



Distr.: General  
7 August 2006

Original: English



**United Nations  
Environment  
Programme**

**Stockholm Convention on Persistent Organic Pollutants  
Persistent Organic Pollutants Review Committee  
Second meeting**

Geneva, 6–10 November 2006

Item 5 (a) of the provisional agenda\*

**Consideration of draft risk profiles:  
pentabromodiphenyl ether**

**Draft risk profile: pentabromodiphenyl ether**

**Note by the Secretariat**

1. At its first meeting, the Persistent Organic Pollutants Review Committee adopted decision POPRC-1/3 on pentabromodiphenyl ether.<sup>1</sup> In paragraph 2 of the decision, the Committee decided to establish an ad hoc working group to review further the proposal to list pentabromodiphenyl ether in Annex A to the Convention (UNEP/POPS/POPRC.1/5 and UNEP/POPS/POPRC.1/INF/5) and to develop a draft risk profile in accordance with Annex E.
2. The members of the ad hoc working group on pentabromodiphenyl ether and its observers are listed in annex VI to document UNEP/POPS/POPRC.1/10.
3. A standard workplan for the preparation of a draft risk profile was adopted by the Committee at its first meeting.<sup>2</sup>
4. The process for developing draft risk profiles is summarized in document UNEP/POPS/POPRC.2/INF/14.
5. In accordance with decision POPRC-1/3 and the standard workplan adopted by the Committee, the ad hoc working group on pentabromodiphenyl ether prepared the draft risk profile set forth in the annex to the present note. The draft risk profile has not been formally edited.

\* UNEP/POPS/POPRC.2/1.

<sup>1</sup> UNEP/POPS/POPRC.1/10, annex I.

<sup>2</sup> Ibid., para. 42 and annex II.

### **Possible action by the Committee**

6. The Committee may wish:

- (a) To adopt, with any amendments, the draft risk profile set forth in the annex to the present note;
- (b) To decide, in accordance with paragraph 7 of Article 8 of the Convention and on the basis of the risk profile, whether the chemical is likely as a result of its long-range transport to lead to significant adverse human health and/or environmental effects such that global action is warranted and that the proposal shall proceed;
- (c) To agree, depending on the decision taken under (b) above:
  - (i) To invite all Parties and observers to provide information pursuant to Annex F to the Convention, to establish an ad hoc working group to develop a draft risk management evaluation and to agree on a work plan for completing the draft; or
  - (ii) To make the risk profile available to all Parties and observers and set it aside.

**Annex**

**PENTABROMODIPHENYL ETHER**

**DRAFT RISK PROFILE**

Draft prepared by the ad hoc working group on  
Pentabromodiphenyl Ether  
under the Persistent Organic Pollutant Review Committee  
of the Stockholm Convention

This draft risk profile is based on the draft prepared by  
National Veterinary Institute, Norway

**August 2006**

## CONTENTS

Executive Summary .....	5
1. Introduction.....	7
1.1 Chemical identity of the proposed substance .....	7
1.2 Conclusion of the Review Committee regarding Annex D information .....	7
1.3 Data sources.....	7
1.4 Status of the chemical under other international conventions .....	8
1.4.1 The OSPAR Convention .....	8
1.4.2 The UNECE Convention on Long-range Transboundary Air Pollution.....	8
1.4.3. The Rotterdam Convention .....	8
1.4.4 Other international forum of relevance .....	8
2. Summary information relevant to the risk profile .....	9
2.1 Sources.....	9
2.1.1. Production and use .....	9
2.1.2 Global demands for brominated flame retardants in the future.....	11
2.1.3 Releases to the environment during production .....	12
2.1.4 Releases to the environment during product use.....	13
2.1.5 Emissions from waste containing PentaBDE .....	14
2.2 Environmental fate .....	16
2.2.1 Persistence .....	16
2.2.2 Bioaccumulation.....	17
2.2.3 Long-range environmental transport .....	21
2.3 Exposure .....	25
2.3.1 Levels .....	25
2.3.2 Trends.....	26
2.3.3. Bioavailability .....	28
2.3.4 Human exposure.....	29
2.3.5 Debromination.....	31
2.4 Hazard assessment for endpoints of concern.....	32
2.4.1 Ecotoxicity.....	32
2.4.2 Effects in mammals .....	32
2.4.3 Toxicity to humans .....	35
3. Synthesis of information.....	35
3.1 Summary.....	35
3.2 Synthesis.....	37
3.3 Annex D reprise.....	38
4. Concluding statement .....	39
References: .....	40

## Risk profile for Pentabromodiphenyl ether

### Executive Summary

A substantial range of studies on pentabromodiphenyl ether has been identified and the findings summarised in this risk profile. The commercial product 'pentabromodiphenyl ether' is a mixture of brominated diphenyl ether congeners containing three to seven bromines in the molecule, and this is referred to here as 'PentaBDE'. Molecules with four and five bromines predominate in the commercial product. There are, of course, a number of isomers of pentabromodiphenyl ether, and analytical procedures often report individual isomers. The new findings reported here support the conclusion reached by the POPRC in 2005 that PentaBDE's properties fulfill the screening criteria in Annex D of the Stockholm Convention. Due to the combination of known toxic effects and widespread exposure, it poses significant risks to human health and the environment, and thus also meets the criteria for Annex E.

Production of PentaBDE is phased out or being phased out worldwide. It has been released into the environment during the manufacture of the commercial product, in the manufacture of products, during their use and after they have been discarded as waste. The main source in North America and Western Europe has been the PentaBDE incorporated in polyurethane foam, used in domestic and public furniture. This use is now mainly phased out. The information is too limited to draw conclusions on the importance of other uses, like textiles, electrical and electronic products, building materials, vehicles, trains and aeroplanes, packaging, drilling oil fluid and rubber products. Dismantling and reuse of electric and electronic consumer goods can be a source for releases of PentaBDE in workplace settings. While some representative examples are covered, detailed information on use is lacking for many regions of the world.

The releases of PentaBDE are to air, water and soil, but the major part ends up in soil. The distribution between the environmental compartments is: soil>>>water>air. In the main, PentaBDE in the environment is bound to particles; only a small amount is transported in its gaseous phase or diluted in water but such transport over long periods can be effective in distributing the PentaBDE widely in the environment, especially into Arctic regions.

Due to its high persistency in air, the main route for long-range transport of PentaBDE - as with so many substances that are sufficiently volatile, persistent and bioaccumulative - is through the atmosphere. Modelling and environmental studies indicate that the transport is through a series of deposition/volatilization hops towards the poles but particulate transport is known to be important, too, especially for the less-volatile congeners. Long-range transport through water and emigrating animals is also likely. Several studies show that PentaBDE in soil and sediments is bioavailable, enters the food chain and that it bioaccumulates and biomagnifies in the food webs, ending up in high levels in top predators.

PentaBDE is widespread in the global environment. Levels of PentaBDE have been found in humans in all UN regions. Most trend analyses show a rapid increase in concentrations of PentaBDE in the environment and in humans from the early 1970s to the middle or end of the 1990s. Vulnerable ecosystems and species are affected, among them several endangered species. Some individuals of endangered species show levels high enough to be of concern. The potential for the toxic effects in wild life, including mammals, is evident.

Potential exposure to humans is through food, and through use of products and contact with indoor air and dust. PentaBDE transfers from mothers to embryos and lactating infants. Norwegian data show that the detected levels are considerably lower than observed NOELs in laboratory mammals,

but the impact of this observation is difficult to assess in the absence of correlating data. A Canadian assessment of risk quotients suggests that the highest risks accrue to species high in the food chain. Information is lacking on the effects in humans of short-term and long-term exposure, although it is to be expected that vulnerable groups can be pregnant women, embryos and infants.

Most countries have ceased their production of PentaBDE and uses of it are being phased out in several countries, but the substances are still on the market in big regions of the world.

*Based on the information in this risk profile, PentaBDE is likely, as a result of long-range environmental transport and demonstrated toxicity in a range of non-human species, to cause significant adverse effects on human health or the environment, such that global action is warranted.*

## 1. Introduction

The Stockholm Convention is a global treaty to protect human health and the environment from persistent organic pollutants (POPs), of which twelve are currently listed under the Convention. POPs are chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in living organisms and can cause harm to humans and the environment. Norway, which is a Party to the Stockholm Convention, submitted a proposal in January 2005 to list pentabromodiphenyl ether in Annex A to the Stockholm Convention, and the POPRC agreed that the commercial product 'pentabromodiphenyl ether' ('PentaBDE') – actually a mixture as described below - met the screening criteria of Annex D to the Convention.

### 1.1 Chemical identity of the proposed substance

The proposal concerns the commercial product, pentabromodiphenyl ether, referred to here as PentaBDE. The commercial mixture, while sold as a technical grade under the Chemical Abstracts Service (CAS) Registry number for the penta isomer, is more accurately identified by the CAS Registry numbers of the individual components:

- (a) Pentabromodiphenyl ether (CAS No. 32534-81-9) 50–62% w/w;
- (b) Tetrabromodiphenyl ether (CAS No. 40088-47-9) 24–38% w/w;
- (c) Tribromodiphenyl ether (CAS No. 49690-94-0) 0–1% w/w;
- (d) Hexabromodiphenyl ether (CAS No. 36483-60-0) 4–12% w/w;
- (e) Heptabromodiphenyl ether (CAS No. 68928-80-3) trace.

Within each of groups (a) – (e), isomers may exist due to various distributions of bromine on the two benzene rings of the diphenyl ether skeleton. Individual isomers are identified by code numbers, examples being BDE-47 for 2,2', 4,4'-tetrabromodiphenyl ether and BDE-99, for 2,2',4,4',5-pentabromodiphenyl ether. The numbering system is the same as that used for polychlorobiphenyls (PCBs) (Ballschmiter *et al.* 1993).

The acronym PBDE is used for the generic term polybromodiphenyl ether, covering all congeners of the family of brominated diphenyl ethers. It is sometimes abbreviated to BDE.

### 1.2 Conclusion of the Review Committee regarding Annex D information

The Committee has evaluated Annex D information at its first meeting in Geneva in November 2005 (UNEP/POPS/POPRC.1/10) and has concluded that the screening criteria have been fulfilled for PentaBDE (Decision POPRC-1/3).

### 1.3 Data sources

This risk profile is elaborated using Annex E information submitted by countries and nongovernmental organizations, national reports from web sites for environment protection agencies in different countries, contact and submissions from Norwegian research institutes, the bromine industry, EMEP and AMAP.

Eleven countries have submitted information (Australia, Brazil, Canada, Japan, Norway, Mexico, Poland, Republic of Lebanon, Spain, Switzerland and United States of America). Seven countries submitted information on production and use. Only one country submitted information on releases; another reported that they did not have release data. All except one country provided monitoring data. There was no information on stock-piles from submitting countries and only a few have submitted information on trade. Two observers submitted information - World Wide Fund for Nature (WWF) and the International POPs Elimination Network (IPEN).

## **1.4 Status of the chemical under other international conventions**

### 1.4.1 The OSPAR Convention

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the OSPAR Convention) is guiding international cooperation on the protection of the marine environment of the North-East Atlantic. The OSPAR Convention was signed in Paris in 1992 and entered into force on 25 March 1998. The OSPAR Commission is made up of representatives of the Governments of 17 Contracting Parties and the European Commission, representing the European Community. In 1998, the OSPAR Commission placed PBDEs on its "List of Chemicals for Priority Action." An OSPAR Commission background document on PBDEs was reviewed by Sweden in 2001. The next full review of this document is not planned before 2008. At the 4th North Sea Conference, it was decided to phase out the use of brominated flame retardants by 2020.

### 1.4.2 The UNECE Convention on Long-range Transboundary Air Pollution

United Nations Economic Commission for Europe (UNECE) works for sustainable economic growth among its 55 member countries. The UNECE Convention on Long-range Transboundary Air Pollution was signed by 34 Governments and the European Community in 1979 in Geneva. Under it, Parties shall endeavour to limit and, as far as possible, gradually reduce and prevent air pollution including long-range transboundary air pollution. It entered into force in 1983 and has been extended by eight specific protocols. There are today 50 countries that are parties to the Convention. The Protocol for persistent organic pollutants (POPs) was adopted on 24 June 1998 in Aarhus (Denmark). It focuses on a list of 16 substances that have been singled out according to agreed risk criteria, for total ban, elimination at a later stage or restrictive use. PentaBDE was nominated as a new POP to the Convention in 2005 by Norway. In December 2005 it was considered by the Executive Body of the Convention to meet the screening criteria for POPs, set out in EB decision 1998/2. In 2006 the management options for PentaBDE will be assessed to give a basis for later negotiations.

### 1.4.3. The Rotterdam Convention

The Rotterdam Convention is a multilateral environmental agreement designed to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals. It is an instrument to provide importing Parties with the power to make informed decisions on which chemicals they want to receive and to exclude those they cannot manage safely.

The text of the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade was adopted at the Diplomatic Conference held in Rotterdam on 10 September 1998. The Convention entered into force on 24 February 2004 and became legally binding for its Parties. Today there are 102 states that are parties to the Convention. The EU notified PentaBDE to the Rotterdam Convention in 2003. For it to become a candidate, bans of the substance must be notified by two parties under the Convention.

### 1.4.4 Other international forum of relevance

The Arctic Council is a high-level intergovernmental forum that provides a mechanism for addressing the common concerns and challenges faced by the Arctic governments and the people of the Arctic. Member states are Canada, Denmark (including Greenland and the Faeroe Islands), Finland, Iceland, Norway, Russia, Sweden and United States of America. Six international organizations representing many Arctic indigenous communities have the status of Permanent Participants of the Arctic Council.

Significant monitoring and assessment of pollution in the Arctic is performed under the auspices of the Arctic Council (The Arctic Monitoring and Assessment Programme, AMAP). This work is important in identifying pollution risks, their impact on Arctic ecosystems and in assessing the effectiveness of international agreements on pollution control, such as the Stockholm Convention on Persistent Organic Pollutants (POPs). Under this umbrella important scientific findings have shown up PentaBDE as one important pollutants of the Arctic.

In the autumn of 2004, the Arctic Council adopted a new Arctic project concerning the reduction of brominated flame retardants. The project will be managed by Norway.

