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Canadian Environmental Protection Act, 1999 Environmental Screening Assessment Report on Polybrominated Diphenyl Ethers (PBDEs)

## February 2004

### **Environment Canada**

$$Br_{x}$$
  $Br_{y}$  where  $x + y = 1$  to 10

Figure 1. PBDE structure

### Introduction

The Canadian Environmental Protection Act, 1999 (CEPA 1999) requires the Minister of the Environment and the Minister of Health to conduct screening assessments of substances that meet the categorization criteria set out in the Act and Regulations to determine, in an expeditious manner, whether substances present or may present a risk to the environment or to human health. Based on the results of a screening assessment, the Ministers can propose taking no further action with respect to the substance, adding the substance to the Priority Substances List (PSL) for further assessment, or recommending that the substance be added to the List of Toxic Substances in Schedule 1 and, where applicable, the implementation of virtual elimination.

A screening assessment involves an analysis of a substance using conservative assumptions to determine whether the substance is "toxic" or capable of becoming "toxic" as defined in CEPA 1999. This environmental screening assessment examines various supporting information and develops conclusions based on a weight of evidence approach as required under Section 76.1 of CEPA 1999. The screening assessment does not present an exhaustive review of all available data; rather, it presents the most critical studies and lines of evidence supporting the conclusions. One line of evidence includes consideration of risk quotients to identify potential for ecological effects. However, other concerns that affect current or potential risk, such as persistence, bioaccumulation, chemical transformation and trends in ambient concentrations, are also examined in this report.

Seven polybrominated diphenyl ethers (PBDEs) were identified in a pilot project list of 123 substances for screening assessment under CEPA 1999, on the basis of their potential persistence and/or bioaccumulation in the environment and inherent toxicity to environmental organisms.

Data relevant to the environmental screening assessment of PBDEs were identified in original literature, review documents, and commercial and government databases and indices. In addition to retrieving the references from a literature database search, direct contacts were made with researchers, academics, industry and other government agencies to obtain relevant information on PBDEs. Ongoing scans were conducted of the open literature, conference proceedings and the Internet for relevant PBDE information. Data obtained as of October 2003 were considered in this document. In addition, an industry survey on PBDEs was conducted for the year 2000 through a Canada Gazette Notice issued pursuant to Section 71 of CEPA 1999. This survey collected data on the Canadian manufacture, import, uses and releases of PBDEs (Environment Canada). Toxicological studies were also submitted by industry under Section 70 of CEPA 1999.

This environmental screening assessment report and associated unpublished supporting working documentation was written by a team of Environment Canada evaluators at the Environmental Protection Branch, Pacific and Yukon Region, Vancouver, B.C., with the assistance of evaluators and management at the Existing Substances Branch, Gatineau, Quebec. The substance matter in this report has been subjected to external review by Canadian and international experts selected from government and academia, including M. Alaee (Environment Canada, National Water Research Institute), L. Birnbaum (U.S. Environmental Protection Agency), C. de Wit (Stockholm University), S. Dungey (UK Environment Agency), R. Hale (College of William and Mary, Virginia), R. Law (UK Centre for Environmental, Fisheries and Aquaculture Science), F. Luckey (U.S. Environmental Protection Agency), J. Maguire (Environment Canada, National Water Research Institute), R. Norstrom (Environment Canada, National Wildlife Research Centre), D. Stewart (Environment Canada, Ontario Region).

The environmental and human health screening assessment reports were approved by the joint Environment Canada/Health Canada CEPA Management Committee. The supporting working documentation for the environmental assessment is available upon request by e-mail from PSL.LSIP@ec.gc.ca. Information on environmental screening assessments under CEPA 1999 is available at http://www.ec.gc.ca/substances/ese. The supporting working documentation for the human health assessment is available upon request by e-mail from ExSD@hc-sc.gc.ca. Additional background information on health screening assessments conducted under this program is available at http://www.hc-sc.gc.ca/hecs-sesc/exsd/splash.htm.

The critical information and considerations upon which the assessment is based are summarized below.

