

商業用オクタブロモジフェニルエーテルの危険性の概要

分解性	蓄積性	人畜影響	動物への影響
<p>【生分解性】 分解せず(OECD TG 301D)</p> <p>【半減期】 ・大気中:(Hexa-Nona BDE)30.4-161.0日(OHラジカルとの反応)(AOPWIN)</p>	<p>【BCF(経鰓的生物濃縮係数)】 ・3I:(HexaBDPE)BCF=2580-5640 ・3I:(HeptaBDE)BCF<1.1-3.8 ・3I:(OctaBDE)BCF<9.5 ・3I:(c-OctaBDE)BCF<10-36</p> <p>【BMF(経口的生物濃縮係数)】 ・飼育中のタイセイヨウサケの餌に含まれるHeptaBDE 183をモニターした結果、95%がサケに蓄積。</p> <p>【BSAF(生物相-底質濃縮係数)】 ・2種の淡水魚:(HexaBDE)BSAF =1, (HeptaBDE)BSAF =2 ・(BDE 154) BSAF =9.1±1.1</p>	<p>【反復投与毒性】 ラット(28日):10mg/kg/dayでT4濃度減少(octa-BDE:30.7%, hepta-BDE:45.1%)</p> <p>【催奇形性・発生毒性】 ウサギ(経口 妊娠7~19日): 5mg/kg/dayで胎児毒性、 15mg/kg/dayで児の肝重量増加、体重増加量減少、骨形成遅延</p> <p>マウス(生後10日目単回):0.45mg/kgで2、4及び6月齢での異常行動並びに成長後の空間認識能・記憶の影響(BDE153)</p>	<p>アメリカチョウゲンボウ <i>Falco sparverius</i>:18.7 µg PBDEs/egg 及び15.6±0.3 ng PBDEs/g bw/dayで29日間曝露した雛鳥において、PHA応答(T細胞媒介性免疫)が増大し、抗体媒介性反応が減少した。脾臓(胚中心の減少)、滑液囊(アポトーシスの減少)、胸腺(マクロファージの増大)に構造的変化あり。脾臓の体細胞指標とPBDEs間及び滑液囊の体細胞指標とBDE-47間に負の相関性あり。</p>



Distr.: General
4 December 2007

English only



**United Nations
Environment
Programme**

**Stockholm Convention on Persistent Organic Pollutants
Persistent Organic Pollutants Review Committee
Third meeting
Geneva, 19–23 November 2007**

**Report of the Persistent Organic Pollutants Review Committee
on the work of its third meeting**

Addendum

Risk profile on commercial octabromodiphenyl ether

At its third meeting, the Persistent Organic Pollutants Review Committee adopted the risk profile on commercial octabromodiphenyl ether, on the basis of the draft contained in document UNEP/POPS/POPRC.3/14. The text of the risk profile, as amended, is set out below. It has not been formally edited.

**COMMERCIAL
OCTABROMODIPHENYL ETHER**

RISK PROFILE

Adopted by the Persistent Organic Pollutants Review Committee
at its third meeting

November 2007

TABLE OF CONTENTS

Executive summary.....	4
1. Introduction.....	6
1.1 Chemical identity of the proposed substance.....	6
1.2 Conclusion of the POP Review Committee of Annex D information.....	7
1.3 Data sources.....	7
1.4 Status of the chemical under international conventions.....	8
2. Summary information relevant for the risk profile.....	8
2.1 Sources.....	8
2.2 Environmental fate.....	9
2.2.1 Persistence.....	9
2.2.2 Bioaccumulation.....	9
2.2.3 Long range environmental transport.....	11
2.3 Exposure.....	11
2.3.1 Atmosphere.....	11
2.3.2 Water.....	12
2.3.3 Sediments.....	12
2.3.4 Soil.....	12
2.3.5 Waste Effluent and Biosolids.....	12
2.3.6 Biota.....	13
2.3.7 Humans.....	14
2.4 Hazard assessment for endpoints of concern.....	15
2.4.1. Experimental studies.....	15
2.4.2. Monitoring data on effects.....	16
3. Synthesis of the information.....	16
4. Concluding statement.....	18
References.....	19

Executive summary

The European Union and its Member States, which are Parties to the Stockholm Convention, submitted a proposal in July 2006 for listing octabromodiphenyl ether in Annex A of the Stockholm Convention pursuant to paragraph 1 of Article 8 of the Convention, and the POPRC agreed that the commercial product Commercial octabromodiphenyl ether (c-OctaBDE) – actually a mixture as described below - met the screening criteria of Annex D to the Convention. This risk profile reviews the available information on the commercial mixture and its main components: Hexa, Hepta, Octa and NonaBDE.

The polybrominated diphenyl ethers in general are used as flame retardants of the additive type. They are physically combined with the material being treated rather than chemically combined (as in reactive flame retardants). The commercial products cover several congeners and bromination levels. The information provided by the bromine industry indicates that (c-OctaBDE) has been produced in The Netherlands, France, USA, Japan, UK and Israel, but since 2004, it is no longer produced in the EU, USA and the Pacific Rim and there is no information that indicates it is being produced in developing countries. According to the Bromine Science and Environmental Forum (BSEF), OctaBDE was commercialized sometime in the mid 70's. By the early 2000's global production was <4000 tonnes/year and by the time production ceased, demand was <500 tonnes; assuming 30 years of production at 6000 tonnes per year total production volume would be around 180,000 tonnes.

