LEVEL
Macroalgae *(Fucus gardneri)**	6.1 ± 0.2	1.0
Zooplancton *(Calanus hyperboreus)***	7.9 ± 0.1	2.0
Bivalves *(Mytilus eduils)***	9.1 ± 0.7	2.3
Salmon *(Salmo salar)**	11.9 ± 1.2	3.1
Capelin *(Mallotus villosus)**	12.8 ± 0.13	3.3
Arctic cod *(Boreogadus saida)**	13.5 ± 0.5	3.5
Sculpin *(Myoxocephalus scorpioides)**	14.1 ± 0.9	3.6
Eider duck *(Somateria mollissima)**	12.1 ± 0.5	3.5
White-winged scoters *(Melanitta fusca)**	13.8 ± 0.8	3.9
Beluga whale *(Delphinapterus leucas)**	15.3 ± 0.7	4.0
Ringed seal *(Pusa hispida)***	17.5 ± 0.2	4.5
Polar bear *(Ursus maritimus)***	21.1 ± 0.3	5.5

* Data obtained from Kelly et al.(2008) [156]
** Data obtained from Hobson et al.(2002) [155]

Fig. 5 Representation of trophic levels of a Canadian Arctic marine food web by stable isotope characterisation (mean + SD)

in an organism from a low trophic level, such as an invertebrate species, it may result in a buildup in the adipose tissue of successive trophic levels such as fish, birds or marine mammals. When eaten by another organism, fats carrying the contaminant are absorbed in the gut, and the chemical will accumulate in the fat of the predator.

To improve the food web characterization, a stable nitrogen isotope analysis technique has been developed, assessing predator–prey interactions and organism trophic levels by determining the $\delta_{15}N$, the concentration ratio of $_{15}N/_{14}N$, expressed relative to a standard (i.e. atmospheric N_2). This ratio increases with increasing trophic levels due to the preferential excretion of the lighter $_{14}N$ isotope [155, 156] (Fig. 5).

There are several ways to calculate the biomagnification of a chemical. One of them is by determining the biomagnification factor (BMF), which accounts for the ratio of lipid-normalized contaminant concentrations in predator and prey. Biomagnification occurs when BMFs are greater than 1, indicating that predators are less capable of metabolizing these compounds compared with their prey.

The trophic magnification factor (TMF) is the average biomagnification at several trophic levels, and it can be derived from the slope of the line in a plot of concentrations in an organism vs the trophic level.

$$\text{BAF, BCF} = \frac{C_{\text{organism}}}{C_{\text{water/air}}} \quad \text{BSAF} = \frac{C_{\text{organism}}}{C_{\text{soil}}} \quad \text{BMF} = \frac{C_{\text{predator}}}{C_{\text{prey}}}$$

3.1 Bioaccumulation Studies

Some BFR levels in wildlife and humans have substantially increased since the 1980 [157]. The evidence of bioaccumulation in wildlife and its potential trophic magnification ability has been investigated since, with interesting conclusions

regarding to the principal congeners bioavailability and its behaviour once they interact with the environment [158, 159].

The different concentrations of the BFRs detected along the food webs from separate locations are usually related to several factors such as the proximity to a production source and the potential degradation of BFRs in different matrices. Concentrations of PBDEs detected in temperate environment marine mammals were about 1,000 times higher than the ones found in Arctic environment, which evidences the decrease in concentration as a function of the distance from release sources and also their ubiquity in apparently less-exposed areas due to their transportation ability [159].

When focusing on a particular ecosystem, difficulties arise establishing the food chain interactions regarding to the predatory–prey preferences and the species-specific differences in the ability to metabolize and biotransform BFR compounds. These differences may change the congener profile in the organism showing congeners that are not detected in the environmental media and leading to a trophic enrichment of less brominated congeners [160, 161]. The dietary absorption efficiency also influences the biomagnification of BFRs along food webs which could lead to an underestimation of their BMF at higher trophic levels.

The bioaccumulation potential of BFRs has been investigated in several aquatic food webs. Gustafsson et al. [162] estimated BAFs in laboratory studies from water to Baltic blue mussels (*Mytilus edulis*), showing that BDE47 and BDE99 are very accumulative in this species with values of 1.3 and 1.4×10^6 followed by BDE153 (0.22×10^6). In a field study in the Netherlands, BCFs of PBDEs in blue mussels collected from several sites along the coast and in the Scheldt estuary were determined. It was concluded that BDE47, BDE28, BDE99, BDE100 and BDE153 bioaccumulate to a significant extent [163]. A study along the river Viskan (Sweden) detected high fish (pike) to sediment ratios for BDE47, BDE99, BDE100 and HBCD, indicating the bioavailability of these compounds. The low concentrations of octa- and nona-BDE congeners suggested limited bioavailability for these congeners [164].