### **Identity, Uses and Sources of Release**

PBDEs comprise a class of substances consisting of 209 possible congeners with 1–10 bromine atoms. The following seven PBDE homologues are on the Domestic Substances list (DSL) and were identified in the pilot project list of 123 substances and are considered in this assessment:

- tetrabromodiphenyl ether (benzene, 1,1'-oxybis-, tetrabromo derivative; tetraBDE) (CAS No. 40088-47-9);
- pentabromodiphenyl ether (benzene, 1,1'- oxybis-, pentabromo derivative; pentaBDE) (CAS No. 32534-81-9);
- hexabromodiphenyl ether (benzene, 1,1'-oxybis-, hexabromo derivative; hexaBDE) (CAS No. 36483-60-0);
- heptabromodiphenyl ether (benzene, 1,1'-oxybis-, heptabromo derivative; heptaBDE)(CAS No. 68928-80-3);
- octabromodiphenyl ether (benzene, 1,1'-oxybis-, octabromo derivative; octaBDE) (CAS No. 32536-52-0);
- nonabromodiphenyl ether (benzene, 1,1'-oxybis-, nonabromo derivative; nonaBDE) (CAS No. 63936-56-1); and
- decabromodiphenyl ether; bis(pentabromophenyl) ether (benzene, 1,1'-oxybis[2,3,4,5,6-pentabromo-; decaBDE) (CAS No. 1163-19-5).

These PBDEs are found in three commercial mixtures, typically referred to as Pentabromodiphenyl Ether (PeBDE), Octabromodiphenyl Ether (OBDE) and Decabromodiphenyl Ether (DBDE). PeBDE is predominantly a mixture of pentaBDE, tetraBDE and hexaBDE congeners, but may also contain trace levels of heptaBDE and tribromodiphenyl ether (triBDE) congeners. OBDE is a mixture composed mainly of heptaBDE, octaBDE and hexaBDE, but may also contain small amounts of nonaBDE and decaBDE. Current formulations of DBDE are almost completely composed of decaBDE and a very small amount of nonaBDE.

PBDEs are used mainly as additive flame retardants in polymer resins and plastics and, to a lesser extent, adhesives, sealants and coatings. Additive flame retardants are physically combined with the material being treated rather than chemically bonded as in reactive flame retardants; therefore, they are more susceptible, to a certain extent, to migration and loss from the polymer matrix. It has been estimated that approximately 90% or more of PeBDE produced globally is used in polyurethane foams in office and residential furniture, automotive upholstery, sound insulation and wood imitation products (WHO 1994; European Communities 2000; RPA Ltd. 2000). Most OBDE produced globally is added to polymers (mainly acrylonitrile butadiene styrene), which are then used to produce computers and business cabinets, pipes and fittings, automotive parts and appliances (WHO 1994; European Communities 2002b). DBDE is used as a flame retardant, to a large extent in high-impact polystyrene and other polymers, with broad use in computer and television cabinets and casings, general electrical/electronic components, cables and textile back coatings (OECD 1994; European Communities 2002a).

The total worldwide market demand for PBDEs was about 67 390 tonnes in 2001, including 56 100 tonnes of DBDE, 7500 tonnes of PeBDE and about 3790 tonnes of OBDE (BSEF 2003). There are significant differences in the usage of PBDEs by continent (see Table 1). The most apparent difference is that PeBDE is used almost exclusively in the Americas.

Table 1. Market demand of PBDEs in 1999 (BSEF 2003)

Commercial	Ame	ericas <sup>a</sup>	Eu	urope <sup>b</sup>	Asia <sup>c</sup>		
product	Market Estimated		mated Market Estimated		Market	Estimated	
	demand	consumption	demand	consumption	demand	consumption	
		(tonnes)		(tonnes)		(tonnes)	
DBDE	44%	24 500	13%	7 600	43%	24 050	
OBDE	40%	1 500	16%	610	44%	1 680	
PeBDE	95%	7 100	2%	150	3%	250	

<sup>&</sup>lt;sup>a</sup> All countries in North, South and Central America were included.

