

2.1.4 Releases to the environment during product use

C-PentaBDE is used solely as an additive in physical admixture with the host polymer, and can thus migrate within the solid matrix and volatilize from the surface of articles during their life cycle (EU 2000). Approximately 3.9 % of the PentaBDE present in articles was estimated to be released each year through volatilization during their assumed service life of 10 years in the EU risk assessment, but each congener will have its own characteristic migration and volatility coefficients. Based on the quantities of shown in Table 2.2, and the 3.9% loss rate, it can be estimated that 585-1053 tonnes of PentaBDE enters the environment in this way each year.

Wilford *et al.* (2003) conducted controlled chamber experiments in which they passed air through samples of C-PentaBDE -treated foam products containing 12% PBDE w/w. They found that PBDEs volatilized from polyurethane foam at measurable levels. Average total PBDE levels of 500 ng/m³/g foam were released from the chamber. For BDE-47, BDE-99 and BDE-100 (4,5 and 5 bromines, respectively), the loss rates were 360, 85 and 30 ng/m³/g foam, respectively. The average temperature range during sampling was 30-34°C.

Given the use of C-PentaBDE in domestic items such as furniture, carpeting and appliances, exposure to indoor air house dust containing PentaBDE has been examined in a number of studies (Shoeib *et al.* 2004, Wilford *et al.* 2005). US researchers (Stapleton *et al.* 2005) report results for a study conducted in 2004 in the Washington, DC, metropolitan area and one home in Charleston, South Carolina. The concentrations of PBDEs in house dust from sixteen homes ranged from 780 ng/g dry mass to 30,100 ng/g dry mass. The dominant congeners were those associated with C-PentaBDE and DecaBDE. It was estimated that young children (1-4 years) would ingest 120-6000 ng/day of PBDEs. For five of the homes, clothes dryer lint was also analyzed, showing PBDE concentrations of 480-3080 ng/g dry mass. The exposures are higher than those observed in Europe, a fact that the researchers attribute to the fact that most markets for C-PentaBDE has been in the United States.

The information in the preceding paragraph highlights the fact that while PentaBDE can volatilize from the products in which it is incorporated, as well as during their whole life-cycle, and during recycling or after disposal, a major route for dissemination of this chemical into the environment will be in the form of particles on which it is absorbed or adsorbed. When emitted from products, the flame retardants are likely to adsorb to particles, and these may adhere to surfaces within appliances or on other surfaces in the indoor environment, or they may spread to the outdoor environment during airing of rooms. Industrial environments where equipment is dismantled may suffer much higher exposures (Danish EPA 1999). There are also releases from products due to weathering, wearing, leaching and volatilization at the end of their service life during disposal or recycling operations (dismantling, grinding or other handling of waste, transport and storage, for example). The annual releases in the EU region from the product life-cycle of polyurethane products were estimated to be distributed among the different compartments as follows: 75% to soil, 0.1% to air and 24.9% to surface water (EU 2000).

The inclusion of C-PentaBDE in materials used for car undercoating, roofing material, coil coating, fabric coating, cables, wires and profiles, and shoe soles can result in slow release to the environment. Emission factors for such releases in the EU risk assessment were judged to be 2-10% during the lifetime of the product, with the higher factors applying to uses with high wear rates such as car undercoating and shoe soles. A further 2% was assumed to be emitted during disposal operations. Taking these into account, the losses in the EU region were estimated to be 15.86 tonnes/year to soil, 5.26 tonnes/year to surface water, and 0.021 tonnes/year to air. No actual measurements were found in the literature with which one might compare these estimates.

Hale *et al.* (2002) demonstrated that flame-retardant treated polyurethane foam exposed to direct sunlight and typical Virginia summer conditions with temperatures up to 30-35°C and humidity of 80% or greater, became brittle and showed evidence of disintegration within four weeks. The authors postulate that the resulting small, low density foam particles would be readily transportable by

stormwater runoff or air currents. Such degradation processes may provide an exposure route to organisms via inhalation or ingestion of the foam particles and their associated PentaBDE.

2.1.5 Emissions from waste containing C-PentaBDE

Waste can be generated from production of C-PentaBDE, from processes for manufacture of C-PentaBDE -containing materials, and from end-of-service-life management of products containing PentaBDE.

In production, the C-PentaBDE producers have stated that the major source of release was from filter waste and reject material, but quantities are small to negligible. In general, the waste was disposed of to landfill (EU 2000), although it is noted that waste containing more than 0.25% PentaBDE is classified as 'hazardous waste'.

After curing and cooling, blocks of polyurethane foam generally have to be cut to the required size, although for some applications the foam is produced in a mould of the desired shape so cutting is not required. Some flame retardant is lost in the scrap foam that results from the cutting process. Such foam scrap is often recycled into carpet underlay (rebond), particularly in the United States. Interestingly, the EU exports about 40,000 tonnes/year of scrap foam to the US for such use (EU 2000). In other uses, scrap foam is ground and used as filler in a number of applications such as cars seats or used for addition to virgin polyol in slab foam production. It is also possible that some foam scrap will be disposed of to landfill, or even incinerated.

During the production of printed circuit boards a substantial part of the laminate is cut off and becomes solid waste. In most countries, however, C-PentaBDE is no longer used in this application. There is limited information about waste generated in other applications of C-PentaBDE, such as its use in electrical and electronic appliances. While some such appliances are recycled on account of their metal content, many are burned in municipal waste incinerators and this often the fate of non-metallic portions of this waste stream. In the EU, from December 2006, plastics containing brominated flame retardants must be separated from such waste prior to recovery and recycling.

Used vehicles, often containing solid or foam components with C-PentaBDE are stored outdoors and then dismantled in shredder plants. In some countries, restrictions require that components containing substances like PentaBDE be treated as hazardous waste. Wastes generated from production of building materials, textiles and furniture are disposed of in landfills, or incinerated. This is easy enough for small, easily dismantled components, but most material containing flame retardants is harder to segregate and so these materials end up in the waste from shredder plants and are usually landfilled.