In a study on Baltic and North Atlantic Sea food webs, several BDEs were analysed in zooplankton (copepods), planktivorous fish (sprat, small and large herring) and predatory fish (salmon) [165]. BDE47 appeared to biomagnify to the largest extent, showing higher assimilation efficiencies compared to BDE99 and BDE153, which was in agreement with previous studies of uptake in fish [166, 167]. The BMFs for all BDEs studied were positive, meaning that all congeners have the ability to biomagnify in this food web. However, the BMFs of the tetra- and penta-BDEs were higher than those of the tri-BDEs and hexa-BDEs reported in a previous study [168].

A trophic characterisation of PBDEs in a North Sea food web was carried out by Boon et al. [158]. Invertebrate sentinel species were investigated together with predatory gadoid fish species and marine mammals representing the higher trophic levels of this food web. All six major BDE congeners present in the penta-BDE formulation were detected, whereas no evidence of the octa-BDE formulation was found, as its major congener, BDE183, was not detected. Since BDE209 was the main BDE congener usually found in sediments from

the area, the main reason for its low concentrations in biota was concluded to be either due to a low uptake rate for this very large molecule (log K_{ow} 9–10), and so would be predominantly particle bound, or to a rapid excretion after biotransformation. The major biomagnification step in this study was found to occur from fish to marine mammals. Another study carried out in a North Sea estuary food web showed evidence of the bioaccumulation of α-HBCD [9]. It was argued that the higher water solubility of the α-isomer compared to the other two isomers could be the cause of the preferential uptake of α-HBCD in aquatic organisms, or that a rapid elimination from the organism of the β- and γ-isomer was occurring. TBBP-A was detected in lower concentrations than HBCD and appeared to have a lower bioaccumulation potential. Due to its more polar nature, TBBP-A may more easily be metabolized and eliminated from the aquatic organisms. This was confirmed by the low accumulation potential observed for the TBBP-A in a study involving uptake efficiency in zebrafish [169]. The bioaccumulation of HBCD in rainbow trout showed high levels after dietary uptake, with different values depending on the diastereomer determined. The highest BMF was found for α-HBCD (BMF = 9.2) followed by the γ- and β-diastereomer (BMF = 4.3) [170]. In aquatic invertebrates, marine fish, birds and marine mammals, the presence of the HBCD is mainly as its α-diastereomer, and the concentration of this isomer was found to increase with increasing trophic level [171]. Uptakes and elimination rates in zebrafish were recently determined for BDE28, BDE183 and BDE209, and the highest uptake was observed for BDE28, whereas the lowest was observed for BDE209 [172]. Bioaccumulation and trophic magnification were determined for several PBDEs in a Canadian Arctic marine food web [156]. The results showed that only BDE47 had a TMF above 1. The food web was characterized using stable nitrogen isotope analysis, involving zooplankton, invertebrate species and different fish, eider ducks and marine mammal species. Another study carried out to determine the biomagnification of PBDEs in a Canadian Arctic marine food web showed a similar pattern of trophic magnification for BDE47 and a low TMF for BDE209, with decreasing values at higher trophic levels [173]. A similar study was carried out for a freshwater food web in South China where three PBDEs were investigated [174]. There, BDE47, BDE100 and BDE153 showed a TMF significantly above 1.

The biomagnification potential of PBDEs was studied in a polar bear food chain from the Norwegian Arctic. The BDE47 BMFs for polar bear (assuming ringed seal as the prey species) were relatively low, between 1 and 7 [159, 160]. However, mean BMFs for BDE153 in polar bears (bear/ringed seal) from the Canadian Arctic and Alaska ranged between 91 and 130 [159], even though it has been reported that polar bears have a large capacity to metabolize organohalogenated compounds [175]. BDE153 is apparently one of the most stable BDEs. Relatively high BMFs for BDE47, BDE99 and BDE100 (between 20 and 60) were reported for beluga whales from Svalbard in the Arctic Ocean [160]. In the northwest Atlantic, no biomagnification was detected for several tetra-BDE congeners (BDE49, BDE66 and BDE75) in a study involving harbour seals. This suggests that this species may possess an efficient metabolism for these congeners [103].