Although the commercial OctaBDE seems to be not longer produced, releases during the service life of articles containing the commercial mixtures and at the end of article service life during disposal operations are still relevant. Switzerland reported for this country diffuse emission from the use of products containing OctaBDE of about 0.37 t/a (based on worst-case estimations) for a total stock of 680 tons.

The persistence of c-OctaBDE components in the environment is well documented. The only relevant degradation pathways identified until now are photolysis, anaerobic degradation and metabolism in biota, acting through debromination and producing other BDE which may have higher toxicity and bioaccumulation potential.

Assessing the bioaccumulation potential of c-OctaBDE components constitutes a main challenge in this risk profile. A high potential for bioaccumulation (including a moderate potential for bioconcentration) and food-web biomagnification has been demonstrated for HexaBDE, and it is fully in line with the reported elimination rates. The food-web biomagnification has been reported for HeptaBDE, although at a lower extent than expected from the Kow; this fact can be explained by metabolism resulting in a relatively short half-life (experimentally demonstrated and explained by the authors by debromination). The presence of Octa and NonaBDE in biota is well documented but its potential for bioaccumulation from water and food is much lower than expected from their Kow. Reduced availability, metabolisms or both can justify this fact. The number of scientific papers demonstrating debromination of Octa to DecaBDE to other PBDEs is continuously increasing; this is critical for the assessment as would indicate that the supposed low bioaccumulation potential could be in reality the consequence of metabolism to bioaccumulative PBDEs. A quantitative estimation cannot be presented yet, but the debromination process has been already reported for aquatic organisms, mammals and birds. This is an active research field, and new results will need to be assessed by the POPRC as they appear in refereed literature.

Biota monitoring data in remote areas offer the best demonstration on the potential for long range transport of the c-OctaBDE components, Hexa and HeptaBDE. The role of atmospheric transport is confirmed based on its detection in alpine lakes. The potential for long range transport has been observed for DecaBDE. The lack of confirmation for Octa and NonaBDE may be related to the lower relative contribution and/or metabolism via debromination.

No relevant effects have been observed in aquatic, sediment and soil laboratory studies; however, the measured endpoints and the exposure conditions employed in these assays are clearly insufficient for a proper assessment of chemicals such as Hexa to NonaBDE.

The available information on mammals and birds offer relevant information. The lowest reported NOAEL for traditional endpoints is 2-5 mg/kg bw/d. The effects are relevant for the health and the ecological assessments and therefore useful for assessing risks for humans and wildlife. In addition, immuno-toxicological effects and particularly delayed neurotoxic effects observed after a single dose require specific attention. A critical body burden for HexaBDE 153 of 2000 µg/kg lipid has been estimated based on a NOEL of 0.45 mg/kg; it should be noted that HexaBDE 153 concentrations close to these value have been found in several species and geographic sites and total PBDE concentrations frequently exceed this threshold by a large margin.

The evaluation of the human and environmental risk of commercial OctaBDE associated to its potential for long range transport must consider that the commercial product is a mixture of components with different properties and profiles, which may also be released to the environment due to its presence as components of other PBDE commercial products and also produced in the environment by debromination of commercial DecaBDE.

The greatest difficulty appears for the estimation of the potential hazard of the commercial mixture and its components. There are traditional ecotoxicological and toxicological studies where no effects have been observed even at unrealistically high concentrations. However, an in-depth assessment of these studies considering in particular the properties and toxicokinetic of PBDE indicates that the test design, exposure conditions and measured endpoints are not appropriate for a sound assessment of these types of chemicals. Thus, the lack of effects reported in those tests should be considered with care. Specific studies have reported particular hazards such as delayed neurotoxicity and immunotoxicity which may be particularly relevant in the assessment of both human health and ecosystem risks; although a quantitative evaluation of these effects in terms of hazard for human health and ecosystem is not possible based on the current level of information, it may become feasible soon if additional scientifically sound information is produced at a similar rate than in recent years.

Based on the existing evidence, it is concluded that the Hexa and HeptaBDE components of the octabromodiphenyl ether are likely, as a result of LRET, to lead to significant adverse human health and/or environmental effects, such that global action is warranted.

The increasing evidence related to debromination of Octa and Nona BDE into BDEs with POPs properties and considering that under Article 8, paragraph 7(a) of the Convention states that the lack of full scientific certainty shall not prevent a proposal from proceeding, it is concluded that the Octa and NonaBDE components of the octabromodiphenyl ether are likely, as a result of LRET, to lead to significant adverse human health and/or environmental effects, 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. The European Union and its Member States, which are Parties to the Stockholm Convention, submitted a proposal in July 2006 for listing octabromodiphenyl ether in Annex A of the Stockholm Convention pursuant to paragraph 1 of Article 8 of the Convention, and the POPRC agreed that the commercial product Commercial octabromodiphenyl ether – actually a mixture as described below – met the screening criteria of Annex D to the Convention.

1.1 Chemical identity of the proposed substance

This proposal concerns the c-OctaBDE. There are several components in the commercial product, with different properties and potential risks. Thus this risk profile focuses on the assessment of individual components of the commercial product, and the final compilation for an overall assessment of the commercial product itself.