Movement of polymer foam particles containing PentaBDE within the landfill could provide a mechanism for transport of the brominated material to leachate or groundwater. It is not currently possible to assess the significance of such processes. However, given the physico-chemical properties of the substance, it is considered unlikely that significant amounts of PentaBDE will leach from landfills, since it has low water solubility, high octanol-water partition coefficient, and adsorbs strongly to soils (EU 2000). Norwegian screening studies have found levels of PentaBDE of concern in landfill leachates (Fjeld *et al.* 2003, Fjeld *et al.* 2004, Fjeld *et al.* 2005). The quantity of PentaBDE disposed of annually in the EU, and going to landfill or incineration, is estimated to be approximately 1,036 tonnes (EU 2000).

In a Dutch project, the emissions of PentaBDE in the EMEP region were estimated and distribution between sources was as follows: 0.33 tonnes/year from industrial combustion and processes, 9.45 tonnes/year from solvent and product use and 0.05 tonnes/year from waste incineration (van der Gon *et al.* 2005).

At the operating temperatures of municipal waste incinerators almost all flame retardants will be destroyed, but based on experience with other organic compounds, trace amounts could be passing the combustion chamber (Danish EPA 1999). Studies of recipients to municipal solid waste incinerators have detected above-background levels of PentaBDE in both gaseous and particulate fractions in the air in the vicinity of the facility (Agrell *et al.* 2004, Law 2005, ter Schure *et al.* 2004b). Potentially toxic products like brominated dibenzo-*p*-dioxins and dibenzofurans may be produced during incineration of articles containing C-PentaBDE (Danish EPA 1999, Ebert and Bahadir 2003, Weber and Kuch 2003, Birnbaum and Staskel 2004) and possibly released to the environment.

Analyses of dismantled FR2 circuit boards in electrical scrap show that about 35% of the PBDE used was PentaBDE, and for estimation purposes it was assumed that 25% of FR2 laminates in older appliances had been treated with the C-PentaBDE (Swiss agency 2002). Prevedouros *et al.* (2004) estimated production, consumption, and atmospheric emissions of PentaBDE in Europe between 1970 and 2000 based on literature data. According to that study, the flow of PentaBDE in discarded electrical and electronic appliances in Europe is in the range 17-60 metric tons per year for the period 2000-2005. However, a Swiss experimental study of such flow in a modern recycling plant showed values higher than expected on the basis of the literature study. This could mean that the literature has underestimated the PBDE content of such appliances, and the study acknowledges that companies seldom provide all the information necessary to make accurate estimates (Swiss agency 2002). This same study reported a flow analysis for the life cycles of Penta-, Octa- and Deca-BDE as well as tetrabromobisphenol A (TBBPA). Waste electrical and electronic equipment was the biggest contributor, ahead of automotive shredder residues and construction waste. The plastics in vehicles produced in 1980 contained 0.089 g/kg of PentaBDE (excluding that contained in electrical and electronic components), whereas plastic in those built in 1998 had 0.044 g/kg. At the beginning of this period, almost all unsaturated polyurethane resins were treated with brominated flame retardants, primarily DecaBDE and TBBPA, but also PentaBDE. Even larger quantities, up to 50 g PentaBDE/kg of resin, were used in rail vehicles produced in 1980.

The average concentration of PentaBDE in appliances is estimated to be 34 mg/kg, with the highest concentration – 125 mg/kg – in the plastic fraction (Morf *et al.* 2005). In plants with off-gas filtering, a large proportion of the PentaBDE will be found in the collected fraction (Morf *et al.* 2005). On the other hand, in a facility without an efficient air pollution control device such as that in the modern facility studied, a significant flow of dust-borne PentaBDE may be released to the environment. A case in point was presented by Wang *et al.* (2005), who detected levels of PentaBDE in soil and sediment collected in the vicinity of an open electronic waste disposal and recycling facility located in Guiyu, Guandong, China.

The Swiss study showed that 5% of polyurethane foams produced in 1990 were used in the building industry, and contained up to 220 g/kg of C-PentaBDE. About 10-20% of the thermoplastic sheeting used in construction was treated with brominated flame retardants at levels of 1.3-5% by weight (Danish EPA) but no information about C-PentaBDE content is available. Some polyvinyl chloride sheeting would also have been treated with C-PentaBDE, typically at 49 g/kg. PentaBDE can be assumed to be emitted during dismantling activities but no information is available about the extent of such emissions.

2.2 Environmental fate

2.2.1 Persistence

Estimated half-life values of PDBE in different environmental compartments are scarce in the literature. In table 2.3 half-life estimates found in literature are summarized.

Table 2.3 Half-lives of PentaBDE (BDE-99) in different environmental compartments, estimated with the use of Syracuse Corporation's EPIWIN program.

Environmental compartment	Half-life estimate (d)	References
Soil	150	Palm 2001, Palm <i>et al.</i> 2002
Aerobic sediment	600	Palm 2001, Palm <i>et al.</i> 2002
Water	150	Palm 2001, Palm <i>et al.</i> 2002
Air	19 11	Palm <i>et al.</i> 2002 Vulykh <i>et al.</i> 2004

It is noted that caution should be used in relying on half-life estimates derived from this program, now called EPI Suite (<http://www.epa.gov/opptintr/exposure/docs/episuite.htm>). The EPI Suite's intended use is chemical screening only and may not be appropriate for consideration of substances for global control. Because of interest in this matter, it is likely that half-life data from new studies will be published but the picture provided by existing data seems unlikely to change substantially. The nature of degradation products of the PBDEs is also likely to be elucidated in future, leading to consideration of their toxicity.

With respect to biodegradation, Tetra-, Penta- and Hexa-BDE are predicted to be "recalcitrant" by the BIOWIN program. Using the EPIWIN program, estimated half-lives for PentaBDE are 600 days in aerobic sediment, 150 days in soil, and 150 days in water (Palm 2001). This degree of persistence is supported by the fact that no degradation (as CO₂ evolution) was seen in 29 days in an OECD 301B ready biodegradation test using PentaBDE (Schaefer and Haberlein 1997).