In a Florida coastal marine food web, the highest BMFs for several BDE congeners were measured from forage fish to bottlenose dolphins and bull sharks [106]. Even though BDE209 has shown a lack of biomagnification in studies concerning marine mammals, a biomagnification of this congener in bull sharks was observed, which was explained by their habitat and feeding habits.

The correct characterization of contaminants in different food webs makes their behaviour in the environment more understandable. Trophic magnification can lead to chronic exposure and toxicological effects in organisms, such as endocrine disruption. The potential risk to human exposure considering our omnivorous diet is of special concern. BFRs have already been detected in human tissues, including adipose tissue, blood serum and milk [176–178].

4 Biotransformation

Environmental factors, such as temperature and pH, may influence the mobility and bioavailability of contaminants. The compounds already existing in the environment could favour chemical reactions leading to different compounds, presenting different toxicological risks. Biological processes may cause an increase in bioaccumulation, allowing the entrance of these compounds into the food chain of a specific ecosystem. Biodegradation processes, often mediated by microorganisms, may facilitate the elimination of contaminants from the environment, but can also lead to the formation of more toxic and bioaccumulative compounds.

There are several reactions that can take place once the chemical is deposited in soil, sediments or water which can modify the bioavailability of these chemicals. Abiotic oxidation, reductive debromination, hydrolysis, elimination and substitution reactions may change the structure, its characteristics and properties, and alter its congener profile in the ecosystem. Once inside organisms, several biotransformation processes may occur. Highly brominated BDEs have been shown to be susceptible to substitution of one or more bromines by a methoxy group, while lower brominated BDE congeners were resistant to this reaction [179]. Biotransformation processes can increase BDE elimination rates or lead to the bioformation of lower brominated congeners via debromination of higher brominated ones [180, 181]. Reductive debromination of BDEs has been confirmed in several species of fish, occurring with both highly and lower brominated congeners as precursors. The presence of hydroxylated metabolites has been detected in pike following dietary exposure to ^{14}C-BDE47, although no lower brominated BDE congeners were produced [182].

4.1 Polybrominated Diphenyl Ethers

BDEs are subject to atmospheric transportation adsorbed to dust particles, and their deposition rates are influenced by their structures. It has been estimated that 90% of

BDE47 that enters the troposphere may be removed by photolysis before being deposited, and that the loss of BDE209 from the atmosphere and its enhancement in sediments samples around the world is highly influenced by wet and dry deposition processes [183]. BDEs are highly hydrophobic compounds with high octanol/water partition coefficient values which indicate their potential bioaccumulation ability. The log K_{ow} increases with the degree of bromination which makes BDE209 the most hydrophobic BDE congener. Log K_{ow} values are in the range of 5.9–6.2 for tetra-BDEs; 6.5–7.0 for penta-BDEs; 8.4–8.9 for octa-BDEs and 10 for deca-BDE [184]. While the log K_{ow} values increase with the number of bromine substituents, the water solubility and vapour pressures decrease. Therefore, the highly brominated congeners are less likely to be found either dissolved in water or in the vapour phase. BDE209 solubility is extremely low and its ubiquity in soil and sediments illustrates the high binding affinity to particles. However, their adsorption to particles in air and particulate matter in water allow these chemicals to undergo long-range atmospheric transport. The vapour pressures range from 0.160 Pa (BDE1) to 5.7×10^{-7} Pa (BDE190) at room temperature, and it has been demonstrated that congeners with bromine substitution in the *ortho*-positions to the ether bond have higher vapour pressures [185]. The higher vapour pressures of the lower brominated BDE congeners facilitate aerial transport. The halogenation pattern also influences the boiling points that range from 310 to 430°C [186] and melting points from 20 to 300°C [187].

The key reaction during the biodegradation of halogenated organic compounds is the halogen removal step, which is known to occur under several dehalogenation enzymatic mechanisms, either aerobically or anaerobically [4]. BDEs may undergo anaerobic reductive debromination by isolated bacteria and mixed cultures, in sediments and in sewage sludge [188–191]. Uptake and biotransformation of highly brominated BDE congeners have been demonstrated in fish, resulting in the formation of lower brominated BDE congeners that have the potential to be both more persistent and bioaccumulative than the parent compounds. Rainbow trout exposed to the commercial deca-BDE mixture via diet showed a range of hexa- to nona-BDEs in their congener profile, with increasing levels influenced by the length of exposure [192]. Several species of fish exposed to octa- and deca-BDE mixtures supplied via water and food showed the presence of lower brominated congeners after exposure [193]. In the same study, a comparative in vitro analysis of degradation of BDE209 by liver microsomes from rainbow trout and carp revealed a more efficient debromination in carp than in trout, which shows that absorption efficiency and metabolic capacity are dependent on the fish species.