## 2. Summary information relevant to the risk profile

### 2.1 Sources

#### 2.1.1. Production and use

Based on the last information on total market demand of PentaBDE presented at the Bromine Science and Environmental Forum (BSEF), the estimated cumulative use of PentaBDE since 1970 was 100 000 metric tons (tonnes). The total market demand decreased during the later years of this period, for example from 8,500 tons in 1999 to 7,500 tons in 2001 (BSEF, 2001).

*Table 2.1. PentaBDE volume estimates: Total market demand by region in metric tons (BSEF, 2001).*

	America	Europe	Asia	Rest of the world	Total
<b>1999</b>	8,290	210	-	-	8,500
<b>2001</b>	7,100	150	150	100	7,500

These consumption figures need to be seen in the context of the global demand for polybrominated flame retardants of all types, which vastly outweighs the demand for PentaBDE. Thus, world totals of PBDE were 204,325 (1999), 203,740 (2001), 237,727 (2002) and 223, 482 (2003) tonnes (BSEF 2006).

PentaBDE has been produced in Israel, Japan, U.S. and EU (Peltola *et al.* 2001 and van der Goon *et al.* 2005). Since 2001 actions to regulate or voluntarily phase-out PentaBDE have been conducted in several countries.

Production in EU ceased in the former EU (15) in 1997 (EU 2000). Usage in the EU (15) has been declining during the second half of the 1990s and is estimated to be 300 metric tonnes in 2000 (used solely for polyurethane production) (EU 2000). The use of PentaBDE was banned in the EU (25) in 2004. Use in electrical and electronic appliances ceased on 1 July 2006.

While use is banned in the EU, there is no ban on use in the US, although it will be banned in the state of California from 2008. The sole US manufacturer voluntarily ceased production, but use may be continuing and will cease only when stocks are fully exhausted. Although a patent on production of PentaBDE was taken out in China as recently as 1999 for a PBDE mixture that differs from the traditional penta-mix, the substance is being phased out in that country. Remaining production in China is estimated as less than 100 MT/year and will cease in 2007 when the substance is banned in that country.

The major producer in Israel, The Dead Sea Bromine Group, declares in a public statement on its web site that their products do not contain PentaBDE. This aligns the producer with the ban in the EU, which is an important market for the company's flame retardants.

There is today no production in Japan. The use of PentaBDE was voluntarily withdrawn from the Japanese market in 1990 (Kajiwara *et al.* 2004). Some developing countries around the East China Sea are potential "hot spots" releasing PentaBDE into the marine environment (Ueno *et al.* 2004). Many industrial manufacturers of computers, television sets and other electric household equipment are situated in the coastal areas of Asian developing countries (Ueno *et al.* 2004). There are indications on a phase-out of PentaBDE in manufacture of new electrical and electronic products in the Asian region, although uses there were always subsidiary to the major uses in polyurethane foams. The extent of this is uncertain. Waste electric products used in developed countries have been exported to Asian developing countries, such as China, India and Pakistan. This waste material has been recycled for recovery of valuable metals (Ueno *et al.* 2004) and continuation of this trade can remain a source to PentaBDE releases. No restrictions have so far been implemented in developing countries in the Asia Pacific and the southern hemisphere.

The release of 'banked' PentaBDE during recycling of foam products has its parallel in the release of CFCs and other ozone depleting substances which have similarly remained in the foam during its useful lifetime.

Results from a survey of Canadian industries regarding certain substances on the country's Domestic Substances List conducted for the year 2000 indicated that no PBDEs were manufactured in Canada, but approximately 1300 tonnes of PentaBDE commercial products (for incorporation into finished articles) was imported into the country (Environment Canada 2003). Based on quantities reported, PentaBDE was the PBDE imported in greatest volume, followed by the commercial decabromodiphenyl ether product. A very small amount of octabromodiphenyl ether was imported in 2000. The volumes reported do not include quantities imported in finished articles. In 2004, it was proposed that PentaBDE be added to the Virtual Elimination list in Canada.

In the U.S. the sole producer voluntarily ended their production of PentaBDE in 2004. In 2001 alone, almost 70,000 metric tons of PBDEs were produced globally, almost half of which was used in products sold in the US and Canada. Before the phase-out in U.S. the majority of PentaBDE formulation produced globally was used in North America (>97 %). At the end of 2004 in the US, approximately 7.5% of the more than 2.1 billion pounds of flexible polyurethane foam produced each year in the US contained the commercial PentaBDE formulation (Washington State 2005).

In Australia in 2004, the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) advised that all importers were phasing out imports of PentaBDE by the end of 2005, and this was reconfirmed by the major importers in mid-2005.

PentaBDE is used or has been used in the following sectors (Alaee *et al.* 2003, Danish EPA 1999, EU 2000, Prevedouros *et al.* 2004b, Swiss Agency for the Environment 2002, Birnbaum and Staskel, 2004):

- Electrical and electronic appliances (EE appliances) – computers, home electronics, office equipment, household appliances and other items containing printed circuit laminates, plastic outer casings and internal plastic parts such as small run components with rigid polyurethane elastomer instrument casings.
- Traffic and transport – cars, trains, aircraft and ships containing textile and plastic interiors and electrical components.

- Building materials – foam fillers, insulation boards, foam insulation, pipes, wall and floor panels, plastic sheeting, resins etc.
- Furniture – upholstered furniture, furniture covers, mattresses, flexible foam components.
- Textiles – curtains, carpets, foam sheeting under carpets, tents, tarpaulins, work clothes and protective clothing.
- Packaging – polyurethane foam based packaging materials.

The most common use, accounting for 95-98% of PentaBDE since 1999, has been in polyurethane foam (Hale *et al.* 2002). This foam may contain between 10 and 18% of the commercial PentaBDE formulation. Polyurethane foam is mainly used for furniture and upholstery in domestic furnishing, automotive and aviation industry. Other uses are in rigid polyurethane elastomers in instrument casings, in epoxy resins and phenolic resins in electrical and electronic appliances, and construction materials. For some years now, the more highly brominated Deca-BDE has been preferred in these applications. PentaBDE has also been incorporated in minor amounts in textiles, paints, lacquers, in rubber goods (conveyer belt, coating and floor panels) and in oil drilling fluids. Levels range from 5-30% by weight. Up to the early 1990s, PentaBDE was used in printed circuit boards, usually FR2 laminates (phenolic resins) in Asia. Such FR2 laminates are used in household electronics (television, radio, video), vehicle electronics, white goods (washing machines, kitchen appliances, for example). In the early 1990s the amount PentaBDE used in textile treatment was 60 % of total use in the EU, but this application is now banned.

PentaBDE has been identified as an additive flame retardant in textiles in national substance flow analyses in the ECE region (Danish EPA 1999). Manufacturers of furniture textiles have stated that the textile contained 0.45% PentaBDE in a Norwegian flow analysis reported in 2003. Stringent rules on flammability apply to textiles used in the public sector, the transport sector and business sector, but rules for domestic use are less consistent.

According to information obtained from the bromine industry the use of PentaBDE as hydraulic fluid (as a component of a mixture) in petroleum borings and mining was discontinued 10-20 years ago.

Australia has reported uses in manufacture of polyurethane foams for refrigerators and packaging, and in epoxy resin formulations supplied into aerospace market and for use as potting agents, laminating systems and adhesive systems. The US has reported use of PentaBDE in the aircraft industry. There is no use of PentaBDE in newer aircraft, and thus no exposure of the public, but PentaBDE is still used in military aircraft.

### 2.1.2 Global demands for brominated flame retardants in the future

According to a market analyst consulting company, the global demand for flame retardants is expected to grow at 4.4% per year, reaching 2.1 million metric tons in 2009, valued at \$4.3 billion. Growth will largely be driven by gains in developing countries in Asia (China, in particular), Latin America and Eastern Europe. Strong increases are forecast for most of the flame retardants. Globally, demand will be greatest for bromine compounds, due mainly to strong growth in China. Electrical and electronic uses will grow fastest. Higher value products will continue to make inroads as substitutes for less environmentally friendly compounds, especially in Western Europe, and chlorine compounds will begin to be replaced in China by bromine- and phosphate-based and other flame retardants (Fredonia Group 2005).

After a severe falloff in demand in 2001, electrical and electronic applications will continue to recover. Demand growth for flame retardants will be strongest in such applications. As electronic circuits become smaller, and more densely packed electronics are subjected to ever higher temperatures, the need for flame retardants will increase. Construction markets will be the second

fastest growing globally, but in China second place will be held by motor vehicles, followed by textiles, both of which industries are growing rapidly in that country. Plastics will continue to replace other materials such as metals and glass in a wide range of products, in order to lower both cost and weight and to allow improved design and more flexible production. Plastic usage is already widespread and growing in fields such as transportation, building products and electronics. Plastics must be made flame retardant for many applications, and as a result some 75% of all flame retardants are used in plastics (Fredonia Group 2005).

Environmental restrictions vary by region. In Western Europe, Japan and to a lesser extent in North America, such restrictions will especially limit growth of chlorinated compounds. A ban on some brominated flame retardants in Western Europe is not expected to spread substantially to other regions, but it will drive the development of alternatives in electrical and electronic equipment for sale on the world market. Dozens of Asian, European and US companies announced in 2005 that they have developed or are developing electrical and electronic equipment that does not contain PentaBDE. In Asia, 51% of electronic manufacturers already make products compliant with the ban on PentaBDE in the EU, and 42% expected to have products that are compliant by 1 July 2006. Officials from electronics companies and industry consultants expected that the difficulty of keeping product streams separate would ensure that most electronic equipment sold on the world market would be compliant by 2005 (International Environment Reporter 2006).

### 2.1.3 Releases to the environment during production

PentaBDE is released into the environment during the manufacturing process, in the manufacture of products, during their use and after they have been discarded as waste. In addition to working towards a manufacturing process that does not cause emissions, it is also important to consider the contributions of emissions from products during use as well as after they have been discarded. Most of the PentaBDE is released as diffuse pollution during and after the service life of articles incorporating PentaBDE and as small-scale point source pollution from the waste management chain of the end products.

PentaBDE is synthesised from diphenyl ether by brominating it with elemental bromine in the presence of a powdered iron Friedel-Craft catalyst. The producers of PentaBDE have reported that the major routes of PentaBDE from this process to the environment are filter waste and rejected material, both of which are disposed of in landfills. Waste water releases of PentaBDE may also occur from spent scrubber solutions (Peltola *et al.* 2001).

According to the EU risk assessment of PentaBDE, the emissions in polyurethane production are assumed to occur prior to the foaming process, when handling the additives (discharges to water) and during the curing (emissions to air). Releases to air may occur during the curing phase of foam production, during which the foam stays at elevated temperature for many hours, depending on the production block size. Emission to air at this stage is estimated to be 1 kg/tonne PentaBDE, but it is assumed that some of the volatilized PentaBDE condenses in the production room and ends up in the waste water. The EU risk assessment concludes that 0.6 kg of PentaBDE is released in this way, and 0.5 kg into air, for each tonne of PentaBDE used in polyurethane foam production.

Table 2.2 Global production and use of PentaBDE in polyurethane foam production, and estimation of associated releases in 2000 (foam containing 10-18% PentaBDE).

Polyurethane foam production	Quantity of PentaBDE	Release of PentaBDE into waste water	Emissions of PentaBDE to air during production
150,000 tonnes/year	15,000-27,000 tonnes/year	9,000-16,200 kg/year	7,500-13,500 kg/year

An important source of release has been associated with the use of liquid flame retardant additives such as PentaBDE in production of polymer foams. Approximately 0.01% (that is, 100 g /tonne) of the raw material handled during mixing is estimated to be released to wastewater. There is also potential for release due to volatilization during the curing phase as described above, since foam reaches temperatures of 160°C for several hours. Wong *et al.* (2001) examined the atmospheric partitioning characteristics of BDEs 47, 99 and 153, and predicted that tetra- and pentabromo-congeners will become gaseous at warmer air temperatures. Therefore, although the low measured vapour pressure values for the PBDEs indicate that volatilization is minimal at normal air temperatures, there is potential for release to air at the elevated temperatures reached during curing (European Communities 2001). The European Communities (2001) study estimates the overall release of PentaBDE to be approximately 0.11%, with about one half of this going to air and the other half to wastewater.

#### 2.1.4 Releases to the environment during product use

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 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 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/m<sup>3</sup>/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/m<sup>3</sup>/g foam, respectively. The average temperature range during sampling was 30-34°C.

Given the use of 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 commercial 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 PBDEs have 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 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 PentaBDE

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

In production, the 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 car 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, PentaBDE is no longer used in this application. There is limited information about waste generated in other applications of 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 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 released during incineration of articles containing PentaBDE (Danish EPA 1999, Ebert and Bahadir 2003, Weber and Kuch 2003, Birnbaum and Staskel 2004).

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 technical mixture of 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 under-estimated 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 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). Some polyvinyl chloride sheeting would also have been treated with 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 Syracus 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	Palm <i>et al.</i> 2002
	11	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 CO<sub>2</sub> 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 <sup>14</sup>C-labelled and unlabelled BDE-47 (a TetraBDE) incorporated into sediments. The study showed that <1% of the total radioactivity was recovered as <sup>14</sup>CO<sub>2</sub> and <sup>14</sup>CH<sub>4</sub>, 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<sub>ow</sub>) for PentaBDE in those studies is 6.5 – 7.4. The more recent studies are described in the following text.



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 PentaBDE technical product. 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 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  $\Sigma$ PBDEs. Age was not a significant covariate for individual PBDEs or  $\Sigma$ 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, 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, Ikonomidou *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/m<sup>3</sup> near Lake Superior to about 52 pg/m<sup>3</sup> 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/m<sup>3</sup> with a mean of 58.3 pg/m<sup>3</sup>. 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/m<sup>3</sup>, with the lighter congeners (DBE-17, -28 and -47) dominating (Gouin *et al.* 2002). The concentrations fell to 10-20 pg/m<sup>3</sup>, 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/m<sup>3</sup>. 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 PentaBDE mixture. Back calculation gave total PBDE concentrations in outdoor air of 4.8 pg/m<sup>3</sup> and 42.1 pg/m<sup>3</sup> 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  $\Sigma$ BDE air concentrations estimated from the passive sampler data ranged from 0.5 to 250  $\text{pg m}^{-3}$ . 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  $\Sigma$ BDE, similar to their proportion in the Bromkal 70-5DE PentaBDE technical product.