It is believed that little if any c-OctaBDE is produced since the major supplier located in North America stopped production in 2004. The commercially supplied OctaBDE was complex mixture consisting (as of 2001 within the EU Member States) typically of $\leq 0.5\%$ Pentabromodiphenyl ether isomers, $\leq 1.2\%$ Hexabromodiphenyl ether isomers, $\leq 4.5\%$ Heptabromodiphenyl ether isomers, $\leq 33\%$ OctaBDE isomers, $\leq 10\%$ Nonabromodiphenyl ether isomers and $\leq 0.7\%$ Decabromodiphenyl ether. The composition of older products or products from non-EU countries may be different from this.

The c-OctaBDE is sold as a technical grade under the Chemical Abstracts Service (CAS) Registry number for the OctaBDE isomer.

IUPAC Name: Diphenyl ether, octabromo derivative (octabromodiphenyl ether, OctaBDE)

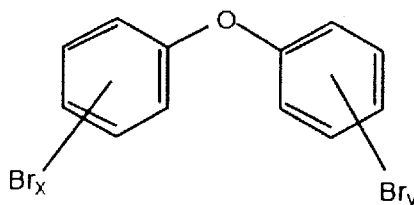
Synonyms: octabromobiphenyl oxide; octabromodiphenyl oxide; octabromo phenoxybenzene and benzene; 1,1' oxybis-, octabromo derivative

CAS Number: 32536-52-0

Molecular formula: $C_{12}H_2Br_8O$

Molecular weight: 801.38

Chemical structure: ($x+y=8$)



Three polybrominated diphenyl ether flame retardants were historically available commercially. They are referred to as penta, octa and decabromodiphenyl ether, but each product is a mixture of diphenyl ethers with varying degrees of bromination. Several synonyms and abbreviations for polybrominated diphenyl ethers exist and these are shown below:

polybrominated biphenyl ethers \equiv polybromobiphenyl ethers – PBBEs
 polybrominated biphenyl oxides \equiv polybromobiphenyl oxides - PBBOs
 polybrominated diphenyl ethers \equiv polybromodiphenyl ethers - PBDPEs
 polybrominated diphenyl oxides \equiv polybromodiphenyl oxides – PBDPOs

The abbreviations PBDE and BDE preceded by the number of bromine atoms (e.g. HeptaBDE) will be used in this document. The commercial mixtures will be identified by a c- (e.g. c-OctaBDE).

The compositions of the commercial polybrominated diphenyl ethers based on composite samples from the EU suppliers are shown in Table 1-1 below. These are the substances that have been used in the recent tests and used as a basis for the EU risk assessment reports (RAR) for the three commercial substances. La Guardia et al (2006) have recently reported additional information on the composition of commercial mixtures.

The commercial mixture covered by this entry is therefore a complex combination of isomers and congeners, as defined at POPRC. This risk profile will focus on the series of Hexa, Hepta, Octa and Nona homologues, as the Penta and Deca homologues are covered by their respective commercial mixtures. There is a tendency in scientific literature to present the identities of polybrominated diphenyl ether congeners using the numbering system based on the polychlorinated biphenyl system:

- Hexabromodiphenyl ethers (benzene, 1,1'-oxybis-, hexabromo derivative; HexaBDE) (CAS No. 36483-60-0; IUPAC N° between BDE-128 and BDE-169)
- Heptabromodiphenyl ethers (benzene, 1,1'-oxybis-, heptabromo derivative; HeptaBDE) (CAS No. 68928-80-3; IUPAC N° between BDE-170 and BDE-193)
- octabromodiphenyl ethers (benzene, 1,1'-oxybis-, octabromo derivative; OctaBDE) (CAS No. 32536-52-0; IUPAC N° between BDE-194 and BDE-205)
- Nonabromodiphenyl ethers (benzene, 1,1'-oxybis-, nonabromo derivative; NonaBDE) (CAS No. 63936-56-1; IUPAC N° between BDE-206 and BDE-208)

Table 1-1. Composition of commercial polybrominated diphenyl ethers as described in the EU RAR.

Component	% Composition of commercial product			
	Penta-		Octa-	Deca-
	1997	2000	1997	1997
Tribromodiphenyl ether		0.23		
Tetrabromodiphenyl ether	33.7	36.02		
Pentabromodiphenyl ether	54.6	55.10		
Hexabromodiphenyl ether	11.7	8.58	5.5	
Heptabromodiphenyl ether			42.3	
Octabromodiphenyl ether			36.1	0.04
Nonabromodiphenyl ether			13.9	2.5
Decabromodiphenyl ether			2.1	97.4

The complexity for setting a risk profile for a complex mixture has been already discussed by the POPRC with reference to the commercial mixture of pentabromodiphenyl ether. A full data set for conducting a risk profile is not available for the commercial mixture or for the individual components. Thus the available pieces of information have been combined in this risk profile. The information was particularly scarce for Hepta- to NonaBDEs but there is an increasing interest in the scientific community for covering these congeners. A quantitative assessment is still not possible nowadays, but may become feasible soon if additional scientifically sound information is produced at a similar rate than in recent years,

1.2 Conclusion of the POP Review Committee of Annex D information

The POPRC has evaluated Annex D information and has concluded that proposal fulfils the requirements of Article 8 and Annex D of the Convention (POPRC-2/6)

1.3 Data sources

The EU risk assessment report (EC, 2003), the Canadian assessment (Environment Canada, 2004), and references from the WHO (1994) report were the main source of information used by the POP RC in Annex D screening. Additional information has been submitted by Canada, the Czech Republic, Germany, Japan, Lithuania, Norway, Switzerland, Turkey, UK, USA, the NGO Environmental Health Fund on behalf of the International POPs Elimination Network (IPEN), and the industry organization Bromine Science and Environmental Forum (BSEF), as well as during the consultation period. Considering the large amount of new scientific information produced nowadays, a review of recent scientific literature has also been conducted and used as an essential data source in this report.