Results from a Section 71 *Notice with Respect to Certain Substances on the Domestic Substances List* (*DSL*) conducted for the year 2000 indicated that no PBDEs were manufactured in Canada, although approximately 1300 tonnes of PBDE commercial products (for manufacturing into finished articles) were imported into the country (Environment Canada 2001). Based on quantities reported, PeBDE was imported in the greatest volume, followed by DBDE. A very small amount of OBDE was imported into Canada in 2000. The volumes reported do not include quantities imported in finished articles.

PBDEs may be released to the environment during manufacturing and polymer processing operations, throughout the service life of articles containing them and at the end of article service life during disposal operations.

### **Fate, Exposure and Effects**

With their low vapour pressures, very low water solubility and high log octanol/water partition coefficient ( $K_{ow}$ ) values (Table 2), it is expected that PBDEs entering the environment will tend to bind to the organic fraction of particulate matter. For instance, if it is assumed that equal quantities of pentaBDE are released to air, water and soil compartments, Level III fugacity modelling (EPI v. 3.10, Syracuse Research Corporation) indicates that much of the substance would be expected to partition to sediment (approximately 59%), followed by soils (approximately 40%), water (1.2%) and air (0.2%). Partitioning characteristics for the other PBDEs subject to this assessment are very similar.

<sup>&</sup>lt;sup>b</sup> All countries in Eastern and Western Europe were included.

<sup>&</sup>lt;sup>c</sup> Australia, New Zealand and the Indian subcontinent were included.

The lower brominated PBDEs (tetra- to heptaBDEs) are slightly more soluble in water and have a greater propensity for volatilization and atmospheric transport than highly brominated PBDEs. In the atmosphere, these homologues would also tend to partition to particulates. The higher brominated PBDEs are reported to have higher  $LogK_{ow}$  and  $Log_{aw}$  values and a greater propensity to remain in a solid form, and thus, any transport would likely be in a particle form. Researchers have noted that the transport of the lower brominated PBDEs may be characterized by a series of deposition/revolatilization hops which are dependent on seasonally and diurnally fluctuating temperatures (Gouin and Harner 2003).

Wania and Dugani (2003) examined the long range transport potential of PBDEs with various models (i.e., TaPL3-2.10, ELPOS-1.1.1, Chemrange-2 and Globo-POP-1.1) using various physical and chemical properties (i.e., solubility in water, vapour pressure, logK<sub>ow</sub>, logK<sub>oa</sub>, logK<sub>aw</sub> and estimated half-lives in different media). They found that all models yielded comparable results with tetraBDE showing the greatest atmospheric transport potential and decaBDE the lowest transport potential. They estimated a characteristic travel distance (CTD) ranging from 1,113 to 2,483 km for tetraBDE, 608 to 1,349 km for pentaBDEs, and 480 to 735 km for decaBDE. The CTD is the distance a parcel of air has traveled until 1/e or 63% of the chemical has been removed by degradation or deposition processes (Gouin and Mackay 2002).

In an earlier study, Dugani and Wania (2002) also predicted using models that of the various PBDE congeners, those with four to six bromine atoms would have a higher long-range transport potential than lower or higher brominated congeners. They found that the transport of lower brominated congeners is limited by their degradation in the atmosphere, while the transport of the more highly brominated congeners is limited by their low volatility. Atmospheric degradation is reduced at low temperatures, so some of the models may underestimate the long range transport potential of the lighter congeners (Dugani and Wania 2002).

As will be indicated later in this report, PBDE concentrations have increased exponentially in arctic biota over the past two decades and have been measured in arctic air. This suggests efficient long-range atmospheric transport of PBDEs.