Schaefer and Flaggs (2001) carried out a 32-week anaerobic degradation study using a mixture of ¹⁴C-labelled and unlabelled BDE-47 (a TetraBDE) incorporated into sediments. The study showed that <1% of the total radioactivity was recovered as ¹⁴CO₂ and ¹⁴CH₄, indicating that essentially no mineralization had occurred. Overall, the study found that levels of degradation were not statistically significant; however, the HPLC analytical method with radiometric detection indicated that some products had been formed in the 32-week samples. Between one and three such peaks were identified in 26 of 42 samples analyzed. Work is underway to identify these products. It is likely that BDE-47 has the potential to degrade very slowly under anaerobic conditions.

Several studies using sediment cores show that PentaBDE congeners deposited in European marine sediments at the beginning of 1970s are still present in significant amounts, indicating high persistency in sediments (Covaci *et al.* 2002a, Nylund *et al.* 1992, Zegers *et al.* 2000, Zegers *et al.* 2003). The industrial production and use in Europe started in the beginning of the 1970s, with a reduction in more recent years. This is reflected in the sediment core profiles, with no occurrence before this date, and an increase in levels after, with a levelling off in more recent years. In the most recent studies (Zegers *et al.* 2003) sediment cores from Norway, the Netherlands and Germany were studied. Concentrations of PBDEs, normalized to total organic carbon content, were in the range 10-20 µg/g total carbon.

2.2.2 Bioaccumulation

2.2.2.1 Studies on bioaccumulation and biomagnification in local food webs

Several studies have focused on PentaBDE's potential for bioaccumulation and biomagnification. The studies show an increase of concentrations in biota with increasing trophic level in pelagic and Arctic food webs. The calculated bioconcentration factors (BCFs), bioaccumulation factors (BAFs) and biomagnification factors (BMFs) indicate PentaBDE's potential for bioaccumulation and biomagnification. In Table 2.4 the calculated values in the literature are summarized. The octanol/water

partition coefficient (log K_{ow}) for PentaBDE in those studies is 6.5 – 7.4. The more recent studies are described in the following text.

Table 2.4 Calculated bioaccumulation factors (BAFs) and biomagnification factors (BMFs) for one PentaBDE (BDE-99) in the literature from environmental studies in pelagic and Arctic food webs. The data are calculated using the mean lipid weight concentrations, except for the study performed by Sørmo et al. 2006, in which the values in brackets are BMFs calculated from mean whole body concentrations.

Variable	Organism	Area	Value	Reference
BAF	<i>Dreissena polymorpha</i>	Lake Mälaren, Sweden	1.8	Lithner et al. 2003
BMF	Guillemot egg/herring	Baltic sea	17	Sellström 1996
	Grey seal/herring	Baltic sea	4.3	Sellström 1996
	Salmon/sprat	Baltic sea	10	Burreau et al. 1999
	Salmon/sprat	Baltic sea	5.9	Burreau et al. 2000
	Atlantic Salmon/Small Herring	The Northern Atlantic Sea	3.8	Burreau et al. 2000
	Net plankton/Benthic organisms	Lake Ontario, Canada	7.1	Alaee et al. 2002
	Benthic organisms/Forage fish	Lake Ontario, Canada	0.8	Alaee et al. 2002
	<i>T. libellula</i> /Copepods	Svalbard, Arctic Norway	0.65 (1.3)	Sørmo et al. 2006
	<i>G.wilkitzkii</i> /Copepods	Svalbard, Arctic Norway	47.6 (19.0)	Sørmo et al. 2006
	Polar cod/Copepods	Svalbard, Arctic Norway	2.1 (1.6)	Sørmo et al. 2006
	Polar cod/ <i>T. inermis</i>	Svalbard, Arctic Norway	1.9 (1.2)	Sørmo et al. 2006
	Polar cod/ <i>T. libellula</i>	Svalbard, Arctic Norway	3.4 (1.3)	Sørmo et al. 2006
	Polar cod/ <i>G.wilkitzkii</i>	Svalbard, Arctic Norway	0.04 (0.1)	Sørmo et al. 2006
	Ringed seal/ <i>T. inermis</i>	Svalbard, Arctic Norway	26.8 (54.5)	Sørmo et al. 2006
	Ringed seal/ <i>T. libellula</i>	Svalbard, Arctic Norway	43.1 (60.0)	Sørmo et al. 2006
	Ringed seal/ <i>G.wilkitzkii</i>	Svalbard, Arctic Norway	0.6 (3.9)	Sørmo et al. 2006
	Ringed seal/Polar cod	Svalbard, Arctic Norway	13.7 (56.6)	Sørmo et al. 2006
	Polar bear/Ringed seal	Svalbard, Arctic Norway	0.3 (0.29)	Sørmo et al. 2006
	Polar bear/Ringed seal	Arctic Canada	3.4	Muir et al. 2006
Polar bear/Ringed seal	Arctic Canada	11	Muir et al. 2006	
Polar bear/Ringed seal	Arctic Canada	8.0	Muir et al. 2006	
Polar bear/Ringed seal	Greenland	1.0	Muir et al. 2006	
Polar bear/Ringed seal	Svalbard, Arctic Norway	5.9	Muir et al. 2006	

PBDE analyses of zebra mussels (*Dreissena polymorpha*) were included in a larger study undertaken in and around the city of Stockholm, Sweden (Lithner et al., 2003). Mussels were collected from a background site and transplanted in baskets to other downstream sites in Lake Mälaren, Saltsjön and in several small lakes. Freshwater flows from Lake Mälaren, through the middle of Stockholm, then out into the brackish Baltic Sea via Saltsjön. Five PBDE congeners (BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154) were determined. The congener pattern was dominated by BDE-47 and BDE-99 (four and five bromines, respectively) and was similar to the C-PentaBDE. Bioaccumulation factors (BAFs) for the various compounds studied were estimated using data from suspended particulate matter (SPM) collected in sediment traps in 1998-99 at the same sites in Riddarfjärden and Saltsjön (Broman et al., 2001). The concentrations on SPM were assumed to reflect water concentrations. BAFs were calculated using lipid weight concentrations in mussels and organic carbon based concentrations in the SPM.