1.4 Status of the chemical under international conventions

- OSPAR Convention: OctaBDE is included in the list of selected substances for the OSPAR lists (no 236). Under the reviewed list, OctaBDE is put under section C – about the substances put on hold because they are not produced and/or used in the OSPAR catchment or are used in sufficiently contained systems making a threat to the marine environment unlikely.
- UNECE, Convention on Long-range Transboundary Air Pollution (LRTAP) and its Protocol on Persistent Organic Pollutants (POPs): c-OctaBDE is being considered under Protocol procedures for inclusion.

2. Summary information relevant for the risk profile

2.1 Sources

The information provided by the bromide industry indicates that the commercial product has been produced in The Netherlands, France, USA, Japan, UK and Israel, but since 2004, it is no longer produced in the EU, USA and the Pacific Rim and there is no information that indicates it is being produced in developing countries.

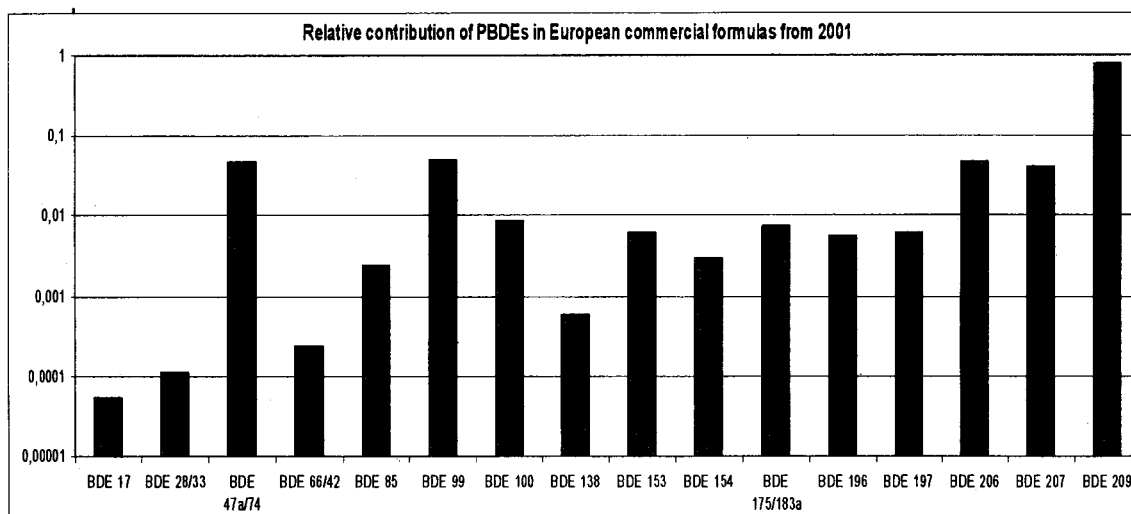
The polybrominated diphenyl ethers in general are used as flame retardants of the additive type. They are physically combined with the material being treated rather than chemically combined (as in reactive flame retardants). This means that there is the possibility that the flame retardant may diffuse out of the treated material to some extent. Industry indicates that octabromodiphenyl ether is always used in conjunction with antimony trioxide. In Europe, it is primarily used in acrylonitrile-butadiene-styrene (ABS) polymers at 12-18% weight loadings in the final product. Around 95% of the total octabromodiphenyl ether supplied in the EU is used in ABS. Other minor uses, accounting for the remaining 5% use, include high impact polystyrene (HIPS), polybutylene terephthalate (PBT) and polyamide polymers, at typical loadings of 12-15% weight in the final product. In some applications, the flame retardant is compounded with the polymer to produce pellets (masterbatch) with slightly higher loadings of flame retardant. These are then used in the polymer processing step to produce products with similar loadings as given above.

The flame retarded polymer products are typically used for the housings of office equipment and business machines. Other uses that have been reported for octabromodiphenyl ether include nylon and low density polyethylene (WHO, 1994), polycarbonate, phenol-formaldehyde resins and unsaturated polyesters (OECD, 1994) and in adhesives and coatings (WHO, 1994).

Assuming that the commercial OctaBDE is not longer produced, the releases to the environment must be associated to historical processes, as well as to releases during the service life of articles containing the commercial mixtures and at the end of article service life during disposal operations. The information review by La Guardia et al (2006) allows estimations of the relative contribution of each congener in different markets and time periods. As an example, Figure 1-1 presents the calculations for European commercial products in 2001.

Although there are some figures on annual production of this mixture, there are no accurate values on the amount of the commercial Octa and/or the individual homologues in articles in service and disposed at the world-wide level, but considering the estimated figure of 6 000 tonnes/year (WHO, 1994) the total amount should be expected in the $10^5 - 10^6$ tonnes range. According to the BSEF, OctaBDE was commercialized sometime in the mid 70's. By the early 2000's global production was <4000 tonnes/year and by the time production ceased, demand was <500 tonnes. While thus, assuming 30 years of production at 6000 tonnes per year gives 180,000 tonnes, a figure within the proposed range.

Figure 1-1. Estimated relative contribution for the different BDE congeners in products in the European market in 2001. Calculated from data published by La Guardia et al., 2006. Note the logarithmic scale.