Table 2. Selected physical and chemical properties of commercial PBDEs and their constituents

Property	PeBDE	OBDE	DBDE		
Molecular weight	485.8 (tetraBDE)	643.6 (hexaBDE)	880.4 (nonaBDE)		
	564.7 (pentaBDE)	722.3 (heptaBDE)	959.2 (decaBDE)		
	(WHO 1994)	801.4 (octaBDE)	(WHO 1994)		
		(WHO 1994)			
Physical state (20°C;	viscous liquid or semi-solid,	powder or flaked material	crystalline powder		
101.325 kPa)	white crystalline solid (pure	(European Communities	(European Communities		
	isomers of pentaBDE)	2002b)	2002a)		
	(European Communities				
	2000)				
Vapour pressure (21°C;	$4.69 \times 10^{-5}$	$6.59 \times 10^{-6}$	$4.63 \times 10^{-6}$		
Pa)	(Stenzel and Nixon 1997 in	(CMABFRIP 1997a)	(CMABFRIP 1997e)		
	European Communities	1.58 x 10 <sup>-6</sup> - 4.68 x 10 <sup>-7</sup>	$2.95 \times 10^{-9}$ (estimated for		
	2000)	(hexa – heptaBDEs, 25°C;	decaBDE; Wania and		
		Tittlemier et al. 2002)	Dugani 2003)		
Water solubility (25°C;	13.3	0.5	< 0.1		
μg/L)	10.9 (tetraBDE)	(CMABFRIP 1997b)	(CMABFRIP 1997f)		
	2.4 (pentaBDE)				
	(Stenzel and Markley 1997)				
$Log K_{ow}$	6.57	6.29	6.27		
	(MacGregor and Nixon	(CMABFRIP 1997c)	(CMABFRIP 1997g)		
	1997)	8.35-8.90	9.97		
		(Watanabe and Tatsukawa	(Watanabe and Tatsukawa		
		1990 in European	1990 in European		
		Communities 2002b)	Communities 2002a)		
Log K <sub>oa</sub>	10.53-	12.78- 13.61 (hepta- and	14.44 -		
	11.31 (tetra- and	octaBDEs)	15.27 (estimated for nona-		
	pentaBDEs)	(Tittlemeier et al. 2002)	and decaBDE)		
	(Harner and Shoeib 2001)		(Tittlemier et al. 2002)		
Henry's law constant	11	10.6 (estimated)	>44 (estimated)		
$(25^{\circ}\text{C; Pa·m}^3/\text{mol})$	(European Communities	(European Communities	(European Communities		
	2000)	2002b)	2002a)		

PBDEs have been detected in all environmental media (see Tables 3 and 4), and there is evidence that their levels in the North American environment are increasing. Gouin et al. (2002) measured total PBDEs (sum of 21 congeners) ranging from 10 to 1300 pg/m³ in air samples collected at a rural southern Ontario site in early spring of 2000. Total PBDEs (congeners not specified) up to 28 pg/m³ were detected in air samples from the Canadian Arctic collected over the period 1994-1995 (Alaee et al. 2000).

Luckey et al. (2002) measured total (dissolved and particulate phases) PBDE (mono- to heptaBDE congeners) concentrations of approximately 6 pg/L in Lake Ontario surface waters in 1999. More than 60% of the total was composed of BDE47 (tetraBDE) and BDE99 (pentaBDE), with BDE100 (pentaBDE) and BDEs 153 and 154 (heptaBDE congeners) each contributing approximately 5 to 8% of the total. Stapleton and Baker (2001) analyzed water samples from Lake Michigan in 1997, 1998 and 1999 and found that total PBDE concentrations (BDEs 47, 99, 100, 153, 154 and 183) ranged from 31 to 158 pg/L.