When compared to other compounds (PCBs, DDTs, HCB), the BDEs had the highest BAFs, ranging from 1 to 2. The BAF (= level in mussel/level in SPM) for PentaBDE was 1.8.

Concentrations of BDE-47 and BDE-99 in Lake Ontario pelagic food web show increasing concentrations with increasing trophic position (Alaee *et al.* 2002). In this study, concentrations of PBDEs in archived plankton, *Mysis*, *Diporeia*, alewife, smelt, sculpin and lake trout samples collected in 1993 were determined. The trophodynamics of PBDEs in the Lake Ontario pelagic food web were also investigated. Lake Ontario pelagic food web consists of three trophic levels. The lake trout (*Salvelinus namaycush*) is a top predator fish species in Lake Ontario, feeding on forage fish including alewife (*Alosa pseudoharengus*), rainbow smelt (*Osmerus mordax*) and slimy sculpin (*Cottus cognatus*); in turn these fish feed on *Mysis* and *Diporeia*, which feed on phytoplankton, and zooplankton sampled as net plankton. Concentrations were increasing at each step up the food chain. The exception to this trend was the biomagnification of BDE-99 from benthic organisms to forage fish, which had a biomagnification factor of 0.8. This is an indication of the breakdown of BDE-99. In fact, the PBDE profile in the plankton; *Mysis* and *Diporeia* resembled the C-PentaBDE formulation, which indicates that BDE-99 bioaccumulates in the invertebrates and starts to be metabolized by forage fish.

Further studies of metabolism involving reductive debromination are discussed in Section 2.3.5.

Whittle *et al.* (2004) conducted surveys of PBDE levels in fish communities of Lake Ontario and Lake Michigan in 2001 and 2002 and evaluated biomagnification in the local pelagic food web (net plankton/*Mysis/Diporeia* → forage fish (smelt/sculpin/alewife) → lake trout). Their analysis, which included a total of forty one PBDE congeners, showed that BDE 47, 99 and 100 were prominent at each trophic level. The biomagnification factors (BMFs) representing total PBDEs for forage fish to lake trout ranged from 3.71 to 21.01 in Lake Michigan and from 3.48 to 15.35 in Lake Ontario. The BMF for plankton to alewife as 22.34 in Lake Ontario.

A recent study of an Arctic food chain shows the same result (Sørmo *et al.* 2006) as Alaee's study. Concentrations of PBDEs were investigated in an Arctic marine food chain, consisting of four invertebrate species, polar cod (*Boreogadus saida*), ringed seals (*Pusa hispida*) and polar bears (*Ursus maritimus*). The most abundant PBDEs, BDE-47 and BDE-99, were found in detectable concentrations even in zooplankton, the lowest trophic level examined in this study. Most of the investigated PBDEs biomagnified as a function of trophic level in the food chain. A noticeable exception occurred at the highest trophic level, the polar bear, in which only BDE-153 was found to increase from its main prey, the ringed seal, indicating that polar bears appear to be able to metabolize and biodegrade most PBDEs. The authors suggested that this discrepancy in the fate of PBDEs among the different species may be related to greater induction of oxidative detoxification activities in the polar bear. Absorption and debromination rates may be more important for bioaccumulation rates of PBDEs in zooplankton, polar cod and ringed seals. BDE-99 showed no biomagnification from pelagic zooplankton to polar cod, probably as a consequence of intestinal or tissue metabolism of BDE-99 in the fish. Also among pelagic zooplankton, there was no increase in concentrations from calanoid copepods to *T. libellula*. Lipid-weight based concentrations (LWCs) and whole-body based concentrations (WBCs) of PBDEs were used to assess biomagnification factors (BMFs). Whole body concentrations gave the most realistic BMFs, as BMFs derived from LWCs seem to be confounded by the large variability in lipid content of tissues from the investigated species. This study demonstrates that PentaBDEs have reached measurable concentrations even in the lower trophic levels (invertebrates and fish) in the Arctic and biomagnifies in the polar bear food chain.

Polybrominated diphenyl ethers (PBDEs) were determined in adipose tissue of adult and sub-adult female polar bears sampled between 1999 and 2002 from sub-populations in Arctic Canada, eastern Greenland, and Svalbard, and in males and females collected from 1994 to 2002 in northwestern Alaska (Muir *et al.* 2006). Only four congeners (BDE-47, BDE-99, BDE-100, and BDE-153) were consistently identified in all samples. BDE-47 was the major PBDE congener representing from 65% to 82% of the

Σ PBDEs. Age was not a significant covariate for individual PBDEs or Σ PBDE. Higher proportions of BDE-99, BDE-100, and BDE-153 were generally found in samples from the Canadian Arctic than from Svalbard or the Bering- Chukchi Sea area of Alaska. All four major PBDE congeners were found to biomagnify from ringed seals to polar bears. The polar bear-seal BMFs were relatively consistent despite the large distances among sites. The exceptions were the BMFs for BDE-99, BDE-100, and BDE-153 in East Greenland which had lower BMFs than those at all other sites. This may imply differences in the transformation of PBDEs in the marine food web leading to polar bears or to food web differences. Species differences in bioaccumulation and biotransformation of PBDEs have been noted for fish and this could lead to differences in congener patterns in fish-eating mammals and their predators.

Studies of the biomagnification of Tri- to DecaBDEs were carried out in three different food chains, two in the Baltic Sea and one in the Atlantic Ocean (Law 2005). All of Tri- to HeptaBDE congeners biomagnified, but the maximum biomagnification was for the PentaBDEs.