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  $100 \pm 35 \text{ pg/m}^3$ , 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  $31 \text{ pg/m}^3$  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 ( $1.0 \text{ }\mu\text{g/L}$ ) and low vapour pressure ( $7.6 \times 10^{-6} \text{ Pa}$ ). 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.  $\Sigma$ BDE concentrations at Mace Head, Ireland, were 0.22 to  $5.0 \text{ pg/m}^3$  with a mean of  $2.6 \text{ pg/m}^3$  and were controlled primarily by advection.  $\Sigma$ BDE concentrations at Hazelrigg (NW England) were 2.8 to  $37 \text{ pg/m}^3$  with a mean of  $12 \text{ pg/m}^3$ , and at Chilton (SW England) were 3.4 to  $33 \text{ pg/m}^3$  with a mean of  $11 \text{ pg/m}^3$ . The congener profile was, on average, similar to that of the commercial 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  $\Sigma$ BDE ranged from 65 to 12,000  $\text{ng/kg}$  dry weight. BDE congeners BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154, covering the major constituents of the commercial 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  $\Sigma$ BDE concentration ( $\Sigma$ BDE is the sum of the concentrations of the congeners determined in each study) was 8.6 pg/m<sup>3</sup>, 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 ± 18% of  $\Sigma$ BDE was found to be particle-associated. The volume weighted mean concentration of  $\Sigma$ BDE (nine congeners) in rain was 209 pg/l, and the total deposition rate was 2 ± 1 ng  $\Sigma$ BDE/m<sup>2</sup>/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<sub>ow</sub>, log K<sub>oa</sub>, log K<sub>aw</sub>,

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/m<sup>3</sup> (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/m<sup>3</sup> near Lake Superior in 1997 to 77 pg/m<sup>3</sup> 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/m<sup>3</sup>. 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, Norstrøm *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 ΣBDE concentrations were as high as 39,000 µg kg<sup>-1</sup> 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/compartment	Levels of PentaBDE	References	Comments
Europe	Atmosphere Gas phase	10-120 pg/m <sup>3</sup>	Jaward <i>et al.</i> 2004	22 countries
Japan	Atmosphere Particulate Gas phase	0.05-0.9 pg/m <sup>3</sup> 0.05-19 <sup>3</sup> pg/m <sup>3</sup>	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	
Taiwan	Skipjack tuna	4.7 ng/g LW	Ueno <i>et al.</i> 2005	Offshore waters
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	Indo-Pacific humpback dolphin	33.6-720 ng/g LW	Ramu <i>et al.</i> 2005	Coastal waters 12% of ΣPBDEs
United Kingdom	White beaked dolphin	1480 ng/g LW	Law <i>et al.</i> 2003	Endangered species
Hong Kong	Finless porpoises	27.6-117.6 ng/g LW	Ramu <i>et al.</i> 2005	Coastal waters 12% of ΣPBDEs
Japan	Northern fur seal	2.64-4.56 ng/g LW	Kajiwara <i>et al.</i> 2004	Pacific coast 12% of ΣPBDEs
Svalbard, Arctic Norway	Polar bear	0.7-4.7 ng/g LW	Gabrielsen <i>et al.</i> 2004	
Canadian Arctic	Polar bear	1.04-11.3 ng/g LW	Muir <i>et al.</i> 2006	
Bjørnøya, Arctic Norway	Glacous gulls	0-7.9 ng/g LW	Herzke <i>et al.</i> 2003	
Norway	White-tailed sea eagle	6-184 ng/g LW	Herzke <i>et al.</i> 2005	In eggs. Endangered Species
Sweden	Peregrine falcons	110-9200 ng/g LW	Lindberg <i>et al.</i> 2004	Endangered species
Australia	Melon-headed whale	4.8 ng/g LW	Law <i>et al.</i> 2003	
Canada	Beluga whale	108 ng/g LW	Law <i>et al.</i> 2003	Vulnerable species
Netherlands	Mussels	0.3-11 ng/g LW	Law <i>et al.</i> 2003	Marine+freshwater
Sweden	Frog	5.6 ng/g LW	De Wit <i>et al.</i> 2004	
Canada	Zooplankton	0.46 ng/g LW	Law <i>et al.</i> 2003	

### 2.3.2 Trends

Most trend analysis show an increase in concentrations of PBDEs in the environment and in humans from the beginning of the 1970s, with a peak around the mid-1990s and a stabilisation or subsequent levelling off in Europe (Covaci *et al.* 2002, Fängström *et al.* 2005, Thomsen *et al.* 2005 and Knudsen *et al.* 2005), but with a continuous increase in the Arctic (Vorkamp *et al.* 2005, AMAP 2002 and AMAP 2005). PentaBDEs are reported in the studies to follow the same trend as ΣPBDEs. This increase has also been seen in North America, in air, soil and sediment, and wildlife, but insufficient data exist to allow comment on trends in the human population.

In the Asia-Pacific region a study on northern fur seals on the Pacific coast of Japan shows an increase of PBDEs to about 150 times between 1972 and 1994, and then levels decreased to about 50% in 1998 (Kajiwara *et al.* 2004). The reduction in PBDEs values was assumed to be due to the voluntary phase out of PentaBDE in Japan in 1990. BDE-99 levels showed the same pattern as  $\Sigma$ PBDEs.

Analysis of archived herring gull eggs (sampled in 1981, 1983, 1987, 1989, 1990, 1992, 1993, 1996, 1998, 1999 and 2000) enabled Norstrom *et al.* (2002) to establish temporal trends in PBDE concentrations over the period 1981-2000. At Lake Michigan, Lake Huron and Lake Ontario sampling sites, concentrations of tetra- and pentabromodiphenyl ethers (that is, BDE-47, BDE-99 and BDE-100) increased by 71-112-fold over these two decades (from 4.7 to 400.5  $\mu\text{g}/\text{kg}$  ww at Lake Ontario; from 8.3 to 927.3  $\mu\text{g}/\text{kg}$  ww at Lake Michigan; from 7.6 to 541.5  $\mu\text{g}/\text{kg}$  ww at Lake Huron). These increases were found to be exponential at all three locations ( $r^2 = 0.903 - 0.964$ ,  $p < 0.00001$ ).

Wakeford *et al.* (2002) undertook sampling of eggs of the great blue heron in 1983, 1987, 1991, 1996, 1998 and 2000 in southern British Columbia and found that total PBDE concentrations (sum of tetra-, penta- and hexabromo-congeners) increased from 1.31 to 287  $\mu\text{g}/\text{kg}$  ww between 1983 and 1996, but then dropped slightly to 193  $\mu\text{g}/\text{kg}$  ww in 2000. They also undertook sampling of the eggs of thick billed murre in the Canadian North in 1975, 1987, 1993 and 1998, and observed a trend of gradually increasing PBDE concentrations (sum of tetra-, penta- and hexabromo-congeners) in these eggs from 0.43-0.89  $\mu\text{g}/\text{kg}$  ww in 1975, to 1.83-3.06  $\mu\text{g}/\text{kg}$  ww in 1998.

PBDEs have been detected in a variety of marine mammals. Alae *et al.* (1999) reported average PBDE (di-to hexaBDE) concentrations in the blubber of marine mammals from the Canadian Arctic as 25.8  $\mu\text{g}/\text{kg}$  lipid in female ringed seals (*Phoca hispida*), 50.0  $\mu\text{g}/\text{kg}$  lipid in male ringed seals, 81.2  $\mu\text{g}/\text{kg}$  lipid in female beluga (*Delphinapterus leucus*) and 160  $\mu\text{g}/\text{kg}$  lipid in male beluga. BDE-47, a tetrabromodiphenyl ether, was the predominant congener, followed by the pentabromo BDE-99. Ikonomou *et al.* (2000, 2000b) reported PBDE concentrations in biota samples from the west coast and Northwest Territories of Canada. The highest concentration of total PBDE residues, 2269  $\mu\text{g}/\text{kg}$  lipid, was found in the blubber of a harbour porpoise from the Vancouver area. With a concentration of about 1200  $\mu\text{g}/\text{kg}$ , one congener, BDE-47, accounted for slightly more than half of the total PBDE in the sample. Ikonomou *et al.* (2002a) analyzed temporal trends in Arctic marine mammals by measuring PBDE levels in the blubber of Arctic male ringed seals over the period 1981-2000. The mean total concentrations increased exponentially, from 0.572  $\mu\text{g}/\text{kg}$  lipid in 1981 to 4.622  $\mu\text{g}/\text{kg}$  in 2000, a greater than eightfold increase. They determined that Penta- and HexaBDEs are increasing at approximately the same rate (doubling time 4.7 and 4.3 years, respectively), more rapidly than TetraBDEs, for which the doubling time was 8.6 years. Once again, BDE-47 was predominant, followed by BDE-99 and BDE-100.

A marked increase in tissue PBDE levels was also evident in blubber samples collected from San Francisco Bay harbour seals over the period 1989 to 1998 (She *et al.* 2002). Total PBDEs (the sum of BDEs 47, 99, 100, 153 and 154) rose from 88  $\mu\text{g}/\text{kg}$  lipid to a maximum of 8325  $\mu\text{g}/\text{kg}$  lipid over this short period. Stern and Ikonomou (2000) examined PBDE levels in the blubber of male SE Baffin Bay beluga whales over the period 1982-1997, and found that the levels of total PBDEs (tri-to hexa-congeners) increased significantly. Mean total PBDE concentrations were about 2  $\mu\text{g}/\text{kg}$  lipid in 1982, and reached a maximum value of about 15  $\mu\text{g}/\text{kg}$  lipid in 1997. BDE-47 was the dominant congener, with a mean concentration of approximately 10  $\mu\text{g}/\text{kg}$  lipid in 1997. Total PBDE residues (concentrations for individual congeners not provided) in the blubber of St Lawrence estuary belugas sampled in 1997-1999 amounted to 466 ( $\pm 230$ )  $\mu\text{g}/\text{kg}$  ww blubber in adult males, and 655 ( $\pm 457$ )  $\mu\text{g}/\text{kg}$  ww blubber in adult females. These values were approximately twenty times higher than concentrations in beluga samples collected in 1988-1990 (Lebeuf *et al.* 2001).

The results from a modelling exercise utilizing the European variant (EVn) BETR multimedia environmental fate model were presented for the technical PentaBDE product by Prevedouros *et al.* (2004). To predict future atmospheric concentration trends, the model was used in its fully dynamic mode over the period 1970-2010. It predicted that atmospheric concentrations would have peaked around 1997, and then declined with an overall “disappearance” half-life of 4.8 years. The model steady state simulations gave generally good agreement with measured data for BDE-47 and BDE-99. The empirical data for North America presented above, however, show continuing increases in concentrations, at least up the year 2000, and so while the model results match some European data with fair agreement, they are not in accord with data from North America.

Three dated sediment cores from locations in Western Europe were analyzed for 14 BDE congeners (Zegers *et al.*, 2003). Cores from the Drammenfjord (Norway), the western Wadden Sea (The Netherlands) and Lake Woserin (Germany) showed a time dependent pattern in the distribution of BDEs since the start of production of PBDE formulations. Two of the three commercial formulations could be distinguished. The penta-mix formulation is clearly present from the beginning of the 1970s. This is in agreement with data for the industrial production of this formulation. In the cores from the Netherlands and Germany, concentrations of BDE congeners associated with the commercial PentaBDE were levelling off in the most recent layers (1995 & 1997), whereas those in the Drammenfjord were still increasing in 1999. The absence of all BDE congeners in the older (deeper) layers of all three cores, as well as in several 100 to 150 million year old layers of clay from Kimmeridge, UK, indicated that these BDE congeners are not produced naturally.

Human exposure to polychlorobiphenyls and PBDEs in Japan in 1980 and 1995 showed that levels of the latter had increased substantially over the twenty-year period, although there was great variation between regions. The main congeners detected in serum were BDE-47 and BDE-99. Most total PBDE levels had more than doubled, and in one area increased twenty-fold, with 1995 values falling in the range 0.6 – 41.4 ng/g lipid Koizumi *et al.* 2006).

### 2.3.3. Bioavailability

Environmental studies on bioavailability have detected uptake of PentaBDE in soil organisms (Matscheko *et al.* 2002), sediment dwelling organisms (Magnusson *et al.* 2003) and aquatic organisms (Lithner *et al.* 2003, Voorspoels *et al.* 2003, Marsch *et al.* 2004, Kierkegaard *et al.* 2004, and Sinkkonen *et al.* 2004), making PentaBDE's way into the food webs evident. Subsequent bioaccumulation and biomagnification of the compound has been detected and described in Section 2.2.2.

Soil exposed to PBDEs in various ways was analyzed for BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-183 (Matscheko *et al.*, 2002). Earthworms collected at all soil sampling sites were analyzed as well. The BDE congener profile in all soil samples was dominated by BDE-47 and BDE-99. Accumulation of the compounds in earthworms from the sites yielded a direct relationship between the concentrations in the soil and concentrations in the worms. The biota-soil accumulation factors (BSAFs) of BDE congeners BDE-47, BDE-99 and BDE-100 were around 5 (organic matter/lipids). Thus, earthworms living in contaminated soils will accumulate tissue BDE concentrations and, as these animals represent the base of the terrestrial food chain for many organisms, this form a pathway for the accumulation of BDEs in organisms at higher trophic levels.