Morf et al., (2002) reported for Switzerland diffuse emission from the use of products containing OctaBDE of about 0.37 t/a (based on worst-case estimations) for a total stock of 680 tons.

2.2 Environmental fate

2.2.1 Persistence

No aerobic biodegradation of the Hexa- to NonaBDEs is expected based on BIOWIN estimates as recalcitrant with respect to biodegradation, and no degradation, based on oxygen uptake, occurred in a 28-day closed bottle test OECD 301D (EC, 2003).

Gerecke et al. (2005) reported the degradation of NonaBDE 206 and 207 and DecaBDE to OctaBDEs under anaerobic conditions using sewage sludge inoculum; and this degradation has been confirmed in other studies (Gaul et al, 2006; He et al, 2006).

AOPWIN predicts half-lives for reaction with atmospheric hydroxyl radicals ranging from 30.4 to 161.0 d for Hexa- to NonaBDEs, respectively. However, in the atmosphere, Hexa to NonaBDEs are expected to strongly adsorb to suspended particles in the air and be removed via wet and/or dry deposition. Note that predicted half-lives have not been empirically substantiated, but are provided for reference purposes.

The photodecomposition of several BDEs has been studied in different matrices such as sealed polyethylene tube exposed to natural sunlight for up to 120 min (Peterman et al. 2003); or water (Sanchez-Prado et al., 2006); in general degradation was faster for the higher brominated DEs than for the lower brominated congeners. Rayne et al. (2006) suggest a short photochemical half-life for the Hexa BDE153 in aquatic systems, with rapid photohydrodebromination to some of the most prevalent Penta- and Tetra-brominated diphenyl ether congeners.

2.2.2 Bioaccumulation

The bioaccumulation potential differs strongly among the components of the commercial mixture. For facilitating, the assessment, the different bioaccumulation processes will be presented independently.

2.2.2.1. Bioconcentration from water

Bioconcentration from water is considered relevant only for HexaBDE. The UK has re-analyzed the CITI (1982) bioconcentration data and suggests BCFs of up to ~5,640 l/kg and ~2,580 l/kg for components D and E (both HexaBDE).

Bioconcentration factors were reported (EC, 2003) for carp. Assuming that the actual concentrations of the c-OctaBDE components were at or around the reported water solubility for the substance of 0.5 µg/L, then the BCF for OctaBDE would be <9.5; for HeptaBDE about <1.1-3.8 and for c-OctaBDE about <10-36. These BCF values are lower

than would be expected from the substance's octanol-water partition coefficients. This can be explained by a reduced bioavailability, metabolisms or both

2.2.2.2 Bioaccumulation and biomagnification from food exposures.

Oral exposure is expected to be the most relevant exposure pathway for these chemicals. Van Beusekom et al. (2006) reported biota-sediment accumulation factors between 1 and 3 for Hexa and HeptaBDE on two freshwater fish species in Spain and concluded that 100% of the exposure was associated to food or food plus sediment for bleak (*Alburnus alburnus*) and barbel (*Barbus graellsii*), respectively.

A controlled feeding trial assessed transfer and accumulation of PBDEs from feed to farmed Atlantic salmon (*Salmo salar*). On average, 95% of the total PBDE content in the feed accumulated in whole salmon including HeptaBDE 183 (Isosaari, et al. 2005).

The potential for biomagnification has been demonstrated for Hexa and HeptaBDE (Burreau et al., 2004, 2006; Sormo et al., 2006; Tomy et al., 2004), and more recently suggested for the DecaBDE (Law et al., 2006).

Food-web biomagnification was not been observed for Octa and NonaBDE in an aquatic ecosystem, but the congeners were detected in biota from zooplankton to fish species (Burreau et al. 2006).

2.2.2.3. Bioaccumulation from sediment exposures

Ciparis and Hale (2005) have reported a rapid bioaccumulation of HexaBDE in the aquatic oligochaete, *Lumbriculus variegatus*, exposed via sediment, with differences between isomers and in the contamination pathway. A biota-sediment accumulation factor of 9.1 ± 1.1 was observed for BDE 154, the highest concentration was found on day 15 and the depuration rate constant was $0.032 \pm 0.016 \text{ days}^{-1}$.

2.2.2.4. Toxicokinetics and relevance of metabolisms

The potential for bioaccumulation and biomagnification of these types of molecules can be calculated using toxicokinetic models, based on metabolism and elimination. Differences among isomers and the reported debromination processes introduce additional uncertainty when reviewing field data.

Stapleton et al. (2004) in a dietary study on carps found depuration rates of $0.051 \pm 0.036 \text{ days}^{-1}$ and assimilation efficiencies of $4\% \pm 3$ for the HexaBDE 153. Stapleton and Baker (2003) and Stapleton et al. (2004b) in dietary studies on common carp (*Cyprinus carpio*) found significant and rapid debromination of HeptaBDE183 to HexaBDE154 and to another unidentified HexaBDE congener within the intestinal tissues of the carp after consuming its food. *In vitro* studies have demonstrated the microsomal debromination in fish (Stapleton et al. (2006).