Matscheko *et al.* (2002) investigated the accumulation of seven PBDEs, eight PCBs and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCCD/Fs) by earth worms collected from Swedish soils in spring and autumn 2000. The selected sampling sites were agricultural lands receiving applications of sewage sludge, and a field flooded by a river known to contain the target substances in its sediment. Reference sites were rural and urban soils with no known sources of the target substances other than background. Earthworms (primarily *Lumbricus terrestris*, *Lumbricus spp.*, *Aporrectodea caliginosa*, *A. rosea* and *Allolobophora chlorrotic*) were collected from all field sites, starved for 24 h to clear gut contents, and then analyzed for the presence of the target substances. Biota-soil accumulation factors (BSAFs) were calculated as the ratio of concentration of target substance in worm lipids to that in soil organic matter. BSAFs for BDE-47, BDE-66, BDE-99 and BDE-100 ranged from 1 to 10. They were comparable to those determined for the PCBs but higher than those for PCCD/Fs. BSAFs of greater than 10 were determined at one agricultural site, where factors of 11, 18 and 34 were calculated for BDE 99, 47 and 100 respectively. Data collected for BDE-153, BDE-154 and BDE-183 were not used, as levels in the earthworm blanks were deemed to be unacceptable high.

2.2.2.2 Monitoring results indicating bioaccumulation

A large range of studies show concentrations of concern in top predators. High levels in top predators are usually an indication on the potential of a compound to bioaccumulate in the top predator food chain.

Several studies (Jaspers *et al.* 2004, Herzke *et al.* 2005, Lindberg *et al.* 2004, D'Silva *et al.* 2004, Law *et al.* 2005, Sinkkonen *et al.* 2004, Sellström *et al.* 2003) indicate that PentaBDE is widespread in top predatory birds in Europe, such as peregrine falcon (*Falco peregrine*), merlin (*Falco columbarius*), goshawk (*Accipiter gentiles*), golden eagle (*Aquila chrysaetos*), and buzzard (*Buteo buteo*). High levels are detected in top predatory eggs of white-tailed sea eagle, peregrine falcon, osprey, and golden eagle (Herzke *et al.* 2005, Lindberg *et al.* 2004). High levels have also been detected in European harbour porpoises (*Phocoena phocoena*) (Thron *et al.* 2004 and Covaci *et al.* 2002).

In the Arctic, C-PentaBDE is detected in high levels in top predatory birds and mammals (Verrault *et al.* 2005, Verrault *et al.* 2004, Norström *et al.* 2002, Herzke *et al.* 2003, Vorkamp *et al.* 2004a and b, Wolkers *et al.* 2004, Thron *et al.* 2004, Thomas *et al.* 2005, Ikonomou *et al.* 2002), such as glaucous gulls (*Larus hyperboreus*), polar bears (*Ursus maritimus*), ringed seals (*Phoca hispida*) and beluga whales (*Delphinapterus leucas*).

2.2.3 Long-range environmental transport

2.2.3.1 Environmental studies on transport and distribution

There are several factors indicating long-range transboundary transport of PentaBDE in the environment. It has a high persistency in air, with a half-life of 11-19 days (Palm *et al.* 2002, Vulykh *et al.* 2004)). Monitoring studies have detected a widespread occurrence in the European atmosphere (ter Shure *et al.* 2004, Lee *et al.* 2004, Jaward *et al.* 2004, Harrad and Hunter 2004, Harrad *et al.* 2004) and Arctic (AMAP 2002 and AMAP 2005, Peltola *et al.* 2001).

Sampling of air in the Great Lakes region of North America was undertaken in 1997-1999 and reported by Strandberg *et al.* (2001). PBDEs, mainly BDE-47 and BDE-99, were detected in all samples from four locations, and there was little variation over the time period. PBDE concentrations ranged from 5 pg/m³ near Lake Superior to about 52 pg/m³ in Chicago. At the temperatures of collection, 20±3°C, approximately 80% of the tetrabromo congeners were in the gas phase, but 70% of the hexabromo congeners were associated with particles.

Results for the far-northern Pacific covered particulate matter collected in July-September 2003 from the Bohai Sea to the high Arctic, 37° – 80° N (Xin-Ming Wang *et al.* 2005). The dominant congeners were BDE-47, BDE-99, BDE-100 (all present in the commercial pentamix) and BDE-209, with concentrations falling from mid- to high-latitudes, probably resulting (according to the authors) from dilution, deposition and decomposition of the PBDEs during long-range transport. Total PBDE concentrations were in the range 2.25 – 198.9 pg/m³ with a mean of 58.3 pg/m³. The source of the PBDEs is believed to be the North American continent from which they distill to an Arctic 'cold trap'.

The emphasis on any assessment of the dispersal of PentaBDE into the environment has to be on long-range transport, specially to Arctic regions, but there also is a growing body of data on dispersal of the substance and related congeners within regions. Air sampling in Southern Ontario in the Spring of 2000, before bud burst, showed PBDE concentrations of 88-1250 pg/m³, with the lighter congeners (DBE-17, -28 and -47) dominating (Gouin *et al.* 2002). The concentrations fell to 10-20 pg/m³, a change that the researchers attributed to, firstly, enhanced levels caused by expiration from the winter snowpack, followed by possible sorption by emergent foliage. Other studies in Ontario (Harner *et al.* 2002) found air levels of total PBDE in the range 3.4-46 pg/m³. In later work, organic films on indoor and outdoor windows in Southern Ontario were examined for their content of PBDEs by Butt *et al.* (2004). While the PBDE content was dominated by BDE-209 from the decabromo mixture, there were significant quantities of congeners deriving from the C-PentaBDE. Back calculation gave total PBDE concentrations in outdoor air of 4.8 pg/m³ and 42.1 pg/m³ for indoor air.