PBDEs have been detected in sediment and soil samples collected throughout North America, and high concentrations have been measured in sewage sludge. Rayne et al. (2003) measured PBDE concentrations (sum of 8 di- to pentaBDE congeners) ranging from 2.7 to 91 µg/kg OC in 11 surficial sediments collected in 2001 from several sites along the Columbia River system in southeastern British Columbia. Domestic wastewaters arising from septic field inputs were identified as potentially dominant sources of PBDEs in the region. Dodder et al. (2002) reported concentrations of total tetra, penta- and hexaBDE ranging from approximately 5 to 38 µg/kg dw in sediment from a lake in the U.S. located near suspected PBDE sources. Preliminary results from a study by Muir et al. (2003) describe concentrations of BDE209 along a north-south transect from southern Ontario/upper New York state to Ellesmere Island. The highest concentrations of BDE209 (up to 12 µg/kg dw) occurred in sediments collected from the western basin of Lake Ontario. However, sediments from two Arctic lakes also had measurable concentrations of 0.075 and 0.042 µg BDE209/kg dw. One of the two Arctic lakes was located near an airport and so inputs of PBDEs from this source could not be ruled out. However, the second lake was completely isolated and was only visited for sampling purposes. The authors speculate that BDE209 was likely transported on particles to the Canadian Arctic due to its low vapour pressure and high octanol-water partition coefficient. Hale et al. (2002, 2003) reported concentrations of total PBDEs (tetra- and pentaBDE) of 76 µg/kg dw in soil near a polyurethane foam manufacturing facility in the United States, and 13.6 µg/kg dw in soil downwind from the facility.

La Guardia et al. (2001) analyzed 11 sludge samples before land application from a sewage treatment facility in the Toronto area and from10 facilities throughout the continental United States. Total PBDEs (sum of 11 tetra- to decaBDE congeners) in the sample of sewage sludge were 8280  $\mu g/kg$  dw at the Toronto site, while those in the U.S. ranged from 730 to 24, 900  $\mu g/kg$  dw. Kolic et al. (2003) investigated PBDE levels in sewage sludge from 12 sites in southern Ontario and found concentrations of total PBDEs (21 mono- to decaBDE congeners) ranging from 1414 to 5545  $\mu g/kg$  dw. Hale et al. (2002) measured total PBDEs (sum of BDEs 47, 99, 100 and 209) of 3005  $\mu g/kg$  dw in sludge sample collected in 2000 from a regional sewage treatment plant discharging to the Dan River in Virginia.

Alaee et al. (1999) reported average concentrations in the blubber of marine mammals from the Canadian Arctic as 25.8  $\mu$ g/kg lipid in female ringed seals (*Phoca hispida*), 50.0  $\mu$ g/kg in the blubber of male ringed seals, 81.2  $\mu$ g/kg lipid in female beluga (*Delphinapterus leucus*) and 160  $\mu$ g/kg lipid in male beluga. In these samples, congeners of tetraBDE and pentaBDE were predominant. Ikonomou et al. (2000) reported PBDE concentrations in biota samples from the west coast and Northwest Territories of Canada. The highest concentration of total PBDE residues, 2269  $\mu$ g/kg lipid, was found in the blubber of a harbour porpoise from the Vancouver area. With a concentration of about 1200  $\mu$ g/kg lipid, a tetraBDE congener accounted for slightly more than half of the total PBDE in the sample. Ikonomou et al. (2002a,b) analyzed temporal trends in Arctic marine mammals by measuring PBDE levels in the blubber of Arctic male ringed seals over the period 1981–2000. Mean total PBDE concentrations increased exponentially from approximately 0.6  $\mu$ g/kg lipid in 1981 to 6.0  $\mu$ g/kg lipid in 2000, a greater than 8-fold increase. TetraBDE was again predominant, followed by pentaBDE. A marked increase in tissue PBDE levels was also evident in blubber samples collected from San Francisco Bay harbour seals over the period 1989–1998 (She et al. 2002). Concentrations of total PBDEs (tetra-, penta- and hexaBDE) rose from 88  $\mu$ g/kg lipid in 1989 to a maximum of 8325

 $\mu$ g/kg lipid in 1998, a period of only 10 years. Stern and Ikonomou (2000) examined PBDE levels in the blubber of male southeast Baffin beluga whales over the period 1982–1997 and found that the levels of total PBDEs (tri- to hexaBDE) increased significantly. Mean total PBDE concentrations were about 2  $\mu$ g/kg lipid in 1982 and reached a maximum value of about 15  $\mu$ g/kg lipid in 1997. Total PBDE residues in the blubber of St. Lawrence estuary belugas sampled in 1997–1999 amounted to 466 ( $\pm$  230)  $\mu$ g/kg wet weight (ww) blubber in adult males and 665 ( $\pm$  457)  $\mu$ g/kg ww blubber in adult females. These values were approximately 20 times higher than concentrations in beluga samples collected in 1988–1990 (Lebeuf et al. 2001).