Tomy et al (2004) exposed juvenile lake trout (*Salvelinus namaycush*) to three dietary concentrations of 13 BDE congeners (3-10 Br atoms) in the laboratory for 56 days, followed by 112 days of clean food. Half-lives ($t_{1/2}$'s) for some BDE congeners (e.g., BDE-85 and -190) were much lower than expected based on their Kow, whereas $t_{1/2}$'s of other BDE congeners (e.g., BDE-66, -77, -153, and -154) were much longer than anticipated based on Kow. This was explained by debromination. The detection of three BDE congeners (an unknown PentaBDE, BDE-140, and an unknown HexaBDE) in the fish that were not present in the food or in the control fish provided further evidence for the debromination of BDEs.

The role of exposure levels in the elimination rate of several chemicals including HexaBDE 153 has been studied by the LPTC). Université Bordeaux I and the INIA's Laboratory for Ecotoxicology within the context of LRI-Cefic Research Project ECO-1AINIA-1100. Depuration rates of 0.03-0.05 for *Sparus aurata* and *Mytilus edulis*, were obtained (Alonso et al., 2006)

The debromination of PBDEs has also indicated in mammals, e.g. for a c-PentaBDE formulation in mice (Qiu et al., 2007) and for DecaBDE in cows (Kierkegaard et al., 2007).

A recent study (Drouillard et al., 2007) has reported a depuration rate constant for the HexaBDE 0.016 days^{-1} in juvenile American kestrels (*Falco sparverius*), with a retention of about 50% of the administered dose in a 36 days study.

Van den Steen et al. (2007) used silastic implants to expose European starlings (*Sturnus vulgaris*) to DecaBDE209 and found Octa- (BDE196, BDE197) and NonaBDEs (BDE206, BDE207, BDE208) in muscle and liver in addition to DecaBDE209, resulting in the first indications of debromination in birds.

2.2.2.5 *Integrated assessment of the bioaccumulation potential.*

A high potential for bioaccumulation (including a moderate potential for bioconcentration) and food-web biomagnification has been demonstrated for HexaBDE; and it is fully in line with the reported elimination rates.

The food-web biomagnification has been also demonstrated for HeptaBDE, although at a lower extent than expected from the Kow; this fact can be explained by metabolism resulting in a relatively short half-life (experimentally demonstrated and explained by the authors by debromination).

The presence of Octa and NonaBDE in biota is well document but its potential for bioaccumulation from water and food is much lower than expected from their Kow. Reduced availability, metabolisms or both can justify this fact. The number of scientific papers demonstrating debromination of Deca-, Nona, and Octa- BDE to other PBDEs is continuously increasing; this is critical for the assessment as would indicate that the supposed low bioaccumulation potential could be in reality the consequence of metabolism to bioaccumulative PBDEs. A quantitative estimation cannot be presented yet, but the debromination process has been already reported for aquatic organisms, mammals and birds.

2.2.3 Long range environmental transport

The presence of components of commercial Octa BDE in remote areas (e.g. Norway info, Norway Info 2; Canada info 2; Switzerland info2, Japan info) is considered the best demonstration for the potential for long range transport of these chemicals. As debromination in biota has been demonstrated, hypothetically, the presence of Hexa to NonaBDEs could be explained by a long range transport of DecaBDE and its subsequent debromination, however, since Hexa to Deca congeners have similar atmospheric transport characteristics in terms of gas-partitioning and reactivity it is evidence of long range transport for DecaBDE and is indirect evidence of long range transport for the Nona to Hexa congeners.

Previous model predictions suggested a low potential for long-range atmospheric transport for highly brominated BDEs (e.g. Wania and Dugani, 2003). However, in a recent paper on DecaBDE, Breivik et al., (2006) have reported that chemicals that are both sorbed to particles and potentially persistent in the atmosphere, such as BDE-209, may have a larger potential for LRT than anticipated on the basis of earlier model evaluations. This explanation could be also applied to c-OctaBDE components.

Recently Wegmann, et al, (2007) applied the OECD Pov and LRTP Screening Tool to the current POPs candidates, including c-OctaBDE. The authors noted that they believed that the substance property values for c-OctaBDE in Wania and Dugani (2003) were more accurate than the values in the POPRC document and therefore included the Wania and Dugani values in their Monte Carlo uncertainty analysis. Although there were considerable uncertainties, the results indicated that c-OctaBDE has Pov and LRTP properties similar to those of several known POPs.

2.3 Exposure

2.3.1 Atmosphere

Strandberg et al. (2001) analyzed air samples from urban, rural and remote sites in the United States near the Great Lakes. The average total c-OctaBDE-related congeners (i.e., sum of BDEs 153, 154 and 190) present in the samples ranged from approximately 0.2 to 0.9 pg/m³.

Bergander et al. (1995) analyzed air samples from two areas of Sweden remote from industry, HexaBDE and HeptaBDE were found in the particulate phase samples.

In a monitoring study carried out in coastal areas of Korea over one-year period, twenty individual PBDE congeners were found in atmospheric samples collected from urban, suburban and rural sites. DecaBDE (BDE 209) was the predominant congener (<93%) The depositional fluxes ranged from 10.1 to 89.0 µg/m²/year (Moon et al., 2007a). In northwest China, the measurements of total PBDEs (8.3 ± 4.0 pg/m³) in the samples collected at the Waliguan Baseline Observatory (April to May, 2005) were at comparable concentration levels with other remote areas (Cheng et al., 2007).

PBDEs have also been detected over the Indian Ocean (mean concentration of 2.5 pg/m³) and along the coastal line of Java, Indonesia (values of 15 pg/m³). Air back trajectory analysis is suggested in relation to the potential of PBDEs for long-range atmospheric transport from remote regions of areas more industrialized (Wurl et al. 2006).