Jaward *et al.* (2004a) studied a total of 71 passive air samples using semi permeable membrane devices (SPMDs) for eight BDE congeners (BDE-28, BDE-47, BDE-49, BDE-75, BDE-99, BDE-100, BDE-153 and BDE-154) during a six week period in 2002 at remote/rural/urban locations across 22 countries in Europe. BDEs were detected in approximately 50% of the samples, and the equivalent Σ BDE air concentrations estimated from the passive sampler data ranged from 0.5 to 250 pg m³. The focus of the most elevated concentrations was the UK, which has a history of PBDE production and has also been a major user of PBDE formulations due to stringent fire regulations within the country. The UK is clearly a regional source for BDEs to the European atmosphere and, in contrast, levels reaching Europe from the west (over the Atlantic Ocean) are low. Other high values were detected in urban centres in mainland Europe – samples from Athens, Bilthoven (Netherlands), Geneva, Milan and Seville, for example. Non-detectable/very low values occurred in remote/background sites, especially in Iceland, Ireland, Norway and Sweden, and values in Eastern Europe were generally low. BDE-47 and BDE-99 contributed ca. 75% to Σ BDE, similar to their proportion in the Bromkal 70-5DE C-PentaBDE.

In the US, high-volume samplers were used to examine concentrations of gaseous and particulate PBDEs at five sites (urban, semi-urban, agricultural and remote) from the Midwest to the Gulf of Mexico, every twelve days during 2002-2003 (Hoh and Hites 2005). The mean concentration of total PBDEs at the Chicago site was 100 ± 35 pg/m^3 , some 3-6 times higher than those at other sites and significantly higher than measurements made in 1997-1999 (Strandberg *et al.* 2001). The mean concentration of PentaBDE was 31 pg/m^3 at the Chicago site, some 2-4 times the values for other sites.

Fugacity model results indicate that PBDEs will largely partition to organic carbon in soil and sediment and that their persistence will be strongly influenced by degradation rates in these media (although these are not well known). Only a small proportion of PBDEs exist in air and water. If this is the case, it suggests that these compounds have limited LRAT potential (Prevedouros *et al.* 2004a, Gouin and Harner 2003). This corresponds with PentaBDE's affinity for carbon, low solubility in water (1.0 $\mu\text{g/L}$) and low vapour pressure (7.6×10^{-6} Pa). However, Gouin and Harner (2003) suggest that because of their physical-chemical properties, PBDEs may experience active surface-air exchange as a result of seasonally and diurnally fluctuating temperatures. Subsequently, this may result in the potential for LRAT of the PBDEs through a series of deposition/volatilization hops, otherwise known as the "grasshopper" effect. This assumption is supported by environmental data. Lee *et al.* (2004) detected atmospheric concentrations of BDEs at two rural/semirural sites in England, and one remote site on the west coast of Ireland in 2001 and in 2000, respectively. Σ BDE concentrations at Mace Head, Ireland, were 0.22 to 5.0 pg/m^3 with a mean of 2.6 pg/m^3 and were controlled primarily by advection. Σ BDE concentrations at Hazelrigg (NW England) were 2.8 to 37 pg/m^3 with a mean of 12 pg/m^3 , and at Chilton (SW England) were 3.4 to 33 pg/m^3 with a mean of 11 pg/m^3 . The congener profile was, on average, similar to that of the C-PentaBDE. At the two English sites in the summer, PBDE concentrations were strongly influenced by temperature, indicating that land/air exchange processes play an important role in determining atmospheric concentrations.

The concentrations of PBDEs were determined in soil samples collected along a latitudinal transect through the UK and Norway, at remote/rural woodland (both coniferous and deciduous) and grassland sites (Hassanin *et al.* 2004). Concentrations for Σ BDE ranged from 65 to $12,000$ ng/kg dry weight. BDE congeners BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154, covering the major constituents of the C-PentaBDE, dominated the average congener pattern in the soils. This was interpreted as evidence that transfer of the congeners from materials treated with the commercial product from source to air to soil occurs with broadly similar efficiency, and that there is little degradation of the congeners by processes acting either during atmospheric transport or within the soils themselves. There was evidence of latitudinal fractionation of the BDE congeners, with the relative amounts of BDE-47 and the lighter congeners increasing to the north (with increasing distance from source areas) while the proportion of BDE-99 and the heavier congeners decreased. Plots of BDE congener concentrations against percentage soil organic matter yielded different slopes for different congeners. Steeper slopes were generally observed for lighter congeners such as BDE-47, indicating that they have undergone some air-surface exchange ("hopping"), whilst those of heavier congeners such as BDE-153 were close to zero, indicating that they are retained more effectively by soil following deposition. A Japanese study detected seasonal variations in the partitioning of PBDEs between the gas and particulate phase. The fraction of particulate PBDEs was higher in samples collected in winter than those in the summer (Hayakawa *et al.* 2004). PentaBDE is expected to be transported in the environment mostly by being absorbed onto particles due to its low volatility, low solubility and high affinity for carbon compounds. There are results from environmental studies which indicate that PBDEs are transported on air borne particles, and that they are susceptible to wet deposition (ter Schure *et al.* 2004a, ter Schure and Larsson 2002). Further transport depends on the fate of the particles. Fate after depositions on land depends on the level of wind erosion, that can vary with the season. Fate after deposition into the sea depends on oceanographic processes, such as water layering and transport by currents in the surface layers.

Ter Schure *et al.* (2004a) collected air and atmospheric bulk deposition samples on the island of Gotska Sandön in the Baltic Proper during a 10 week period in autumn 2001. The sampling site was chosen because of its central position in the Baltic Sea, and because of the absence of local point sources of

pollution. Ten PBDE congeners were determined (BDE-17, BDE-28, BDE-47, BDE-85, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209). The median Σ BDE concentration (Σ BDE is the sum of the concentrations of the congeners determined in each study) was 8.6 pg/m^3 , and the BDEs were mainly associated with particles. A comparison to levels of PCB in the atmosphere indicated that, as PCB concentrations in Baltic air have been declining, the input of BDEs by atmospheric deposition to the Baltic Proper now exceeds that of the PCBs by a factor of almost 40 times.