Table 3. Measured concentrations of PBDEs in the North American ambient environment and sewage sludge

Medium	Location; year	Total PBDEs	Reference
Air	Alert, Canada; 1994–1995	$1-28 \text{ pg/m}^3$	Alaee et al. 2000
Air	Great Lakes; 1997–1999	$5.5-52 \text{ pg/m}^3$	Strandberg et al. 2001
Air	Southern Ontario; 2000	$10-1300 \text{ pg/m}^3$	Gouin et al. 2002
Air	Ontario; 2000	$3.4-46 \text{ pg/m}^3$	Harner et al. 2002
Water	Lake Michigan; 1997–1999	31–158 pg/L	Stapleton and Baker 2001
Water	Lake Ontario; 1999	6 pg/L	Luckey et al. 2002
Sediment	Lake Michigan; 1998	4.2 μg/kg dw	Stapleton and Baker 2001
Sediment	British Columbia; 2001	2.7–91 μg/kg OC	Rayne et al. 2003
Soil	United States; 2000	<0.1–76 µg/kg dw	Hale et al. 2002
Sewage sludge	Toronto, Canada	8280 µg/kg dw	La Guardia et al. 2001
	United States	730–24 900 μg/kg dw	
Sewage sludge	United States; 2000	3005 μg/kg dw	Hale et al. 2002

dw = dry weight; OC = organic carbon

Table 4. Measured concentrations of PBDEs in North American biota

Organism	Location; year	Total PBDEs	Reference		
Dungeness crab	West coast, Canada; 1993–	4.2–480 µg/kg lipid	Ikonomou et al. 2002b		
hepatopancreas	1995				
Mountain whitefish	Columbia River, British	0.726–131 µg/kg ww	Rayne et al. 2003		
(muscle)	Columbia; 1992–2000				
Heron egg	British Columbia; 1983–2000	1.308–288 µg/kg ww	Wakeford et al. 2002		
Murre egg	Northern Canada; 1975–1998	0.442–2.93 µg/kg ww			
Fulmar egg	Northern Canada; 1975–1998	0.212–2.37 μg/kg ww			
Beluga whale blubber	Canadian Arctic	81.2–160 µg/kg lipid	Alaee et al. 1999		
Herring gull egg	Great Lakes; 1981–2000	9.4–1544 μg/kg ww	Norstrom et al. 2002		
Lake trout	Lake Ontario; 1997	95 μg/kg ww	Luross et al. 2002		
	Lake Erie; 1997	27 μg/kg ww			
	Lake Superior; 1997	56 μg/kg ww			
	Lake Huron; 1997	50 μg/kg ww	7		
Rainbow trout	Spokane River, Washington,	297 µg/kg ww	Johnson and Olson		
Mountain whitefish	USA; 1999	1250 μg/kg ww	2001		
Largescale sucker		105 µg/kg ww			
Carp	Virginia, USA; 1998-1999	1140 μg/kg ww	Hale et al. 2001		

These studies indicate that PBDE levels in Canadian biota are rising, with dramatic increases in tissue concentrations evident over the last two decades. The highest levels in biota are associated

with industrialized regions; however, the increasing incidence of PBDEs in Arctic biota provides increasing evidence for long-range atmospheric transport of these compounds (Stern and Ikonomou 2000). Although the tetraBDE predominates in wildlife, there are recent indications of a shift in tissue congener profiles. Ikonomou et al. (2002a) determined that over the period 1981–2000, penta-and hexaBDE levels in the blubber of Arctic ringed seals increased at rates that were roughly equivalent and about twice that of tetraBDE.