The western Scheldt estuary is subject to a variety of suspected PBDE sources, such as a brominated flame retardant manufacturing plant, Antwerp harbour, and the textile industry located further upstream. PBDE concentrations in samples of biota, including crab, shrimp, starfish, benthic fish (such as dab, goby, plaice and sole) and gadoid fish (such as bib and whiting) from the estuary were

compared to those in samples from the Belgian North Sea beyond the mouth of the estuary (Voorspoels *et al.*, 2003). Eight BDE congeners (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) were determined. Concentrations observed in the estuarine samples were up to 30 times higher than in those from the Belgian North Sea, with an increasing gradient towards Antwerp. Concentrations in the North Sea ranged from 0.02 to 1.5 µg/kg wet weight in benthic invertebrates and goby, from 0.06 to 0.94 µg/kg wet weight in fish muscle, and from 0.84 to 128 µg/kg wet weight in fish liver. The corresponding ranges in samples from the estuary were from 0.2 to 30, 0.08 to 6.9, and from 15 to 984 µg/kg wet weight, respectively. The ratio BDE-99/BDE-100 was found to be highly location- and species-dependent, possibly relating to differences in metabolism. In shrimp, the value of this ratio (4:1) was very similar to that observed in the Bromkal formulation and in estuarine sediment, and was similar in shrimp from both the North Sea and the estuary, implying both that these congeners are readily bioavailable and that shrimp lack the ability to metabolize either congener. On a lipid weight basis, concentrations of BDE-47 ranged from 3 to 108 µg/kg lipid weight in samples from the North Sea, and from 8 to 1,550 µg/kg lipid weight in estuarine samples. BDE-47 was the most abundant congener in all samples, comprising 43 to 75% of ΣBDE.

Thomas *et al.* (2004) conducted an input-output balance study of BDEs on three captive, juvenile grey seals. The animals were fed a diet of herring for six months, and the study was performed during the last three months of this period. BDE analysis was undertaken using GC-ECNIMS. Consistently high absorption (89 - 99%) was observed for all PBDE congeners studied (BDE-28, BDE-47, BDE-49, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-209).

#### 2.3.4 Human exposure

Studies, assessments and reviews referred to in this section have shown that the main routes for human exposure are food, and exposure to dust in indoor air at home and workplaces due to levels in products like furniture and electronic devices. Fish and agriculture products are the main food sources of PentaBDE for humans, and mother's milk for the nursing child. Fatty fish from contaminated areas are a major source (Sjödin *et al.* 2003). PentaBDE has been detected in various foods (VKM 2005, Burniston *et al.* 2003 and Bocio *et al.* 2003) as well as in indoor dust (Shoeib *et al.* 2004 and Wilford *et al.* 2005). Levels in foods in the US have been reported by Schecter *et al.* (2004), Schecter *et al.* 2006, and Huwe *et al.* (2005). There are several hazard assessments in EU and US, looking into the exposure of humans (VCCEP 2003, COT 2004, VKM 2005). They conclude that the available hazard or exposure information is inadequate to fully characterize the risks.

Domestic house dust is likely to be a significant source where furniture, carpet or appliances contain PentaBDE. This has been discussed in Section 2.1.1. It is not clear which sources are the greatest, and there could be wide variations depending on lifestyle and diet.

Several studies have detected levels of PentaBDE in sewage sludge (Matscheko *et al.* 2002, Fabrellas *et al.* 2004, Motche and Tanner 2004 and Sjödin *et al.* 2003, Hale 2002). Sewage sludge is considered to be one of the main sinks for PBDEs. The application of sewage sludge to agricultural land is one of the reasons for detected levels of PentaBDE in food products. This can explain the detected levels in vegetables and root crops in experimental studies. Levels in fish and root crops can be the source of exposure to domestic animals like chickens and pigs, and the source of PBDEs in meat products for human nourishment.

A Canadian global study showed that PentaBDE is widespread in human milk in populations all over the world (Ryan 2004). There are data on levels in human blood serum and milk from USA, Canada, Mexico, Japan, the EU region, the Arctic region and Scandinavia. A meta-analysis by Hites (2004),

using data published up to mid-2003, showed that serum and milk levels in the US were much higher than those in Europe - ~35 ng/g vs ~ 2 ng/g lipid – and were doubling on average every 4-6 years. BDE-47 and BDE-99 were the major congeners detected.

Levels increasing from the 1980s to the 2000s have been observed in mother's milk from Sweden as well as in blood from Germany and Norway (Sjödin *et al.* 2003). A more recent study in Sweden (Fängström *et al.* 2005) assessed the temporal trends of polybrominated diphenyl ethers (PBDEs), in mothers' milk in the Stockholm area. The pooled samples were covering the time period 1980 to 2004, with emphasis on samples from the last ten years. Concentrations of BDE-47, BDE-99 and BDE-100 reached a peak in the mid-1990s and are now clearly showing decreasing levels. The concentrations are however still much higher than in 1980.

The objective of a recent Norwegian study was to complete and extend a previous study on time trends of PBDEs in Norwegian pooled serum samples (Thomsen *et al.* 2005). These levels were compared with levels in other human samples from Norway in order to put together an overview of the PBDE body burden in the general population from 1977 to 2004. The temporal trend of the sum of seven PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-183) in the pooled serum from the present study are in close agreement with the levels found in a previous study by the same authors, except for the pools from 1991 and 2002 which were found to be considerably higher than expected from earlier results of preceding and following years. This was surprising as the pools contained at least twenty individual samples (mean age 40 – 50 years). In the samples from 2002, the mean of sum seven PBDEs is 3.8 ng/g lipid (serum from the youngest group excluded) and 3.5 ng/g lipids in men age 25-59 years. In general, for similar time periods the levels in breast milk seem to be somewhat lower than in the serum, but the same overall trend is observed. This confirms that the PBDE body burdens in these regions have risen rapidly from 1977 to about 1997, but now seem to have stabilized or even to have decreased. This is in accordance with the trends observed in Swedish breast milk, as an indicator of the European situation, but may not be true of levels in North America. The PBDE level was previously found to be about twice as high in a serum pool from infants up to four years of age compared to serum pools from elderly persons. This finding was confirmed in the Norwegian study. However, in 2002, children between the ages of 5 and 14 years showed higher levels of PBDEs than the average adult.

Contemporary PBDE concentrations in Europe and Asia are remarkably similar, with low median values on a lipid basis for all countries and relatively small variations. The situation in North America is completely different with median values for individual studies in the range of 20-50 ng/g LW (Ryan 2004). However, in parallel with the regional differences that were reported above for biota, the levels in breast adipose tissue taken from women living in San Francisco Bay area in 2000 were almost two orders of magnitude higher than what has been reported in human milk from Sweden (Sjödin *et al.* 2003). A more recent study of levels in human adipose tissue in New York was published by Johnson-Restrepo *et al.* (2005). The study of 40 males and 12 females of a range of ages and ethnicities showed wide variations in lipid PBDE concentrations, with mean values substantially higher than the medians. Median concentrations were: BDE-47, 29.3 ng/g lipid; BDE-99, 10.3 ng/g lipid; BDE-100, 12.0 ng/g lipid.

In a preliminary screening of PBDEs in plasma and milk samples from Mexican women, the levels were well above European levels of PBDEs reported so far (López *et al.* 2004). The mean level of PBDEs (with BDE-209 excluded) in Mexican women living in urban areas was approx. 20 ng/g LW in plasma. The levels in women living in rural areas in Mexico were however comparable with women living in rural areas in Sweden. (BDE-209 levels were only detected in women living in the Mexican city).

Ryan (2004) detected a big individual variation in levels in the general population in a study from Canada. The values span more than three orders of magnitude, with a few values showing a much greater level. Levels detected in the Canadian Arctic in Ryan's study (2004) were increasing. Values in human milk from the Faroe Islands showed the same trend (Fångström *et al.* 2004).

Two studies in Australia indicated that levels of PBDEs in Australian breast milk and blood serum are higher than those in Europe but lower than those found in North America (Harden *et al.* 2004 and 2005).

Table 2.6 Data on mean levels of PentaBDE (**BDE-99**) (ng/g LW) in humans from different parts of the world.

Data	Country/region	Levels	References	Year	Comments
blood	The Netherlands	0.8	Weiss <i>et al.</i> 2004	unknown	
blood	Norway	1.0	Thomsen <i>et al.</i> 2004	1999	
blood	Mexico	2.0	López <i>et al.</i> 2004	2003	Urban population
blood	Australia	2.3	Harden <i>et al.</i> 2004	2003	
milk	Germany	0.2	Harden <i>et al.</i> 2004	2000	
milk	Sweden	0.3	Fångström <i>et al.</i> 2005	2003	Urban population
milk	Mexico	0.6	López <i>et al.</i> 2004	2003	Rural population
milk	Sweden	0.5	López <i>et al.</i> 2004	2003	Rural population
milk	United Kingdom	0.9	Harden <i>et al.</i> 2004	?	median
milk	Faroe Islands	1.0	Fångström <i>et al.</i> 2004	1999	Rural population
milk	Australia	1.9	Harden <i>et al.</i> 2005	2002/2003	
milk	Canada	4	Ryan <i>et al.</i> 2002	2002	Rural population
milk	USA	28	Päpke <i>et al.</i> 2001	2000	Urban population

Although they are less relevant than environmental data, results from occupational studies bear out the facility with which the PBDEs are taken up by human bodies. In Sweden, occupational exposure to PBDE has been identified among electronics recycling personnel (Sjødin *et al.*, 1999) and in technicians responsible for repair and maintenance of computers (Jacobsson *et al.*, 2002) as well as in nearby soil and sediment (Wang *et al.* 2005). Also workers in industry manufacturing PentaBDE, or polyurethane foam and electronic equipment containing it can be exposed to PentaBDE. There is an extensive literature on such exposures.

### 2.3.5 Debromination

There is growing interest in the fate of PBDEs in the environment. In experiments reported by Stapleton *et al.* (2004), carp were fed food spiked with individual BDE congeners for 62 days, and tissue and excreta were examined. At least  $9.5 \pm 0.8\%$  of BDE-99 in the gut was reductively debrominated to BDE-47 (one less bromine) and assimilated in carp tissues. Similarly, 17% of the heptabromo congener BDE-183 was reductively debrominated to hexabromo congeners. The authors noted that body burdens of PBDEs may thus reflect direct uptake from exposure as well as debromination of more highly brominated congeners. Highly selective reductive microbial debrominations were observed in experiments reported by He *et al.* (2006). Hepta- and Octa-BDEs were produced in cultures of *Sulfurospirillum multivorans* to which DecaBDE had been added, but OctaBDE was not attacked in a similar system. Cultures of an alternative organism, *Dehalococcoides sp.*, failed to attack the DecaBDE but an OctaDBE mixture was extensively changed, yielding a mixture of Hepta- through Di-BDEs which included the PentaBDE, BDE-99. The authors draw attention to the potential for conversion of higher congeners in the environment to more toxic congeners with fewer bromine substituents.

Hydroxylated BDEs (OH-BDEs) have been detected and identified as metabolites in several species after exposure to specific BDE congeners but have also been found to occur as natural products in marine sponges and ascidians (Marsch *et al.* 2004). Methoxylated BDEs (MeO-BDEs) have also been reported as natural products present in marine sponges and green algae. It would seem that the origin of these substances can be natural, anthropogenic or both. Nine OH-BDEs and six MeO-BDEs were identified in blood of Baltic Sea salmon (*Salmo salar*) using newly synthesized standards (Marsch *et al.*, 2004). All of the identified OH- and MeO-BDEs were substituted with four or five bromine atoms and five of them also had one chlorine substituent. Fourteen have the methoxy or hydroxy group substituted in the position *ortho*-to the diphenyl ether bond. The structures of several of the compounds support natural rather than anthropogenic origins. However, at least one of the OH-BDEs (4'-OH-BDE-49) may be a hydroxylated metabolite of BDE-47. Estrogenic activity of some hydroxylated PBDEs has been reported by Meerts *et al.* (2001).

Other studies of metabolism of PBDEs are summarized in Section 2.2.2.1.

## **2.4 Hazard assessment for endpoints of concern**

Evidence to date suggests that the major congeners of the technical PentaBDE formulation, BDE-47 and BDE-99, are likely to be more toxic and bioaccumulative than other PBDE compounds congeners. The toxicology of PBDEs is not well understood, but some studies on PentaBDE have demonstrated reproductive toxicity, neurodevelopmental toxicity and effects on thyroid hormones. The neurotoxic effects of PBDEs are similar to those observed for PCBs. Children exposed to PBDEs are prone to subtle but measurable developmental problems. It is presumed that PBDEs are endocrine disrupters, but research results in this area are scant (Siddiqi *et al.* 2003).

While further studies follow internationally-accepted guidelines might be needed to make a full risk assessment of the situations of children, there are sufficient data for development of the present risk profile.

It is acknowledged that these conclusions rest to some extent on examination of reviews, rather than reanalysis of primary data, but in general the studies under review have followed internationally accepted experimental protocols. Nonetheless, there is no significant disagreement between some reported results and later analyses, such as that of the US Voluntary Children's Chemical Evaluation Program (VCCEP) (2005).

### 2.4.1 Ecotoxicity

Recent studies show that exposure to BDE-47 can cause growth inhibition in colonies of the plankton algae (*Skeletonema costatum*) and a depression on reproductive output of the zooplankton *Daphnia magna* (Källqvist *et al.* 2006).

A recent paper by Timme-Laragy *et al.* (2006) showed adverse effects on fish development at low concentrations. However, the endpoints that were affected in this report (behavioural learning) are not usually accepted risk assessment endpoints. Other endpoints that would be acceptable, such as growth or survival, were not affected.

### 2.4.2 Effects in mammals

In a review article on toxic effects of brominated flame retardants, Darnerud (2003) drew on a range of primary literature to conclude that exposure to PBDEs gives rise to adverse effects in experimental

*in vivo* models, and depending on type of product different effects are seen, occurring at varying dose levels. Generally, the technical PentaBDE products cause effects at the lower dosages. The critical effects of PentaBDE are those on neurobehavioral development and, although somewhat less sensitive, thyroid hormones in offspring (from 0.6 to 0.8 and 6 to 10 mg/kg body wt., respectively) (Darnerud 2003). Note that some data reported in Table 2.7 show levels below these. More recent information, especially for North America, is available in Birnbaum and Staskal (2004).

Blubber biopsy and blood samples were collected from weaned grey seal (*Halichoerus grypus*) pups and juveniles during 1998 and 1999 (Hall *et al.*, 2003). Fifty four post-weaned pups and fifty five first year juveniles (of which thirteen were recaptured post- weaned pups) were studied. The median concentrations of  $\Sigma$ BDE (14 congeners) were 0.17 and 0.46  $\mu\text{g}/\text{kg}$  lipid weight in the blubber of the pups and the juveniles, respectively. The study indicated that thyroid hormone levels in the blood of grey seals during their first year of life were significantly, and positively, related to  $\Sigma$ BDE concentrations in blubber, after accounting for the effects of possible confounding variables. Such an association is not, in itself, sufficient evidence for a causal relationship, but is in accordance with the hypothesis that these compounds can act as endocrine disrupters in grey seal pups.