BDEs were determined in precipitation falling in southern Sweden during a two week period in 2000 (ter Schure and Larsson, 2002). The particle-associated and "dissolved" phases were separated during sampling and $65 \pm 18\%$ of Σ BDE was found to be particle-associated. The volume weighted mean concentration of Σ BDE (nine congeners) in rain was 209 pg/l , and the total deposition rate was $2 \pm 1 \text{ ng } \Sigma\text{BDE/m}^2\text{/day}$. The congener profile in both phases of the total deposition was dominated by BDE-209, and thereafter BDE-47, BDE-99 and BDE-183, representing inputs from all three commercial PBDE formulations. The authors found that particle associated BDEs are effectively removed during small precipitation episodes, and that particle scavenging was an important mechanism for the wet deposition of BDEs.

A model assessment of potential for long-range transboundary atmospheric transport and persistence of PentaBDE have been carried out by EMEP (Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe). The values of LRTP were considered to be strongly influenced by environmental processes, such as degradation, deposition, gas/particle partitioning, and gaseous exchange with underlying surface. The main process of removal from the atmosphere for the two congeners BDE-47 and BDE-99 was found to be deposition to land and seawater, 78% to land and 15% to sea for BDE-47 and 77% to land and 21% to sea for BDE-99. Only 7% of BDE-47 and 2% of BDE-99 was degraded. The calculated half-life in air was 7 days for BDE-47 and 11 for BDE-99. The findings showed a spatial distribution of BDE-47 that covers the Arctic, Europe, the Mediterranean Sea and northern Africa. BDE-99 spreads over longer distances and spreads to the Arctic, Atlantic Ocean, Asia and Africa. Transport distances (TD) were calculated for the two congeners. The TD was 2300 km for BDE-47 and 2800 km for BDE-99 (EMEP 2004).

Wania and Dugani (2003) examined the long-range transport potential of PBDEs using a number of models – TaPL3-2.10, ELPOS-1.1.1, Chemrange-2, and Globo-POP-1.1 – and various physical and chemical properties – for example, solubility in water, vapour pressure, $\log K_{ow}$, $\log K_{oa}$, $\log K_{aw}$, and estimated half-lives in various media. They found that all models yielded comparable results, with tetrabromodiphenyl ether showing the greatest atmospheric transport potential and decabromodiphenylether the lowest. The researchers estimated a characteristic transport distance (CTD) ranging from 1113 to 2483 km for the tetrabromo, 608 to 1349 for the pentabromo, 525 to 854 for the hexabromo, and 480 to 735 for the decabromo congener. The CTD was defined as the distance a parcel of air has travelled until $1/e$ (approximately 63%) of the chemical has been removed by degradation or deposition processes (Gouin and Mackay 2002).

The EU risk assessment (EU 2000) concluded that the major part of releases end up in soil. From soil, PentaBDE can be expected to be moved mainly through leaching with water in the suspended solids fraction or through wind erosion where it occurs. A small part in the soil can be volatilized, especially in the warm season, and so may be considered a plausible alternative mechanism for transport in addition to volatilization and advective transport of vapor identified in the literature. Although PentaBDE has low water solubility, it has been detected in lakes and seas, and can be transported with water in the soluble and particle phases (Peltola *et al.* 2001). Occurrence in migratory birds and fish indicate the possibility of transport by migration of animals, but the main route seems to be through the atmosphere.

2.2.3.2. Levels in remote areas

The detected levels in the Arctic atmosphere, biota and environment are strong indicators of the PentaBDEs potential for long-range transport (Verreault *et al.* 2005, Verreault *et al.* 2004, Norström *et al.* 2002, Herzke *et al.* 2003, Vorkamp *et al.* 2004a and b, Wolkers *et al.* 2004, Thron *et al.* 2004, Thomas *et al.* 2004, Ikomomou *et al.* 2002, Christensen *et al.* 2002, de Wit *et al.* 2004, AMAP 2002 and AMAP 2005).

There are several studies showing the occurrence of PentaBDE in remote areas in Europe as well (Vives *et al.* 2004, Hassanin *et al.* 2004 and Zenegg *et al.* 2003). Levels in remote regions are considered to be an indication on long-range transport.

PentaBDE (as total BDE) has been detected in Canadian and Russian Arctic air at concentrations up to 28 pg/m³ (Alaee *et al.* 2002). Strandberg *et al.* (2001) reported concentrations of total PBDE (BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-190 and BDE-209) in air from the Great Lakes area during the period 1997-1999. Average concentrations based on four samples from each of four locations ranged from 4.4 pg/m³ near Lake Superior in 1997 to 77 pg/m³ in Chicago in 1998. The average air concentration of total PBDEs (1997, 1998 and 1999) for the sampling sites ranged from 5.5 to 52 pg/m³. Tetra- and pentabromo congeners accounted for approximately 90% of the total mass of PBDE in this study. At 20±3°C, about 80% of the tetrabromo congeners and 55-65% of the pentabromo congeners were in the vapour phase while about 70% of the hexabromo congeners were associated with the particulate phase.

A larger study was performed detecting BDEs in trout (three species) from eleven high mountain lakes in Europe (566 to 2,485m altitude) (Vives *et al.*, 2004). These lakes were selected as being far from local pollution emission sources, and it was considered that the only source of BDEs to these lakes was as a result of atmospheric transport and deposition. The major congeners identified (of 39 determined) were BDE-47 and BDE-99, followed by BDE-100, BDE-153, BDE-154 and BDE-28, and these congeners were found in all samples analysed. The highest concentrations of ΣBDE in fish muscle and liver were found in Lochnagar, Scotland, 1.2 and 11 µg/kg wet weight, respectively (177 and 366 µg/kg on a lipid basis). No correlation was observed between the occurrence of these compounds and altitude, latitude or temperature, and the authors inferred that the environmental distribution of the BDEs has not, as yet, reached a steady-state.