There are several difficulties when assessing the possible debromination pathways of the different BDE congeners. The bioaccumulation of a specific congener may be the result of the biotransformation from higher brominated congeners and its resistance to further degradation. Preferential *meta* debromination processes and specific accumulation of certain BDE congeners in fish have also been observed (Fig. 6).

The substantial accumulation of BDE47 and, to a lesser extent, of BDE99 in aquatic biota is an evidence of their stability due to the lack of *meta* bromine atoms [194–196]. A comparison of BDE congener profiles between fish from the Antarctic

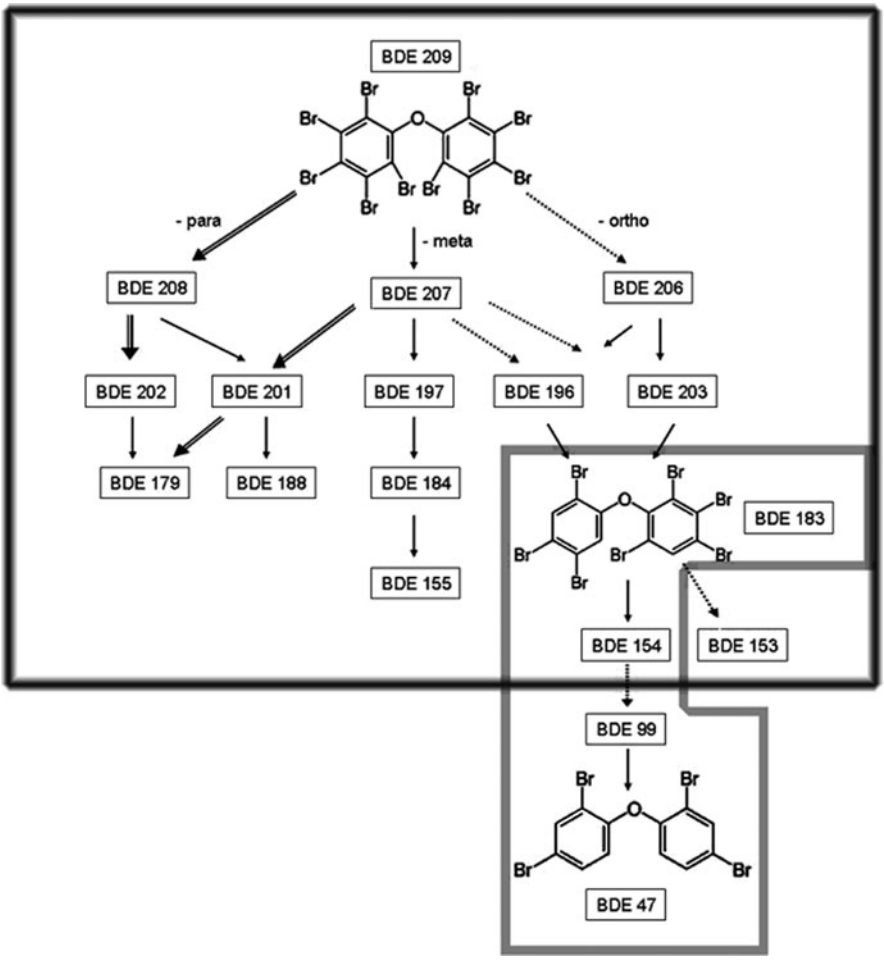


Fig. 6 Main congeners detected in fish after metabolic debromination of BDE209, BDE183 and BDE99. The different *arrows* represent the tentative debromination at the *ortho*-, *meta*- and *para*-positions [190–192]

and the Mediterranean Sea showed a difference in the ratio BDE47:BDE99 which was attributed to the lower ability of the icefish to metabolize the penta-BDE by debromination [197]. The accumulation of BDE99 was concluded to be at least partly dependent upon the differences in metabolic capacity between species [198]. However, the generally lower accumulation of BDE99 compared to BDE47 can be related either to a preferential excretion of BDE99 [196] or to a rapid absorption and conversion into hydroxy- and debrominated hydroxy metabolites [199]. Higher levels of BDE100 than BDE153 and BDE154 detected in tuna from the Mediterranean Sea may be attributed to hexa-BDE congener debromination processes [197]. BDE congeners with substituents in the *ortho*-position appear to be more recalcitrant in fish.