Darnerud (2003) concluded in his review that for PentaBDEs, the critical effects among the available studies seem to be developmental neurotoxicity and, although generally at somewhat higher doses, altered thyroid hormone homeostasis. Regarding the neurotoxicity in mice, no clear mechanism could be defined but effects of the PentaBDEs both via thyroid hormone disruption and directly on signal transmission in brain have been discussed. For example, PBDEs were capable to induce cell death of cerebellar granule cells in culture (Reistad *et al.*, 2002, Reistad and Mariussen 2005). The LOAEL value for PentaBDE could be set to 0.6–0.8 mg/kg body wt., based on the most sensitive effect observed, neurobehavioral effects during early development (Darnerud 2003, although it is not the task of the POPRC to set a LOAEL, for construction of which resort would need to be made a wider range of data.

In a hazard assessment by the Committee on Food Safety in Norway (VKM 2005) the following toxic effects of exposure to BDE-99 or the technical PentaBDE formulation was reported: neurotoxicity, effects on neurobehavioral development, effects on the thyroid hormone system and hispatological alterations in the tyroidea and liver.

*Table 2.7 Overview of No Observed Effect level (NOEL) and Lowest Observed Effect Level (LOEL) after oral administration of **BDE-99** congener or commercial PentaBDE formulations. Bold values are the lowest LOEL or NOEL detected.\**

PENTABDE	Duration	Dose	NOEL mg/kg/ day	LOEL mg/kg/day	Endpoint	Species	Reference
BDE-99	s.d	0.8 or 12.0 mg/kg	n.d.	0.8	Neurotoxicity Behaviour, motor activity level and learning	mouse	Eriksson <i>et al.</i> 2001
BDE-99	s.d	0.6, 6, or 30 mg/kg	n.d.	0.6	Developmental- and neurotoxicity Behaviour - hypoactive	mouse	Branchi <i>et al.</i> 2002

BDE-99	s.d	0.4, 0.8, 4.0, 8.0, or 16 mg/kg	<b>0.4</b>	<b>0.8</b>	Developmental- and neurotoxicity Behaviour	mouse	Viberg <i>et al.</i> 2004 Sand <i>et al.</i> 2004
BDE-99	s.d.	0,06 and 0,3 mg/kg to pregnant female	<b>n.d.</b>	<b>0,06</b>	Developmental- and neurotoxicity Behaviour (increased activity)	rat, F1 gen.	Kuriyama <i>et al.</i> 2005
BDE-99	s.d.	0,06 and 0,3 mg/kg to pregnant female	<b>0,06</b>	<b>0,3</b>	Reduced testis size and number of sperms	rat, F1 gen.	Kuriyama <i>et al.</i> 2005
Penta mix DE-71	30 d	0.01, 0.05, 0.1, 0.5, or 1.0 mg/kg/day	<b>1</b>	n.d.	Growth, food intake, hematology, histopatology Clinical chemistry	rat	Great lakes Chemical Corporation 1985
Penta mix DE-71	30 d	0, 3, 30, or 60 mg/kg/day	3	30	Liver weight, puberty, reproduction, liver enzymes, T <sub>4</sub> -reduction	Male rat	Stoker <i>et al.</i> 2004
Penta mix DE-71	30 d	0, 3, 30, or 60 mg/kg/day	n.d.	3	T <sub>4</sub> -reduction	Female rat	Stoker <i>et al.</i> 2004
Penta mix DE-71	35 d	0, 1, 10 or 30 mg/kg/day	1	10	T <sub>4</sub> -reduction Liver enzymes	pregnant rat	Zhou <i>et al.</i> 2002, Zhou <i>et al.</i> 2001
Penta mix DE-71	90 d	0-0.44 mg/kg/day	n.d.	0.44	Liver enzymes	rat	Carlson 1980
Penta mix DE-71	90 d	0, 2,10, or 100 mg/kg/day	0-2	2-10	Hepatocytomegaly Tyreoida hyperplasi	rat	Great lakes Chemical Corporation 1984

n.d.=not defined, s.d.=single dose

\* Most of the studies are in line with the OECD test guidelines and for those are not, the quality of the study is assessed to be adequate.

The PBDE mixture known as DE-71 (71% bromine by mass, and containing BDE-47, BDE-99, BDE-100, BDE-153, BDE-154) delays the puberty and suppresses the growth of androgen-dependent tissues in male Wistar rat following a peri-pubertal exposure. These effects suggest that DE-71 may be either inducing steroid hormone metabolism or acting as an androgen receptor (AR) antagonist (Stoker *et al.* 2005).

Talsness *et al.* (2005) evaluated the effects of environmentally relevant concentrations (low doses) of BDE-99 on the female reproductive system in rats. Ultra structural changes compatible with altered mitochondrial morphology were observed in the ovaries of the F1 offspring. No statistically significant changes in ovarian follicle counts were observed. External and skeletal anomalies were detected in offspring (F2) from two different dams (F1) with early developmental exposure to 300 µg BDE-99/lkg BW. Exposure to BDE-99 resulted in female reproductive tract changes in the F1 generation which were apparent at adulthood.

*In utero* exposure to a single low dose of BDE-99 disrupts neurobehavioral development and causes permanent effects on the rat male reproductive system apparent in adulthood (Kuriyama *et al.* 2005). Also in this study, the effects of developmental exposure to BDE-99 on juvenile basal motor activity levels and adult male reproductive health were assessed. The exposure to low-dose BDE-99 during development caused hyperactivity in the offspring at both time points (postnatal days 36 and 71) and permanently impaired spermatogenesis by the means of reduced sperm and spermatid counts. The doses used in this study of 60 and 300 µg/kg BW are relevant to human exposure levels, being approximately 6 and 29 times, respectively, higher than the highest level reported in human breast adipose tissue. This is the lowest dose of PBDE reported to date to have an *in vivo* toxic effect in rodents and supports the premise that low-dose studies should be encouraged for hazard identification of persistent environmental pollutants. The study by Viberg *et al.* (2004) shows that neonatal exposure to BDE-99 can induce developmental neurotoxic effects, such as changes in spontaneous behaviour (hyperactivity), effects that are dose-response related and worsen with age. The changes are seen in C57/B1 mice of both sexes. Spontaneous behaviour (locomotion, rearing, and total activity) was observed in two-, five- and eight-month-old mice.

### 2.4.3 Toxicity to humans

Several hazard assessments have been produced in EU and in US. The conclusions in the hazard assessments elaborated are qualified by the lack of sufficient knowledge of the toxicology of PentaBDE to enable assessment of the risk to humans (COT 2004, VKM 2005 and VCCEP 2003). The toxicological importance for humans of detected effects in laboratory animals is not clear. There is still not enough knowledge of the mechanisms, half-life and metabolism of PentaBDE in experimental animals and humans (VKM 2005).

The conclusion in the hazard assessment by the Committee on Food Safety in Norway was that the exposure through food and mother's milk is considerably lower than the observed NOEL in laboratory mammals (VKM 2005). It is believed that long-time exposure to lower doses of PentaBDE can cause health effects, since PentaBDE accumulates in the human body. Since the half-life of PentaBDE in humans is not known it is not possible today to conclude on long-time exposure effects. This is true even for the US situation, where levels may be 10-20 times those observed in Europe, but pharmacokinetics, toxicology, exposure and other critical data are lacking.

Vulnerable groups could however be pregnant women, embryos and infants, because of effects on the thyroid hormone balance, and the embryo's development of the central nervous system. During pregnancy, maintenance of the thyroid hormone balance is a physiological challenge. Embryos and infants are particularly vulnerable for reductions in thyroid hormone levels (VKM 2005). Infants are exposed to PentaBDE through the diets of their mothers' milk, since PentaBDE is lipophilic and accumulates in the milk (VKM 2005).

## **3. Synthesis of information**

### **3.1 Summary**

The pentabromodiphenylether (PentaBDE) commercial product is a mixture of primarily tetra- through hexa-BDE congeners (plus trace amounts of TriBDE and 0-1% HeptaBDE). It is used for flame retardant purposes as an additive in consumer products. The proportion of the PBDE-congeners in commercial PentaBDE mixtures is different in different regions of the world.

A substantial range of studies on PentaBDE has been identified. New findings further support the conclusion that PentaBDE's properties fulfill the screening criteria in Annex D of the Stockholm Convention.

PentaBDE is released into the environment during the manufacture of the commercial PentaBDE mixture, in the manufacture of products, during their use and after they have been discarded as waste. The main source in North America and Western Europe has been products with polyurethane foam, but this use is now mainly phased out. The information is too limited to draw conclusions on the importance of other uses, like textiles, electrical and electronic products, drilling oil fluid and rubber products. Dismantling and reuse of electrical and electronic consumer goods can be an extensive source for releases of PentaBDE. In addition detailed information on use is lacking for many regions of the world.

The releases are to air, water and soil. The major part of the releases ends up in soil. The distribution between the environmental compartments is: soil>>>water>air. The main part of PentaBDE in the environment is bound to particles; only a small amount is transported in its gaseous phase or diluted in water.

Due to PentaBDE's high persistency in air, the main route for long-range transport is through the atmosphere. Modelling and environmental studies indicate that the transport is through a series of deposition/volatilization hops towards the poles. To a lesser extent, long-range transport through water and emigrating animals may also occur. Several studies show that PentaBDE in soil and sediments is bioavailable and thus enters the food chain, and that it bioaccumulates and biomagnifies in the food webs, ending up in high levels in top predators.

PentaBDE is widespread in the global environment and in humans. Most trend analyses show a rapid increase in concentrations of PentaDBE in the environment and humans from the beginning of the 1970s, reaching plateau levels in the some regions in the late 1990s but continuing to increase in others. Vulnerable ecosystems and species are affected, among them several endangered species. Some individuals of endangered species show high levels of concern. The potential for the toxic effects in wild life and mammals is evident.

The exposure to humans is through food, use of products and indoor air and dust. PentaBDE transfers from mothers to embryos and lactating infants. The detected levels are considerably lower than observed NOELs in laboratory mammals but because inter-species comparisons are lacking the significance of this observation cannot be assessed. Similarly, knowledge is too scarce to conclude on the effects of long-term exposure. Vulnerable groups can be pregnant women, embryos and infants.

Most countries have ceased their production and others will soon do so. Uses of PentaBDE have been phased-out in several countries, but are still on the market in many regions of the world, but in any case there is a substantial reservoir of PentaBDE in products which could release it to the environment.

The general pattern of production and use of PentaBDE is clear from studies conducted over the last two decades. The detection of significant quantities of this substance in proximate and remote locations (especially the Arctic) provides evidence of its dispersal into the environment, but direct connections between sources and sinks – especially for particular congeners – have yet to be identified. Recent finding son reductive debromination of highly brominated congeners to their more toxic relatives suggest that the situation may be more complex than was at first envisaged. Much remains to be learned.

One leading researcher (Hites, R. A. 2004) summarised the situation a few years ago in the following terms. 'By now it is clear that PBDEs are ubiquitous environmental pollutants and that their concentrations in most environmental compartments are exponentially increasing with doubling times of about 4-6 years.' Noting that pentaBDE was being phased out in Europe, that its production in the US was ceasing, and that both penta- and octaBDE would be banned in California from 2008, Hites went on to reflect on the likely drop in environmental concentrations as regulation took hold. Already, he noted, PBDE levels in Swedish breast milk had decreased over recent years (Darnerud *et al.* 2002).

### 3.2 Synthesis

PentaBDE easily meets all of the Annex D screening criteria, and details are included (for the sake of completeness) in Table 3.2, below.

In the absence of production controls, the levels detected in humans, other species and the environment have been observed to rise steeply and this increase is observed in remote locations as well as closer to sites of production and use. In the US, where PentaBDE was in high use until recently and where it remains in such materials as polyurethane foam incorporated into consumer products, there has been a build-up in human tissue.

PentaBDE in soil or sediment is readily incorporated into the food chain and bioaccumulates in the fatty tissues of top predators, including humans.

There are toxicological studies of concern that demonstrate neurodevelopmental impacts in animals at low tissue levels that are of relevance to levels observed in populations. Such body burdens remain under close review.

An assessment of the impact of PBDEs on the environment was recently concluded by Environment Canada (2006), taking into account critical studies and lines of evidence that support the conclusion that these commercial substances entering the environment have or may have an immediate or long-term harmful effect on the environment or its biodiversity. Although there is a paucity of relevant toxicological data (compared to observations of the environmental presence of PBDEs), Environment Canada was able to perform a risk quotient analysis for each congener, integrating known or potential exposures with known or potential adverse effects. In its simplest form, the risk quotient may be described by the equation:

$$\text{Risk quotient} = \frac{\text{exposure reference value}}{\text{toxicity reference value}}$$

and it is customary to use conservative values in order to highlight the worst case. A risk quotient value >1 signifies the likelihood or potential for adverse effects to occur, while those <1 imply no danger to organisms. The Canadian results shown in Table 3.1 are based partly on Canadian empirical data and partly on surrogate data from Swedish and US sources.

*Table 3.1 Risk quotient values for PentaBDE (Environment Canada 2006).*

<b>Commercial product</b>	<b>Pelagic organisms</b>	<b>Benthic organisms</b>	<b>Soil organisms</b>	<b>Wildlife consumers</b>
PentaBDE	$4 \times 10^{-3}$	45.2	0.13-0.26	149

These values reflect the bioaccumulation of PentaBDE which causes organisms higher in the food chain to be exposed to greater risk.