2.3 Exposure

2.3.1 Levels

PentaBDE has spread widely in the global environment. A large quantity of monitoring data exist with detected levels in marine and terrestrial birds, sea and terrestrial mammals, sediments, soil, seafood and fish. A global study by Ueno *et al.* (2004) of PentaBDE in skipjack tuna (*Katsuwonus pelamis*) shows a wide spread occurrence in the offshore waters of various regions in the world. Table 2.5 gives an overview over the levels found in different parts of the world.

Contamination of the environment and biota in remote regions can be a threat to vulnerable species and ecosystems. In the Arctic, together with other pollutants of concern, PentaBDE is detected in high levels in top predatory birds and mammals (Verreault *et al.* 2005, Verreault *et al.* 2004, Norström *et al.* 2002, Herzke *et al.* 2003, Vorkamp *et al.* 2004a and b, Wolkers *et al.* 2004, Thron *et al.* 2004, Thomas *et al.* 2004, Ikomomou *et al.* 2002) showing that the Arctic food webs are seriously affected. Wolkers *et al.* (2004) detected levels of PentaBDE in beluga whales (*Delphinapterus leucas*) in the Arctic, a species protected by the Convention on migratory species (the Bonn convention). ΣBDE concentrations (geometric mean; 22 congeners) were 234, 161 and 29 µg/kg in juvenile, adult male and adult female beluga.

In fact, there are detected high levels of PentaBDE in several species, with populations of concern protected by the Bonn convention. Several studies (Jaspers *et al.* 2004, Herzke *et al.* 2005, Lindberg *et al.* 2004, D'Silva *et al.* 2004, Law *et al.* 2005, Sinkkonen *et al.* 2004, Sellström *et al.* 2003, Kannan *et al.* 2005, Ramu *et al.* 2005 and Wolkers *et al.* 2004) indicate that PentaBDE is widespread in peregrine falcon (*Falco peregrine*), merlin (*Falco columbarius*), goshawk (*Accipiter gentiles*), golden eagle (*Aquila chrysaetos*), buzzard (*Buteo buteo*), beluga whales (*Delphinapterus leucas*), irrawaddy dolphins (*Orcaella brevirostris*), and Indo-Pacific humpback dolphin (*Sousa chinensis*), all protected by the Bonn convention. High levels of PBDEs are also detected in peregrine falcon eggs in Sweden (Lindberg *et al.* 2004), for which individual Σ BDE concentrations were as high as 39,000 $\mu\text{g kg}^{-1}$ lipid weight, some of the highest concentrations seen in wildlife so far.

The populations of harbour porpoises (*Phocoena phocoena*) in the North and Baltic seas are protected through the Bonn Convention. Studies have detected high levels in those populations (Thron *et al.* 2004 and Covaci *et al.* 2002). In a study by Thron *et al.* (2004) animals with poor body condition (lower mean blubber thickness) had much higher concentrations than other individuals. Only females showed decreasing concentrations with age, indicating elimination via transfer from mother to offspring.

The harbour porpoise is, together with peregrine falcon and merlin, also on the list for strictly protected (endangered) species in the convention on the conservation of European wildlife and natural habitats (the Bern Convention). The white-tale sea eagle is on the list for endangered species in the Bern Convention. Levels of concern are detected in both individuals and eggs (Herzke *et al.* 2005). Beluga whales and irrawaddy dolphins are on list for protected (vulnerable) species. High levels are found in white-beaked dolphin (*Lagenorhynchus albirostris*), another endangered species. The parties of this convention undertake to take appropriate measures to ensure the conservation of endangered and vulnerable species and their habitats.

Table 2.5 Levels of PentaBDE (BDE-99) in different parts of the world (LW=Lipid weight, DW=Dry weight).

Country/Region	Organism/compartiment	Levels of PentaBDE	References	Comments
Europe	Atmosphere Gas phase	10-120 pg/m^3	Jaward <i>et al.</i> 2004	22 countries
Japan	Atmosphere Particulate Gas phase	0.05-0.9 pg/m^3 0.05-19' pg/m^3	Hayakawa <i>et al.</i> 2004	Measured in the summer
Sweden	Sediments	<0.7-51.4 ng/g DW	Palm <i>et al.</i> 2002	Rivers at point source
United Kingdom	Soil	78 – 3200 pg/g DW	Hassanin <i>et al.</i> 2004	
Western Europe	Sediments	<0.2-6.9 ng/g DW	Palm <i>et al.</i> 2002	Estuaries
Japan, Osaka	Sediments	9-28 ng/g DW	Palm <i>et al.</i> 2002	
North Pacific Ocean	Skipjack tuna	0.18-2.1 ng/g LW	Ueno <i>et al.</i> 2005	
Japan	Skipjack tuna	1.1-1.7 ng/g LW	Ueno <i>et al.</i> 2005	Offshore waters
East China Sea	Skipjack tuna	2.4-4.7 ng/g LW	Ueno <i>et al.</i> 2005	
Philippines	Skipjack tuna	2.1 ng/g LW	Ueno <i>et al.</i> 2005	Offshore waters
Brazil	Skipjack tuna	1.9 ng/g LW	Ueno <i>et al.</i> 2005	Offshore waters
Canada	Atlantic tomcod	77 ng/g LW	Law <i>et al.</i> 2003	
Chilika Lake, India	Irrawaddy dolphin	0.12-0.78 ng/g LW	Kannan <i>et al.</i> 2005	Endangered species
Hong Kong, China	Indo-Pacific humpback dolphin	33.6-720 ng/g LW	Ramu <i>et al.</i> 2005	Coastal waters 12% of Σ PBDEs
United Kingdom	White beaked dolphin	1480 ng/g LW	Law <i>et al.</i> 2003	Endangered species
Hong Kong, China	Finless porpoises	27.6-117.6 ng/g LW	Ramu <i>et al.</i> 2005	Coastal waters 12% of Σ PBDEs
Japan	Northern fur seal	2.64-4.56 ng/g LW	Kajiwara <i>et al.</i> 2004	Pacific coast 12% of Σ PBDEs