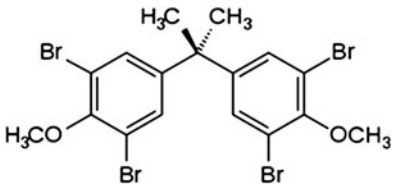


Fig. 7 Structure of TBBP-A *di-o*-methyl ether

The metabolic debromination of BDE209 was investigated in a study involving the European starling. This terrestrial bird species showed the ability to debrominate BDE209 to octa- and nona-BDE congeners, and to lesser extent hexa-BDEs [200]. The low levels of BDE209 in aquatic food webs compared with terrestrial animals may be attributable to a lower uptake, but the potential debromination of PBDEs in fish after dietary exposure, as observed in several studies, should also be considered when investigating their BAF.

4.2 Tetrabromobisphenol A

TBBP-A can undergo substitution reactions in the environment. Methylation of TBBP-A by microorganisms may cause the formation of a dimethylated derivative of TBBP-A in sediments (MeTA) [201]. MeTA has log K_{ow} of 6.4 [184] making it more lipophilic than the parent compound which has a log K_{ow} of 4.5 [202]. TBBP-A can also be microbially metabolized in a process involving reductive debromination under anaerobic conditions, resulting in bisphenol-A [203].

The possibility of *o*-methylating TBBP-A has been also tested under aerobic conditions, giving a highly lipophilic derivative with higher bioaccumulation potential (TBBP-A *di-O*-methyl ether [14]) (Fig. 7).

TBBP-A has been subjected to photolytical decomposition when exposed to UV light, resulting in different breakdown products such as di- and tri-bromobisphenol A and several bromophenols [11]. pH variations in the matrix change the solubility of TBBP-A in the environment, which may make its mobility in soil favourable and increase its potential for groundwater contamination [204].

4.3 Hexabromocyclododecane

The differences in structure of the individual HBCD diastereomers result in differences in polarity and, consequently, in water solubility. The variation of these properties will influence the bioavailability and the rates of biological uptake and metabolism of an organism [171]. Due to the low water solubility of the HBCD, hydrolysis could be assumed to be an insignificant degradation route. However, HBCD is susceptible of biodegradation in aerobic and anaerobic soil and aquatic sediments, resulting in the loss of two bromines from vicinal carbons with the

subsequent formation of a double bond between neighbouring carbon atoms [205, 206]. Experiments carried out for the evaluation of HBCD degradation under different conditions showed that there were differences in the degradation rates of the three diastereomers, and that the fastest degradation occurred under anaerobic conditions [207]. In sediment degradation tests, α-HBCD degraded more slowly than the other diastereomers [208].

The technical HBCD mixture has low water solubility (lower for the γ-diastereomer), and its log K_{ow} is 5.62 [209]. Juvenile rainbow trout were exposed to α-, β- and γ-HBCD for 56 days with a 112 days depuration period [210]. The analysis of muscle and liver samples did not show the presence of debrominated or hydroxylated metabolites. However, it was observed that the HBCD diastereomer pattern changed in biological samples. Muscle tissues of fish exposed solely to β-HBCD showed a shift to α- and γ-HBCD. Fish exposed to γ-HBCD showed the α-congener as the major diastereomer, and fish exposed to α-HBCD did not show any diastereomeric shift. A study of metabolization rates in microsomal liver preparations of common dab showed diastereomer and enantiomer-selective metabolism, with α-HBCD the least bio-transformed of the three main diastereomers [210]. Several hydroxylated metabolites of HBCD and pentabromocyclododecene (PBCDe) were identified in tern eggs and in the blubber of harbour seals [211]. In the same study, four different groups of hydroxylated metabolites were detected in rats after exposure to HBCD, and debromination to penta- and tetrabromocyclododecene was suggested as a metabolic pathway.

The blubber of female harbour porpoises and common dolphins stranded on western European coasts was investigated to determine the presence of HBCD. All samples analysed contained exclusively the α-diastereomer of HBCD. It was also seen that microsomal preparations of liver samples of harbour porpoises studied in vitro were capable of metabolizing β- and γ-HBCD when incubated in the presence of NADPH as an electron donor [26]. Three bromine-containing metabolites derived from β-HBCD could be observed, while two were found for γ-HBCD, including hydroxyl-metabolites. Therefore, biotransformation by the cytochrome P-450 system is also expected to occur in other marine mammals, thus explaining the higher rate of occurrence of α-HBCD in blubber samples.

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