### 3.3 Annex D reprise

Table 3.2 POP characteristics of PentaBDE (from “Annex to decision POPRC-1/3” in UNEP/POPS/POPRC.1/10)

Criterion	Meets the Criterion	Remark
Potential for Long-Range Atmospheric Transport	Yes	<p>PentaBDE has a low vapour pressure (<math>9.6 \times 10^{-8}</math> to <math>4.7 \times 10^{-5}</math> Pa) and modelling data show an estimated half-life in air greater than two days. The estimated half-lives for BDE-47 and BDE-99 in air are between 10 and 20 days*.</p> <p>Monitoring data show that the substance is found in remote areas. PentaBDE congeners have been found in Arctic air with a concentration of from &lt;1 to 20 <math>\text{pg}/\text{m}^3</math>. There is also a substantial amount of monitoring data in marine animals, birds, fish, lake sediments, etc. in remote areas.</p>
Toxicity (Adverse Effects)	Yes	<p>There is evidence of reproductive toxicity in invertebrates and fish. The <math>\text{EC}_{50}</math> for larval development of marine copepod was 13 and 4 <math>\text{mg}/\text{L}</math> for BDE-47 and BDE-99 respectively. The lowest observed adverse effect level (LOAEL) for developmental neurotoxicity and liver toxicity in rodents ranged from 0.6 to 10 <math>\text{mg}/\text{kg}</math> body weight/day.</p>
Persistence	Yes	<p>The estimated half-life in water for PDBE congeners BDE-47 and BDE-99 is 150 days, which exceeds the BCF criterion.</p> <p>Deposits of PBDE congeners that were present in marine sediments a few decades ago are still present in clearly quantifiable quantities.</p>

Bioaccumulation	Yes	<p>Log <math>K_{ow}</math> is greater than 5 (observed values 6.46-6.97). The reported bioconcentration factors for <i>Cyprinus carpio</i> are 66,700 for BDE-47 and 17,700 for BDE-99.</p> <p>Data from around the world demonstrate increasing levels of PentaBDE congeners with rising trophic position. Recent publications confirm food chain transfer in the Arctic.</p>
-----------------	-----	--

\* BDE-47 and BDE-99 are two major congener components of the PentaBDE commercial mixture (2,2',4,4'-tetrabromodiphenyl ether and 2,2',4,4',5-pentabromodiphenyl ether respectively).

#### 4. Concluding statement

*Based on the information in this risk profile, PentaBDE is likely, as a result of long-range environmental transport and demonstrated toxicity in a range of non-human species, to cause significant adverse effects on human health or the environment, such that global action is warranted.*

References:

- Agrell, C., ter Schure, A.F.H., Sveder, J., Bokenstrand, A., Larsson, P. and Zegers, B.N. 2004. Polybrominated diphenyl ethers (PBDEs) at a solid waste incineration plant. I: atmospheric concentrations. *Atmos. Environ.* 38: 5139-3148.
- Alaee, M., Luross, M.J., Whittle, M.D. and Sergeant D.B. 2002. Bioaccumulation of polybrominated diphenyl ethers in the Lake Ontario pelagic food web. *Organohalogen Compounds* 57: 427-430.
- Alaee, M., Arias, P., Sjödin, A. and Bergman, Å. 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of releases. *Env. Int.* 29: 683-689.
- AMAP Assessment 2002: Persistent organic pollutants in the Arctic. Arctic monitoring and assessment program, Oslo 2004.
- AMAP 2005. Fact sheet: Brominated flame retardants in the Arctic. <http://www.amap.no>
- Ballschmiter, K., Mennel, A. and Buyten, J. 1993. Long-chain Alkyl Polysiloxanes as Non-Polar Stationary Phases in Capillary Gas Chromatography, *Fresenius' J. Anal. Chem.* 346: 396-402.
- Birnbaum, L., Staskal, D.F. and Diliberto, J.J. 2003. Health effects of polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs). *Environ. Int.* 29: 855-860.
- Birnbaum, L. And Staskal, D.F. 2004. Brominated flame retardants: cause for concern? *Environ. Health Perspectives.* 112: 9-17.
- Bocio, A., Llobet, J.M., Domingo, J.L., Corbella, J., Teixidó, A. and Casas C. 2003. J. Agric. Polybrominated Diphenyl Ethers (PBDEs) in Foodstuffs: Human Exposure through the Diet. *Food Chem.* 51: 3191 - 3195; (Article) DOI: 10.1021/jf0340916
- Branchi, I., Alleva, E. and Costa, L.G. 2002. Effects of perinatal exposure to a polybrominated diphenyl ether (PBDE-99) on mouse neurobehavioral development. *Neurotoxicology* 23:375-84.
- Broman, D., Balk, L., Zebühr, Y. and Warman K. 2001. Miljöövervakning i Stockholmskommun Saltsjön och Mälaren . KEMI Slutrapport: Provtagningsåren 96/97, 97/98 och 98/99. Laboratoriet för akvatisk ekotoxikologi, ITM, Stockholms universitet samt Miljölaboratoriet i Nyköping.
- BSEF, Brominated Science and Environmental Forum. 2001. Major brominated flame retardants volume estimates. Total market demand by region 2001. 21 January 2003. [www.bsef.com](http://www.bsef.com).
- BSEF 2006. Information provided by the BSEF in July 2006. Figures for 2004 and 2005 will be forthcoming.

- Burniston, D.A., Symons, R.K., Croft, M., Trout, M. and Korth, W. 2003. Determination of polybrominated diphenyl ethers (PBDEs) in Australian pig fat. *Organohalogen Compounds*, Volumes 60-65 (Dioxin 2003) Boston, MA.
- Burreau, S., Broman, D. and Zebühr Y. 1999. Biomagnification quantification of PBDEs in fish using stable nitrogen isotopes. *Organohalogen Compounds* 40: 363 - 366.
- Burreau, S., Zebühr, Y., Ishaq, R. and Broman D., 2000. Comparison of biomagnification of PBDEs in food chains from the Baltic Sea and the Northern Atlantic Sea. *Organohalogen Compounds* 47: 253-255.
- Burreau, S., Zebühr, Y., Broman, D. and Ishaq, R. 2004. Biomagnification of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) studies in pike (*Esox lucius*), perch (*Perca fluviatilis*) and roach (*Rutilus rutilus*) from the Baltic Sea. *Chemosphere* 55: 1043-1052.
- Butt, C.M., Diamond, M.L., Truong, J., Ikonomou, M.G. and ter Schure, A. 2004. A Spatial Distribution of Polybrominated Diphenyl Ethers in Southern Ontario as Measured in Indoor and Outdoor Window Organic Films. *Environ. Sci. Technol.* 38: 724-731.
- Carlson, G.P. 1980. Induction of xenobiotic metabolism in rats by brominated diphenyl ethers administered for 90 days. *Toxicol. Lett.* 6:207-12.
- Christensen, J.H., Glasius, M., Pécseli, M., Platz, J. and Pritzl, G. 2002. Polybrominated diphenyl ethers (PBDEs) in marine fish and blue mussels from southern Greenland. *Chemosphere* 47: 631-638.
- CITI. 2000. The bioaccumulation of compound S512 by carp. Chemical Biotesting Center, Chemicals Inspection and Testing Institute, Tokyo. As cited in: Risk Assessment of Diphenyl Ether, Pentabromoderivative, Commission of the European Communities, 2000.
- Committee on toxicity of chemicals in food consumer products and the environment. COT statement on brominated flame retardants in fish from Skerne-Tees rivers system. 2004. <http://www.food.gov.k/multimedia/pdfs/bfrstatement.pdf>
- Covaci, A., Gheorghe, A., Steen Redeker, E., Blust, R. and Schepens, P. 2002a. Distribution of organochlorine and organobromine pollutants in two sediment cores from the Scheldt estuary (Belgium). *Organohalogen Compounds* 57: 239-242.
- Covaci, A., Van de Vijver, K., DeCoen, W., Das, K., Bouquegneau, J.M., Blust, R. and Schepens, P. 2002b. Determination of organohalogenated contaminants in liver of harbour porpoises (*Phocoena phocoena*) stranded on the Belgian North Sea coast. *Mar. Pollut. Bull.* 44: 1157-1165.
- Danish EPA. 1999. Brominated flame retardants. Substance flow analysis and assessment of alternatives.
- Darnerud, P.O. 2003. Toxic effects of brominated flame retardants in man and wildlife. *Environ. Int.* 29: 841-853.

Darnerud, P.O., Aune, M., Atuma, S., Becker, W., Bjerselius, R., Cnattingius, S. and Glynn, A. 2002. Time trend of polybrominated diphenyl ether (PBDE) levels in breast milk from Uppsala, Sweden, 1996-2001. *Organohalogen Compd.* 58: 233-236.

de Wit, C., Alae, M. and Muir, D. 2004. Brominated flame retardants in the Arctic – an overview of spatial and temporal trends. *Organohalogen Compounds* 66: 3764-3769.

D'Silva, K., Thompson, H., Fernandes, A. and Duff, M. 2004. PBDEs in Heron Adipose Tissue and Eggs from the United Kingdom. Abstract. BFR 2004.

Ebert, J. and Bahadir, M. 2003. Formation of PBDD/F from flame retarded plastic materials under thermal stress. *Environ. Int.* 29: 711-716.

EMEP. 2004. New substances: Model assessment of potential for long-range transboundary atmospheric transport and persistence of PentaBDE. EMEP contribution to the preparatory work for the review of the CLRTAP protocol on POPs. Information note 10/2004.

Environment Canada. 2006. Ecological Screening Assessment Report on Polybrominated Diphenyl Ethers (PBDEs). January 2006.

Eriksson, P., Jakobsson, E. and Fredriksson, A. 2001. Brominated flame retardants: a novel class of developmental neurotoxicants in our environment? *Environmental Health Perspectives* 109: 903-8.

EU. 2000. Risk Assessment of Diphenyl Ether, Pentabromoderivative (Pentabromodiphenyl Ether). CAS Number: 32534-81-9, EINECS Number: 251-084-2. Final Report of August 2000, Commission of the European Communities. Rapporteur: United Kingdom.

Fabrellas, B., Larrazabal, D., Martinez, M.A., Eljarrat, E. and Barceló, D. 2004. Presence of polybrominated diphenyl ethers in Spanish sewage sludges: important contribution of deca-BDE. *Organohalogen Compounds.* 66: 3755-3760.

Fängström, B., Strid, A., Athanassiadis, I., Grandjean, P., Wiehe, P. and Bergman Å. 2004. A retrospective study of PBDEs in human milk from the Faroe Islands. The third international workshop on brominated flame retardants, BFR 2004.

Fängström, B., Strid, A. and Bergman, Å. 2005. Rapport til Naturvårdsverket för projektet ”Analys av polybromerade difenyletrar (PBDE) och hexabromcyklododekan (HBCDD) i human mjölk från Stockholm – en tidstrend studie. (Dnr 721-2653-05Mm) Stockholm 2005-11-23.

Fjeld E., Mariussen, M., Strand-Andersen, M., Hjerpset, M. og Schlabach M. 2003. Bioakkumulering og fordeling av polybromerte difenyletere i norske innsjøer. NFRs program for forurensninger: kilder, spredning, effekter og tiltak (ProFO). Foredrag, forskerseminar 15. okt. 2003, Olavsgård hotell.

Fjeld, E., Schlabach, M., Berge, J.A., Eggen, T., Snilsberg, P., Källberg, G., Rognerud, S., Enge, E.K., Borgen, A. and Gundersen, H. 2004. Kartlegging av utvalgte nye organiske miljøgifter – bromerte flammehemmere, klorerte parafiner, bisfenol A og triclosan (Screening

of selected new organic contaminants – brominated flame retardants, chlorinated paraffins, bisphenol-A and triclosan). NIVA-rapport 4809-2004, Oslo. (SFT: TA-2006). 106 sider.

Fjeld, E. et al. 2005. Screening of selected new organic contaminants 2004. Brominated flame retardants, perfluorated alkylated substances, irgarol, diuron, BHT and dicofol. NIVA-report 5011-2005, Oslo, pp. 97.

Fredonia Group. 2005. Specialty Plastic Additives to 2009. Study # 1961. Available for a fee from [www.fredonia.ecnext.com](http://www.fredonia.ecnext.com) (accessed July 2006).

Gabrielsen, G.W., Knudsen, L.B., Verreault, J., Push, K., Muir, D.C. and Letcher, J. 2004. Halogenated organic contaminants and metabolites in blood and adipose tissues of polar bears (*Ursus maritimus*) from Svalbard. SFT-report 915/2004. [www.sft.no](http://www.sft.no)

Gouin, T., Thomas, G.O., Cousins, I., Barber, J., Mackay, D. and Jones, K.C. 2002. Air-Surface Exchange of Polybrominated Diphenyl Ethers and Polychlorobiphenyls. *Environ. Sci. Technol.* 36: 1426-1434.

Gouin, T. and Harner, T. 2003. Modelling the Environmental Fate of the PBDEs. *Environment International.* 29:717-724.

Great Lakes Chemical Corporation (1984). 90-day dietary study in rats with pentabromodiphenyl oxide (DE-71). Final report. 1984. Report No.: Project No. WIL-12011, WIL Research Laboratories, Inc.

Hale, R.C., La Guardia, M.J., Harvey, E.P. and Mainor, M. 2002. Potential role of fire-retardant-treated polyurethane foam as a source of brominated diphenyl ethers to the US environment. *Chemosphere.* 46: 729-735.

Hall, A.J., Kalantzi, O.I. and Thomas, G.O. 2003. Polybrominated diphenyl ethers (PBDEs) in grey seals during their first year of life – are they thyroid hormone endocrine disruptors? *Environmental Pollution* 126: 29-37.

Harden, F.A, Toms, L.M.L, Ryan, J.J. and Mueller, J. F. 2004. Determination of the levels of polybrominated diphenylethers (PBDEs) in pooled blood sera obtained from Australians aged 31-45 years. In: *Proceedings of the Third International Workshop on Brominated Flame Retardants*, June 6-9 2004, Toronto, Canada: 59-62

Harden, F., Müller, J. and Toms, L. 2005, Organochlorine Pesticides (OCPs) and Polybrominated Diphenyl Ethers (PBDEs) in the Australian Population: Levels in Human Milk, Environment Protection and Heritage Council of Australia and New Zealand [http://www.ephc.gov.au/pdf/EPHC/OCP\\_PBDE\\_human\\_milk\\_jan%202005.pdf](http://www.ephc.gov.au/pdf/EPHC/OCP_PBDE_human_milk_jan%202005.pdf)

Harner, T., Ikonomou, M., Shoeib, M., Stern, G. and Diamond, M. 2002. Passive air sampling results for polybrominated diphenyl ethers along an urban-rural transect. 4<sup>th</sup> Annual Workshop on Brominated Flame Retardants in the Environment, June 17-18, Canada centre for Inland Waters, Burlington, Ontario, pp. 51-54.