Based on a time trend analysis of PBDE levels in Arctic ringed seals, Ikonomou et al. (2002a) asserted that if present rates of bioaccumulation continue unchanged, PBDEs will surpass polychlorinated biphenyls (PCBs) as the most prevalent organohalogen compound in Arctic seals by 2050. By contrast, there are indications from recent studies conducted in Europe that PBDE levels in some European biota may have peaked. Time trend analyses using Baltic guillemot (*Uria aalge*) eggs (Sellström 1996; Sellström et al. 2003) and pike (*Esox lucius*) from Lake Bolmen in Sweden (Kierkegaard et al. 1999b, Submitted in text) show a levelling off and possible decline in the concentrations of penta-like congeners beginning in the early 1990s. Any observed reduction in the concentrations of PBDEs in European biota may be a consequence of recent reductions in the production and use of commercial PeBDE throughout Europe. These results provide evidence that the PBDE contamination evident in North American biota is predominantly North American in origin and not derived from European sources (Ikonomou et al. 2002a). For further discussion of this issue, the reader should consult references such as de Wit (2002) and Law et al. (2003).

An analysis of archived herring gull eggs (sampled in 1981, 1983, 1987, 1988, 1989, 1990, 1992, 1993, 1996, 1998, 1999 and 2000) enabled Norstrom et al. (2002) to establish temporal trends in PBDE concentrations between 1981- 2000. At Lake Michigan, Lake Huron and Lake Ontario sites, concentrations of total tetra- and pentaBDEs increased 71 to 112 fold over the 1981 to 2000 period (from 4.7 to 400.5  $\mu$ g/kg ww at Lake Ontario; from 8.3 to 927.3  $\mu$ g/kg ww at Lake Michigan; from 7.6 to 541.5  $\mu$ g/kg ww at Lake Huron). These increases were all found to be exponential at all three locations. Overall, the total PBDEs ranged from a low of 9.4  $\mu$ g/kg ww in Lake Ontario to a high of 1544  $\mu$ g/kg ww Lake Michigan in 1998. These increases were largely due to the tetra- and pentaBDE congeners, but hexa- and heptaBDEs also increased during this period.

Empirical and predicted data indicate that all PBDEs subject to this environmental screening assessment are highly persistent, and each satisfies the requirements for persistence as defined by the Persistence and Bioaccumulation Regulations under CEPA 1999 (see Table 5). Specifically, tetra-, penta-, hexa- and heptaBDEs have been measured in the Arctic environment in spite of their very low vapour pressures, providing evidence that they are subject to long-range atmospheric transport. DecaBDE in natural sediments has been shown to be stable and resistant to biodegradation under anaerobic conditions for up to 2 years (de Wit 2000). A preliminary study has also detected decaBDE in Arctic sediments (Muir et al. 2003). In this study, three Arctic lakes were sampled in Nunavut in the Canadian Arctic. Romulus Lake had non-detectable levels (detection limit 0.1  $\mu$ g/kg dry weight [dw]) of PBDEs in its sediment core. Lake AX-AJ and Char Lake had concentrations of 0.075 and 0.042  $\mu$ g/kg dw, respectively (detection limit not specified). The authors speculated that decaBDE was likely transported on particles to the Canadian Arctic due to its low vapour pressure and high octanol-water partition coefficient.

Table 5. Persistence and bioaccumulation criteria as defined in CEPA 1999 Persistence and Bioaccumulation Regulations (Environment Canada 2000)

	Persistence <sup>a</sup>								
Medium	Half-life								
Air	≥2 days or is subject to atmospheric transport from its source to a remote area	BAF ≥ 5000							
Water	≥182 days (≥6 months)	BCF≥ 5000							
Sediment	≥365 days (≥12 months)	$\log K_{ow} \ge 5$							
Soil	≥182 days (≥6 months)	-							

<sup>&</sup>lt;sup>a</sup> A substance is persistent when at least one criterion is met in any one medium.