Wang et al. (2005,) report atmospheric concentrations for c-OctaBDE components for a large number of remote locations, and additional information about the presence of Penta to HeptaBDE congeners in air at several locations can be found in the review paper by de Wit et al. (2006).

2.3.2 Water

Luckey et al. (2002) measured total PBDE (mono- to HeptaBDE congeners) concentrations of approximately 6 µg/L in Lake Ontario surface waters in 1999, with HexaBDE congeners BDE153 and BDE154 each contributing approximately 5 to 8% of the total.

C-OctaBDE was not detected in 1987 in 75 surface water samples taken in Japan at a detection limit of 0.1 µg/L or in 1988 in 147 water samples at a detection limit of 0.07 µg/L (Environment Agency Japan 1991). According to EC (2003), the concentrations are considered to be representative of industrial, urban and rural areas of Japan, but it is not known whether any of the sampling sites were in the vicinity of a polybrominated diphenyl ether production site or a polymer processing site.

There is additional information on concentrations of c-OctaBDE components (HexaBDEs 153 and 154) in the dissolved phase in water in a study by Law et al. (2006).

2.3.3 Sediments

Concentrations of c-OctaBDE in UK sediments ranged from <0.44 to 3030 µg/kg dw (Allchin et al. 1999; Law et al. 1996; Environment Agency UK, 1997). The highest levels were in sediments downstream from a warehouse where c-DecaBDE was stored. C-OctaBDE was detected in 3 of 51 sediment samples from Japan in 1987 at concentrations from 8 to 21 µg/kg (detection limit 7 µg/kg; ww or dw not specified), and in 3 of 135 samples collected in 1988 at concentrations of 15 to 22 µg/kg (detection limit 5 µg/kg; ww or dw not specified) (Environment Agency Japan 1991).

Kolic et al. (2004) presented levels of PBDEs in sediments from tributaries flowing to Lake Ontario, and area biosolids in southern Ontario. Total Hexa- and HeptaBDEs (i.e., BDE 138, 153, 154 and 183) measured in sediment samples taken from fourteen tributary sites (only 6 sites were reported) ranged from approximately 0.5 to 4.0 µg/kg dw.

Historical trends of PBDEs in sediments have been determined in the Lake of Ellasjøen, Norwegian Arctic, where contamination is due to both atmospheric and biological transport. Maximum level of PBDEs was detected in 2001 (0.73 ng/g dw) (Evenset et al., 2007). Marvin et al. 2007, have reported temporal trends in PBDEs in Niagara river suspended sediments from 1988 to 2004. Prior to 1988, PBDEs (sum of 16 congeners including DecaBDE) were generally detected at low-ppb concentrations, but showed a trend toward increasing concentrations over the period 1980–1988. After 1988, PBDE concentrations in the Niagara River showed a more rapidly increasing trend (maximum of approximately 35 ng/g in 1995). DecaBDE was the predominant congener detected, and a similar situation has been observed in Europe (Eljarrat et al., 2005), and Asia (Moon et al. 2007b).

The study by Law et al. (2006) provides additional information on concentrations of c-OctaBDE components (HexaBDEs 153 and 154) for sediments at a background location.

2.3.4 Soil

Hassanin et al. (2004) determined PBDEs in undisturbed surface soils (0-5 cm) and subsurface soils from remote/rural woodland and grassland sites on a latitudinal transect through the United Kingdom and Norway. In total, 66 surface soils were analyzed for 22 tri- to HeptaBDEs. Concentrations of total PBDEs in the surface soils ranged from 0.065 to 12.0 µg/kg dw. Median PBDE concentrations in the surface soils ranged from 0.61 to 2.5 µg/kg dw, with BDEs 47, 99, 100, 153 and 154 dominating the total concentrations. The median concentration of the sum of these five congeners ranged from 0.44 to 1.8 µg/kg dw. The researchers noted that the congener patterns in the European background soils closely matched that reported for the c-PentaBDE mixture. Northward along the latitudinal transect, there was an increasing relative contribution of BDE 47 and other lighter PBDEs in comparison to the heavier PBDEs measured in the samples.

2.3.5 Waste Effluent and Biosolids

Kolic et al. (2004) presented levels of PBDEs in sediments from tributaries flowing to Lake Ontario, and of biosolids from nearby wastewater treatment facilities in southern Ontario. Total Hexa- and HeptaBDEs (i.e., BDEs 138, 153, 154 and 183) measured in biosolids ranged from approximately 111 to 178 µg/kg dw.

La Guardia (2001) analyzed 11 sewage sludge samples before land application from Canada and the United States and found that total Hexa- to OctaBDE congener concentrations ranged from 40 to 2080 µg/kg dw. Kolic et al. (2003) investigated PBDE levels in sewage sludge from 12 sites in southern Ontario and found Hexa- to OctaBDE congener concentrations totaled 124 to 705 µg/kg dw. Hexa- to OctaBDE congeners were not detected in manure samples, and were at very low levels in pulp mill biosolids (up to approximately 3 µg/kg dw).

Martinez et al. (2006) have recently reported concentrations of sum of Hexa to NonaBDE in the range of 15.5 to 160 µg/kg dw in sludge from municipal wastewater treatment facilities in Spain, and up to 268 µg/kg dw in industrial facilities.