Harrad, S. and Hunter, S. 2004. Spatial Variation in Atmospheric Levels of PBDEs in Passive Air Samples on an Urban-Rural Transect. *Organohalogen Compounds*. 66: 3786-3792.

Harrad, S., Wijesekara, R., Hunter, S., Halliwell, C. and Baker, R. 2004. Preliminary Assessment of UK Human Dietary and Inhalation Exposure to Polybrominated Diphenyl Ethers. *Environ. Sci. Technol.* 38: 2345-2350.

Hassanin, A., Breivik, K., Meijer, S.N., Steinnes, E., Thomas, G.O. and Jones, K.C. 2004. PBDEs in European Background Soils: Levels and Factors Controlling Their Distribution. *Environ. Sci. Technol.* 38: 738-745.

Hayakawa K, Takatsuki H, Watanabe I. and Sakai S. 2004. Polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs) and monobromo-polychlorinated dibenzofurans (MoBPXDD/Fs) in the atmosphere and bulk deposition in Kyoto, Japan. *Chemosphere* 57: 343-356.

He, J., Robrock, K.R. and Alvarez-Cohen, L. 2006. Microbial Reductive Debromination of Polybrominated Diphenyl Ethers (PBDEs). *Environ. Sci. Technol.* 40: 4429-4434.

Herzke, D., Gabrielsen, G.W., Evenset, A. and Burkow, I.C. 2003. Polychlorinated camphenes (toxaphenes), polybrominated diphenylethers and other halogenated organic pollutants in Glaucous Gull (*Ularus hyperboreus*) from Svalbard and Bjørnøya (Bear Island). *Environmental Pollution* 121: 293-300.

Herzke, D., Berger, U., Kallenborn, R., Nygård, T. and Vetter, W. 2005. Brominated flame retardants and other organobromines in Norwegian predatory bird eggs. *Chemosphere* 61: 441-449.

Hites, R.A. 2004. Polybrominated Diphenyl Ethers in the Environment and in People: A Meta-Analysis of Concentrations. *Environ. Sci. Technol.* 38: 945-956.

Hoh, E. and Hites, R.A. 2005. Brominated Flame Retardants in the Atmosphere of the East-Central United States. *Environ. Sci. Technol.* 39: 7794-7802.

Huwe, J.K. and Larsen, G.L. 2005. Polychlorinated Dioxins, Furans, and Biphenyls, and Polybrominated Diphenyl Ethers in a U.S. Meat Market Basket and Estimates of Dietary Intake. *Environ. Sci. Technol.* 39: 5606-5611.

Ikonomou, M.G., Raine, S. and Adisson, R.F. 2002. Exponential Increases of the Brominated Flame Retardants Polybrominated Diphenyl Ethers, in the Canadian Arctic From 1981-2000. *Environ. Sci. Technol.* 36: 1886-1892.

International Environment Reporter. 2006. Material available for a fee – see [www.bna.com](http://www.bna.com).

Jakobsson, K., Thuresson, K., Rylander, L., Sjödin, A., Hagner, L. and Bergman, A. 2002. Exposure to polybrominated diphenyl ethers and tetrabromobisphenol A among computer technicians. *Chemosphere* 46: 709-716.

- Jaspers, V., Covaci, A., Maervoet, J., Dauwe, T., Schepens, P. and M. 2004. Brominated flame retardants in Belgian little owl (*Athene noctua*) eggs. *Organohalogen Compounds* 66: 3856-3860.
- Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J. and Jones, K.C. 2004. Passive Air Sampling of PCBs, PBDEs, and Organochlorine Pesticides Across Europe. *Environ. Sci. Technol.* 38: 34-41.
- Johnson-Restrepo, B., Kannan, K., Rapaport, D.P., and Rodan, B.D. 2005. Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Human Adipose Tissue from New York. *Environ. Sci. Technol.* 39: 5177-5182.
- Kajiwara, N., Ueno, D., Takahashi, A., Baba, N. and Tanabe, S. 2004. Polybrominated Diphenyl Ethers and Organochlorines in Archived Northern Fur Seals Samples From The Pacific Coast of Japan, 1972-1998. *Environ. Sci. Technol.* 38: 3804-3809.
- Kannan, K., Ramu, K., Kajiwara, N., Sinha, R.K. and Tanabe, S. 2005. Organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers in Irrawaddy dolphins from India. *Arch. Environ. Contamination* 49: 415-420.
- Källqvist, T., Grung, M. and Tollefsen, K-E. Chronic toxicity of 2,4,2',4'-tetrabromodiphenyl ether (BDE-47) on the marine alga *Skeletonema costatum* and the crustacean *Daphnia magna*. *Environmental Toxicology and Chemistry* (accepted for publication).
- Kierkegaard, A., Bignert, A., Sellström, U., Olsson, M., Asplund, L., Jansson, B. and de Wit, C.A. 2004a. Polybrominated diphenyl ethers (PBDEs) and their methoxylated derivatives in pike from Swedish waters with emphasis on temporal trends, 1967-2000. *Environmental Pollution* 130: 187-198.
- Knudsen, L. B., Gabrielse, G. W., Verreault, J., Barrett, R., Skåre, J.U., Polder, A. and Lie, E. 2005. Temporal trends of brominated flame retardants, cyclododeca-1,5,9-triene and mercury in eggs of four seabird species from Northern Norway and Svalbard. SFT-report 942/2005.
- Koizumi, A., Yoshinaga, T., Harada, K., Inoue, K., Morikawa, A., Muroi, J., Inoue, S., Eslami, B., Fujii, S., Fujimine, Y., Hachiya, N., Koda, S., Kusaka, Y., Murata, K., Nakatsuka, N., Omae, K., Saito, N., Shimbo, S., Takenaka, K., Takeshita, T., Todoriki, H., Wada, Y., Watanabe, T. and Ikeda, M. 2006. Assessment of human exposure to polychlorinated biphenyls and polybrominated diphenyl ethers in Japan using archived samples from the early 1980s and mid-1990s. *Environmental Res.* Accepted for publication December 2004, still 'in press' when accessed at [www.elsevier.com/locate/envres](http://www.elsevier.com/locate/envres) in June 2006.
- Kuriyama, S.N., Talsness, C.E., Grote, K. and Chahoud, I. 2005. Developmental exposure to low dose PBDE-99: effects on male fertility and neurobehavior in rat offspring. *Environmental Health Perspectives* 113(2):149-54.
- Law, R. J., Alae, M., Allchin, C.R., Boon, J.P., Lebeuf, M., Lepom, P. and Stern, G.A. 2003. Levels and trends of polybrominated diphenylethers and brominated flame retardants in wildlife. *Environment International* 29: 757-770.

- Law, R.J., Allchin, C.R., de Boer, J., Covaci, A., Herzke, D., Lepom, P., Morris, S., Tronczynski, J. and de Wit, C.A. 2005. Levels and Trends of Brominated Flame Retardants in European and Greenland Environments. *Chemosphere* 64: 187-208.
- Lee, R.G.M., Thomas, G.O. and Jones, K.C. 2004. PBDEs in the Atmosphere of Western Europe. *Environ. Sci. Technol.* 38: 699-706.
- Lindberg, P., Sellström, U., Häggberg, L. and de Wit, C.A. 2004. Higher Brominated Diphenyl Ethers and Hexabromocyclododecane Found in Eggs of Peregrine Falcons (*Falco peregrinus*) Breeding in Sweden. *Environ. Sci. Technol.* 38: 93-96.
- Lithner, G., Holm, K. and Ekström, C. 2003. Metaller och organiska miljögifter i vattenlevande organismer och deras miljö i Stockholm 2001. ITM Rapport 108, 87 pp., Institute of Applied Environmental Research (ITM), Stockholm University, Stockholm, Sweden, ISBN 91-631-3758-5 (in Swedish).
- López, D., Athanasiadou, M. and Athanassiadis, I. 2004. A preliminary study on PBDEs and HBCD in blood and milk from Mexican women. The third international workshop on brominated flame retardants, BFR 2004.
- Magnusson, K., Agrenius, S. and Ekelund, R. 2003. Distribution of a tetrabrominated diphenyl ether and its metabolites in soft-bottom sediment and macrofauna species. *Mar. Ecol. Prog. Ser.* 255: 155-170.
- Marsch, G., Athanasiadou, M., Bergman, Å. and Asplund, L. 2004. Identification of Hydroxylated and Methoxylated Polybrominated Diphenyl Ethers in Baltic Sea salmon (*Salmo salar*) Blood. *Environ. Sci. Technol.* 38: 10-18.
- Matcheko, N., Tysklind, M., de Wit, C., Bergek, S., Andersson, R. and Sellström, U. 2002. Application of sewage sludge to arable land – soil concentrations of polybrominated diphenyl ethers and polychlorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls, and their accumulation in earth worms. *Environ. Toxicol. Chem.* 21: 2515-2525.
- Meerts, I.A., Letcher, R.J., Hoving, S., Marsh, G., Bergman, A., Lemmen, J.G., van der Burg, B. and Brouwer, A. 2001. *In vitro* estrogenicity of polybrominated diphenyl ethers, hydroxylated PBDEs, and polybrominated bisphenol A compounds. *Environ. Health Perspect.* 109(4): 399-407.
- Moche, W. and Thanner, G. 2004. Levels of PBDE in effluents and sludge from sewage treatment plants in Austria. Proceedings of the Third International Workshop on Brominated Flame Retardants BFR2004, Toronto, Canada, June 6-9 2004. pp. 167-170.
- Morf, L.S., Tremp, J., Huber, Y., Stengele, M. and Zenegg, M. 2005. Brominated flame retardants in waste electrical and electronic equipment: substance flow in a recycling plant. *Environ. Sci. Technol.* 39: 8691-8699.
- Muir, D.C.G., Backus, S., Derocher, A.E., Dietz, R., Evans, T.J., Gabrielsen, G.W., Nagy, J., Norström, R.J., Sonne, C., Stirling, I., Taylor, M.K. and Letcher, R. J. 2006. Brominated flame retardants in polar bears (*Ursus maritimus*) from Alaska, the Canadian Arctic, East Greenland, and Svalbard. *Environ. Sci. Technol.* 40: 449-455.

- Norström, R.J., Simon, M., Moisey, J., Wakeford, B. and Weseloh, D.V.C. 2002. Geographical Distribution (2000) and Temporal Trends (1981-2000) of Brominated Diphenyl Ethers and Hexabromocyclododecane in Guillemot Eggs from Baltic Sea. *Environ. Sci. Technol.* 37: 5496-5501.
- Nylund, K., Asplund, L., Jansson, B., Jonsson, P., Litzén, K. and Sellström, U. 1992. Analysis of some polyhalogenated organic pollutants in sediments and sewage sludge. *Chemosphere*, 24: 1721-1730.
- Päpke, O., Bergman, Å., Fürst, P., Meironyté, G.D., and Herrmann, T. 2001. Determination of PBDEs in human milk from the United States - comparison of results from three laboratories. *Organohalogen Compounds*. 52: 197-200.
- Palm, A. 2001. The Environmental Fate of Polybrominated Diphenyl Ethers in the centre of Stockholm – Assessment of Using a Multimedia Fugacity Model. Master of Science Thesis, Umeå Universitat.
- Palm, A., Cousins, I.T., Mackay, D., Tysklind, M., Metcalf, C. and Alae, M. 2002. Assessing the Environmental Fate of Chemicals of Emerging Concern: A Case Study of the PBDEs. *Environ. Poll.* 117: 195-213.
- Peltola, J. and Yla-Mononen, L. 2001. Pentabromodiphenyl ether as a global POP. *TemaNord 2001*, vol. 579. Copenhagen: Nordic Council of Ministres; ISBN 92-893-0690-4: 78 pp.
- Prevedouros, K., Jones, K.C. and Sweetman, A.J. 2004a. European-Scale Modelling of Concentrations and Distribution of Polybrominated Diphenyl Ethers in the Pentabromodiphenyl Ether Product. *Environ. Sci. Technol.* 38: 5993-6001.
- Prevedouros, K., Jones, K.C. and Sweetman, A.J. 2004b. Estimation of the Production, Consumption, and Atmospheric Emissions of Pentabrominated Diphenyl Ethers in Europe Between 1970 and 2000. *Environ. Sci. Technol.* 38: 3224-3231.
- Ramu, K., Kajiwara, N., Tanabe, S., Lam, P.K.S. and Jefferson, T.A. 2005. Polybrominated diphenyl ethers (PBDEs) and organochlorines in small cetaceans from Hong Kong waters: Levels, profiles and distribution. *Marine Poll. Bull.* 51: 669-676.
- Reistad, T., Mariussen, E. and Fonnum, F. 2002. The effects of polybrominated flame retardants on cell death and free radical formation in cerebellar granule cells. *Organohalogen Compd* 57: 391-394.
- Reistad, T. and Mariussen, E. 2005. A commercial mixture of the brominated flame retardant pentabrominated diphenyl ether (DE-71) induces respiratory burst in human neutrophil granulocytes *in vitro*. *Toxicol. Sci.* 87: 57-65.
- Ryan, J.J., Patry, B., Mills, P. and Beaudoin G. 2002. Recent trends in levels of brominated diphenyl ethers (BDEs) in human milks from Canada. *Organohalogen Compounds*. 58: 173-176.