Gevaio et al. (2006) measured PBDEs in coastal sediments receiving industrial and municipal effluents in Kuwait. Total concentrations varied from 80 to 3800 µg/g dw with HeptaBDE183 dominating the congener distribution which resembled the commercial formulation, Bromkal 79-8DE. Wastewater discharge from industrial activities appeared to be the primary source of the compounds.

2.3.6 Biota

Concentrations of components found in c-OctaBDEs in biota were reviewed in Law et al. (2003). The concentration of c-OctaBDE (reported as the commercial mixture DE-79) in various biota found in aquatic environments in the UK ranged up to 325 µg/kg ww in the liver of dab (Allchin et al. 1999). Concentrations of OctaBDE in muscle tissue from UK fish ranged from <1 to 12 µg/kg ww (Allchin et al. 1999). In Japan, OctaBDE was not detected in 75 fish samples taken in 1987 (detection limit 5 µg/kg ww), nor was it detected in 144 fish samples taken from 48 locations in 1988-89 (detection limit 4 µg/kg; ww or dw not specified) (Environment Agency Japan 1991). HeptaBDE, along with other PBDE congeners, was detected in eggs of peregrine falcons, *Falco peregrinus*, from Sweden, at concentrations from 56 to 1300 µg/kg lipid (Lindberg et al. 2004).

Alaee et al. (1999) sampled lake trout from Lakes Superior, Huron and Ontario and found that the total of HexaBDE and HeptaBDE congeners ranged from an estimated 11 to 53 µg/kg lipid.

Rice et al. (2002) compared PBDE levels and congener patterns in carp and bass sampled from two industrialized regions in the eastern U.S. The fish were collected from the Detroit River, MI. and the Des Plaines River, IL. in May and June of 1999, and analyzed for the presence of BDEs 47, 99, 100, 153, 154, 181, 183 and 190. Both river systems are considered to receive high contributions from municipal and industrial effluents. BDE47 dominated in fish taken from the Detroit River, comprising an average of 53 to 56% of the total PBDEs by wet weight. BDEs 99, 100, 153 and 154 each contributed between 8 and 9%, and BDEs 181 and 183 each comprised about 5% of the total PBDEs. BDE190 was not detected in either fish species. Only carp were sampled from the Des Plaines River, and these exhibited a markedly different PBDE profile from that seen in the Detroit River fish. HeptaBDEs 181 and 183 were predominant, contributing about 21% and 19%, respectively. BDE47 was third in prevalence, comprising about 17% of the total PBDEs. Levels of the two HexaBDE congeners, BDEs 153 and 154 were 8 to 13%, compared with about 5% for each of the Penta- congeners, BDEs 99 and 100. BDE190, not detected in the Detroit River fish, was present at about 12% of total PBDE.

Norstrom et al. (2002) evaluated the geographical distribution and temporal trends (during the 1981 to 2000 period) of PBDEs in herring gull (*Larus argentatus*) eggs from a network of colonies scattered throughout the Great Lakes and their connecting channels in 2000 (see Section 2.1.6.6 and Appendix D). Although samples were analyzed for Octa- to DecaBDE, these were not found at their respective limits of detection (0.01-0.05 µg/kg ww). However, total concentrations of Hexa- and HeptaBDE congeners (i.e., BDEs 153, 154 and 183) increased 6 to 30 fold over the 1981 to 2000 period at the Lake Michigan (from 6.7 to 195.6 µg/kg ww), Lake Huron (from 13.8 to 87.6 µg/kg ww) and Lake Ontario (3.8 to 112.1 µg/kg ww) sites. This increase was not as dramatic as that found for the tetra- and PentaBDE congeners.

Wakeford et al. (2002) conducted sampling of wild bird eggs in western and northern Canada between 1983 and 2000. They determined that the total of Hexa- and HeptaBDE congeners ranged from 0.148 to 52.9 µg/kg ww in Great Blue Heron (*Ardea herodias*) eggs (on Canada's west coast), 0.03 to 0.68 µg/kg ww in Northern Fulmer (*Fulmarus glacialis*) eggs (in the Canadian arctic) and 0.009 to 0.499 µg/kg ww in Thick Billed Murre (*Uria lomvia*) eggs (in the Canadian arctic). OctaBDE, NonaBDE and DecaBDE congeners were subject to analysis by the researchers, but were not detected (detection limit was not specified) in the any of the samples.

Temporal, spatial, and interspecific trends in PBDEs were determined in eggs of marine and freshwater bird species from the province of British Columbia, Canada. Temporal trends in the Fraser River estuary, 1983-2002, were examined by analysis of eggs of great blue herons (*Ardea herodias*) and from the Strait of Georgia marine ecosystem, 1979-2002, in eggs of double-crested cormorants (*Phalacrocorax auritus*). PBDEs increased exponentially with a doubling time of 5.7 years in eggs of both herons and cormorants. The PBDE pattern was relatively consistent in most years and sites, with BDEs 47 > 100 > 99 > 153 > 154 > 28 > 183. This was interpreted as evidence of technical PentaBDE formulations as primary sources of the contamination, with the OctaBDE formulations as secondary. Higher resolution analysis of a subsample of the eggs revealed the presence of up to nine other congeners, including BDE209 (range: 0.9-1.8 microg/kg), indicating exposure and uptake of DecaBDE sourced congeners in North American foodchains (Elliot et al., 2005)

A recent study (Burreau et al., 2006) has demonstrated the presence of Hexa to NonaBDE in biota (zooplankton, sprat, herring and salmon) from the Baltic Sea and Northern Atlantic.