- Ryan, J.J. 2004. Polybrominated diphenyl ethers (PBDEs) in human milk; occurrence worldwide. The third international workshop on brominated flame retardants, BFR 2004.
- Sand, S., von Rosen, D., Eriksson, P., Fredriksson, A., Viberg, H., Victorin, K. and Filipsson, A.F. 2004. Dose-response modeling and benchmark calculations from spontaneous behaviour data on mice neonatally exposed to 2,2',4,4',5-pentabromodiphenyl ether. *Toxicol. Sci.* 81: 491-501.
- Schechter, A., Pöpke, O., Tung, K-C., Staskal, D. and Birnbaum, L. 2004. Polybrominated Diphenyl Ethers Contamination of United States Food. *Environ. Sci. Technol.* 38: 5306-5311.
- Schechter, A., Pöpke, O., Harris, T.R., Tung, K-C., Musumba, A., Olson, J. and Birnbaum, L. 2006. Polybrominated Diphenyl Ether (PBDE) Levels in an Expanded market basket Survey of United States (US) Food and Estimated PBDE Intake by Age and Gender. *Environ. Health Perspectives*. Doi:10.1289/ehp.9121 (prepublication viewed online 13 July 2006).
- ter Schure, A.F.H. and Larsson, P. 2002. Polybrominated diphenyl ethers in precipitation in Southern Sweden (Skåne, Lund). *Atmos. Environ.* 36: 4015-4022.
- ter Schure, A.F.H., Larsson, P., Agrell, C., and Boon, J.P. 2004a. Atmospheric Transport of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls to the Baltic Sea. *Environ. Sci. Technol.* 38: 1282-1287.
- ter Schure, A.F.H., Agrell, C., Bokenstrand, A., Sveder, J., Larsson, P. and Zegers, B.N. 2004b. Polybrominated diphenyl ethers at a solid waste incineration plant. II: atmospheric deposition. *Atmos. Environ.* 38: 5149-5155.
- Sellström, U. 1996. PBDEs in the Swedish environment. Licentiate Thesis, Institute of Applied Research, Stockholm University.
- Sellström, U., Bignert, A., Kierkegaard, A., Häggberg, L., de Wit, C.A., Olsson, M. and Jansson, B. 2003. Temporal Trend Studies on Tetra- and Pentabrominated Diphenyl Ethers and Hexabromocyclododecane in Guillemot Eggs From the Baltic Sea. *Environ. Sci. Technol.* 37: 5496-5501.
- Shoeib, M., Harner, T., Ikonomou, M. and Kannan, K. 2004. Indoor and Outdoor Concentrations and Phase Partitioning of Perfluoroalkyl Sulfonamides and Polybrominated Diphenyl Ethers. *Environ. Sci. Technol.* 38: 1313-1320.
- Siddiqi, M.A., Laessig, R.H. and Reed, K.D. 2003. Polybrominated diphenyl ethers (PBDEs): new pollutants – old diseases. *Clin Med Res.* 1(4):281-90.
- Sinkkonen, S., Rantalainen, A.-L., Paasivirta, J. and Lahtiperä, M. 2004. Polybrominated methoxy diphenyl ethers (MeO-PBDEs) in fish and guillemot of Baltic, Atlantic and Arctic environments. *Chemosphere* 56: 767-775.
- Sjödin, A., Patterson, D.G. and Bergman Å. 2003. A review on human exposure to brominated flame retardants – particularly polybrominated diphenyl ethers. *Environ. Int.* 29: 829-839.

Sjödin, A., Hagmar, L., Klasson-Wehler, E., Kronholm-Diab, K., Jakobsson, E. and Bergman, A. 1999. Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. *Environ. Health perspectives* 107: 643-648.

Stapleton, H.M., Letcher, R.J. and Baker, J.E. 2004. Debrominated Diphenyl Ether Congeners BDE 99 and BDE 183 in the Intestinal Tract of the Common Carp (*Cyprinus carpio*). *Environ. Sci. Technol.* 38: 1054-1061.

Stapleton, H.M., Dodder, N.G., Offenber, J.H., Schantz, M.M. and Wise, S.A. 2005. Polybrominated Diphenyl Ethers in House Dust and Clothes Dryer Lint. *Environ. Sci. Technol.* 39: 925-931.

Stoker, T.E., Laws, S.C., Crofton, K.M., Hedge, J.M., Ferrell, J.M. and Cooper, R.L. 2004. Assessment of DE-71, a commercial polybrominated diphenyl ether (PBDE) mixture, in the EDSP male and female pubertal protocols. *Toxicol Sci.* 78(1): 144-55.

Stoker, T.E., Cooper, R.L., Lambright, C.S., Wilson, V.S., Furr, J. and Gray, L.E. 2005. *In vivo* and *in vitro* anti-androgenic effects of DE-71, a commercial polybrominated diphenyl ether (PBDE) mixture. *Toxicol. Appl. Pharmacol.* 207(1): 78-88.

Strandberg, B., Dodder, N.G., Basu, I. and Hites, R.A. 2001. Concentrations and Spatial Variations of Polybrominated Diphenyl Ethers and Other Organohalogen Compounds in Great Lakes Air. *Environ. Sci. Technol.* 35: 1078-1083.

Swiss Agency for the Environment. 2002. Environmentally hazardous substances: Selected polybrominated flame retardants, PBDE and TBBPA – Substance flow analysis. Environmental series No. 338.

Sørmo, E.G., Salmer, M.P., Jenssen, B.M., Hop, H., Bæk, K., Kovacs, K.M., Lydersen, C., Falk-Pettersen, S., Gabrielsen, G.W., Lie, E. and Skaare, J.U. 2006. Biomagnification of brominated flame retardants in the polar bear food chain in Svalbard, Norway. Accepted for publication in *Environmental Toxicology and Chemistry*.

Talsness, C.E., Shakibaei, M., Kuriyama, S.N., Grande, S.W., Sterner-Kock, A., Schnitker, P., de Souza, C., Grote, K. and Chahoud, I. 2005. Ultrastructural changes observed in rat ovaries following *in utero* and lactational exposure to low doses of a polybrominated flame retardant. *Toxicol. Lett.* 157(3):189-202.

Thomas, G.O., Moss, S.E.W., Asplund, L. and Hall, A.J. 2005. Absorption of decabromodiphenyl ether and other organohalogen chemicals by grey seals (*Halichoerus grypus*). *Environ. Pollut.* 133: 581-6.

Thomsen, C., Frøshaug, M., Becher, G., Kvallem, H.E, Knutsen, H., Alexander, J., Bergsten, C. and Meltzer, H.M. 2004. PBDEs in serum from persons with varying consumption of fish and game. The third international workshop on brominated flame retardants, BFR 2004.

Thomsen, C., Liane, V., Frøshaug, M. and Becher, G. 2005. Levels of brominated flame retardants in human samples from Norway through three decades. *Organohalogen Compounds.* 67: 658-661.

Thron, K.U., Bruhn, R. and McLachlan, M.S. 2004. The influence of age, sex, body-condition, and region on the levels of PBDEs and toxaphene in harbour porpoises from European waters. *Fresenius Environ. Bull.* 13: 146-155.

Timme-Laragy, A.R., Levin, E.D. and Di Giulio, R.T. 2006. Developmental and behavioural effects of embryonic exposure to the polybrominated diphenyl ether mixture DE-71 in the killifish (*Fundulus heteroclitus*). *Chemosphere* 62: 1097-1104.

Ueno, D., Kajiwara, N., Tanaka, H., Subramanian, A., Fillmann, G., Lam, P.K.S., Zheng, G.J., Muchitar, M., Razak, H., Prudente, M., Chung, K. and Tanabe, S. 2004. Global Pollution Monitoring of Polybrominated Diphenyl Ethers Using Skipjack Tuna as a Bioindicator. *Environ. Sci. Technol.* 38: 2312-2316.

Van der Goon, D., van het Bolscher, M., Visschedijk, A.J.H. and Zandveld, P.Y.J. 2005. Study to the effectiveness of the UNECE persistent organic pollutants protocol and cost of possible additional measures. Phase I: Estimation of emission reduction resulting from the implementation of the POP protocol. TNO-report 2005/194.

VCCEP. 2003. US Voluntary Children's Chemical Evaluation Program. 2003. Tier 1 Assessment of the Potential Health Risks to Children Associated With Exposure to the Commercial Pentabromodiphenyl Ether Product, prepared for Great Lakes Chemical Corporation.

VCCEP. 2005. US Voluntary Children's Chemical Evaluation Program (VCCEP), Summary of Tier 1 Hazard Assessment, document 25 August 2005, accessed July 2006. <http://www.epa.gov.chemrtk/vccep/pubs/finalpenoct.pdf>.

Verreault, J., Gabrielsen, G.W., Letcher, R.I., Muir, D.C.G., and Chu, S. 2004. New and established organohalogen contaminants and their metabolites in plasma and eggs of glaucous gulls from Bear Island. SPFO-Report: 914/2004.

Verreault, J., Gabrielsen, G.W., Chu, S., Muir, D.C.G., Andersen, M., Hamaed, A. and Letcher, R.I. 2005. Flame Retardants and Methoxylated and Hydroxylated Polybrominated Diphenyl Ethers in Two Norwegian Arctic Top Predators: Glaucous Gulls and Polar Bears. *Environ. Sci. Technol.* 39: 6021-6028.

Viberg, H., Fredriksson, A. and Eriksson, P. 2002. Neonatal exposure to the brominated flame retardant 2,2',4,4',5-pentabromodiphenyl ether causes altered susceptibility in the cholinergic transmitter system in the adult mouse. *Toxicol. Sci.* 67: 104-7

Viberg, H., Fredriksson, A. and Eriksson, P. 2004. Investigation of strain and/or gender differences in developmental neurotoxic effects of polybrominated diphenyl ethers in mice. *Toxicol. Sci.* 81: 344-53.

VKM 2005. Vitenskapskomiteen for mattrygghet (Norwegian Scientific Committee for food safety.) Utalelse fra faggruppen for forurensninger, naturlige toksiner og medisinrester i matkjeden. Risikovurdering av PBDE. 04/504.

Vives, I., Grimalt, J.O., Lacorte, S., Guillaumon, M., Barceló, D. and Rosseland, B.O. 2004. Polybromodiphenyl Ether Flame Retardants in Fish from Lakes in European High Mountains and Greenland. *Environ. Sci. Technol.* 38: 2338-2344.

Voorspoels, S., Covaci, A. and Schepens, P. 2003. Polybrominated Diphenyl Ethers in Marine Species from the Belgian North Sea and the Western Scheldt Estuary: Levels, Profiles and Distribution. *Environ. Sci. Technol.* 37: 4348-4357.

Vorkamp, K., Christensen, J.H., Glasius, M. and Riget, F.R. 2004a. Persistent halogenated compounds in black guillemots (*Cephus grylle*) from Greenland – levels, compound patterns and spatial trends. *Mar. Pollut. Bull.* 48: 111-121.

Vorkamp, K., Christensen, J.H. and Riget, F.R. 2004b. Polybrominated diphenyl ethers and organochlorine compounds in biota from the marine environment of East Greenland. *Sci. Total Environ.* 331: 143-155.

Vorkamp, K., Thomsen, M., Falk, K., Leslie, H., Møller, S. and Sørensen, P.B. 2005. Temporal Development of Brominated Flame Retardants in Peregrine Falcon (*Falco peregrinus*) Eggs from South Greenland (1986-2003). *Environ. Sci. Technol.* 39: 8199-8206.

Vulykh, N., Dutchak, S., Mantseva, E. and Shatalov, V. 2004. EMEP contribution to the preparatory work for the review of the CLRTAP protocol on persistent organic pollutants. New Substances: Model assessment of potential for lon-range transboundary atmospheric transport and persistence of PentaBDE. EMEP MSC-E Information Note 10/2004. Metrological Synthesizing Centre-East.

Wang, D., Cai, Z., Jiang, G., Leung, A., Wong, M.H. and Wong, W.K. 2005. Determination of polybrominated diphenylethers in soil and sediment from an electronic waste recycling facility. *Chemosphere* 60: 810-816.

Washington State Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final Plan, December 1, 2005.

Weber, R. and Kuch, B. 2003. relevance of BFRs and thermal conditions on the formation pathways of brominated and brominated-chlorinated dibenzodioxins and dibenzofurans. *Environ. Int.* 29: 699-710.

Weiss, J., Meijer, L., Sauer, P., Lindeholm, L., Athanasiadis, I. and Bergman, Å. 2004. PBDE and HBCDD levels in blood from Dutch mothers and infants. The third international workshop on brominated flame retardants, BFR 2004.

Wilford, B.H., Shoeib, M., Harner, T., Zhu, J. and Jones, K.C. 2005. Polybrominated Diphenyl Ethers in Indoor Dust in Ottawa, Canada: Implications for Sources and Exposure. *Environ. Sci. Technol.* 39(18): 7027-7035.

Wolkers, H., van Bavel, B., Derocher, A.E., Wiig, Ø., Kovacs, K.M., Lydersen, C. and Lindström, G. 2004. Congener-Specific Accumulation and Food Chain Transfer of Polybrominated Diphenyl Ethers in Two Arctic Food Chains. *Environ. Sci. Technol.* 38: 1667-1674.

Xin-Ming Wang, Ding, X., Mai, B-X., Xie, Z-Q., Xiang, C-H., Sun, L-G., Sheng, G-Y., Fu, J-M. and Zeng, E.Y. 2005. Polybrominated Diphenyl Ethers in Airborne Particulates Collected During a Research Expedition from the Bohair Sea to the Arctic. *Environ. Sci. Technol.* 39: 7803-7809.

Zegers, B.N., Lewis, W.E. and Boon, J.P. 2000. Levels of Some Polybrominated Diphenyl Ether (PBDE) Flame Retardants in Dated Sediment Cores. *Organohalogen Compounds*, 47: 229-232.

Zegers, B.N., Lewis, W.A., Booij, K., Smittenberg, R.H., Boer, W., de Boer, J. and Boon, J.P. 2003. Levels of polybrominated diphenyl ether flame retardants in sediment cores from Western Europe. *Environ. Sci. Technol.* 37: 3803-3807.

Zennegg, M., Kohler, M., Gerecke, A.C. and Schmid, P. 2003. Polybrominated diphenyl ethers in whitefish from Swiss lakes and farmed rainbow trout. *Chemosphere* 51: 545-553.

Zhou, T., Ross, D.G., DeVito, M.J. and Crofton, K.M. 2001. Effects of short-term in vivo exposure to polybrominated diphenyl ethers on thyroid hormones and hepatic enzyme activities in weanling rats. *Toxicol. Sci.* 61: 76-82.

Zhou, T., Taylor, M.M., De Vito, M.J. and Crofton, K.M. 2002. Developmental exposure to brominated diphenyl ethers results in thyroid hormone disruption. *Toxicol. Sci.* 66: 105-116.