Although all PBDEs subject to this assessment are considered to be persistent, evidence shows that PBDEs are susceptible to some degree of degradation. Studies have shown the transformation of higher brominated PBDEs (e.g., hepta- to decaBDEs) to lower brominated congeners (e.g., tetra- to hexaBDEs), which are associated with high levels of bioaccumulation. A dietary exposure study has shown that congeners of heptaBDE and pentaBDE rapidly biotransform in the gut of carp (*Cyprinus carpio*), and at least 10–12% is debrominated to congeners of hexaBDE and tetraBDE, respectively (Stapleton 2003; Stapleton and Baker 2003). These transformation products then accumulate in the tissues of the carp. Carp have also demonstrated a limited ability to biotransform decaBDE when exposed via food, producing various penta- to octaBDE congeners. In a study described by Stapleton (2003) and Stapleton and Baker (2003), less than 1% of consumed decaBDE was shown to biotransform in carp to form penta- to octaBDEs.

Many studies have also shown that PBDEs found in PeBDE, OBDE and DBDE are susceptible to photodegradation under varied laboratory conditions (e.g., Norris et al. 1973, 1974; Herrmann et al. 2003; Hua et al. 2003; Peterman et al. 2003). For instance, decaBDE in toluene exposed to artificial sunlight has been found to have a half-life of less than 15 minutes. When dispersed in solvent and then applied to substrates, such as soils and sediments, the half-life of decaBDE is slower (up to approximately 200 hours) (Sellström et al. 1998; Tysklind et al. 2001; Söderström et al. 2003). Their persistence in the atmosphere and susceptibility to long range atmospheric transport is supported by the finding showing that PBDEs have slower rates of photodegradation when associated with particulates.

While highly brominated PBDEs have not been observed to biodegrade under anaerobic or aerobic conditions, even when studied for periods of up to 2 years, there is speculation that biodegradation of highly brominated PBDE congeners may occur over the long term under anaerobic conditions, based on reductive dehalogenation observed with polybrominated biphenyls (PBBs) and PCBs (European Communities 2002a).

Globally, DBDE has become the most used technical PBDE product (see Table 1). There is a weight of evidence suggesting that highly brominated PBDEs such as octa- and decaBDE are precursors of the more toxic, bioaccumulative and persistent lower brominated PBDEs. While the degree to which this phenomenon adds to the overall risk presented to organisms from formation of the more toxic

b When the bioaccumulation factor (BAF) of a substance cannot be determined in accordance with generally recognized methods, then the bioconcentration factor (BCF) of a substance will be considered; however, if neither its BAF nor its BCF can be determined with recognized methods, then the log K<sub>ow</sub> will be considered.

and persistent tetra- to hexaBDE congeners is not known, there is sufficient evidence to warrant concern.

Measured data indicate that tetra-, penta- and hexaBDE are highly bioaccumulative, with bioconcentration factors (BCFs) exceeding 5000 for aquatic species; thus, they satisfy the criteria for bioaccumulation as described in the CEPA 1999 Persistence and Bioaccumulation Regulations (see Table 5). A BCF of about 27 400 L/kg for PeBDE was reported by European Communities (2000), based on a recalculation of data contained in a study by CITI (1982), in which carp were exposed for 8 weeks to PeBDE at 10 or 100  $\mu$ g/L. This BCF for the commercial product was driven by a high BCF calculated for the tetraBDE component. The recalculated BCFs for the various components were 66 700 L/kg for tetraBDE, 17 700 and 1440 L/kg for separate pentaBDE congeners (identities not provided) and 5640 and 2580 L/kg for separate hexaBDE congeners (identities not provided). A bioaccumulation factor (BAF) of  $1.4 \times 10^6$  was reported for PeBDE in blue mussels (*Mytilus edulis*) exposed for 44 days (Gustafsson et al. 1999). The same study reported BCFs of  $1.3 \times 10^6$  for tetraBDE and  $2.2 \times 10^5$  for hexaBDE in these organisms. High rates of accumulation in biota are supported by high log  $K_{ow}$  values for PBDEs and reports of biomagnification of tetraBDE and pentaBDE in aquatic food chains (e.g., Alaee and Wenning 2002; de Wit 2002).

Key studies of toxicity to organisms in different environmental media are presented in Table 6. Since testing is frequently carried out using commercial mixtures, effects must frequently be best considered in relation to the total exposures to all congeners involved (see below).

# **Proposed Conclusion for the Environment**

The approach taken in this environmental screening assessment was to examine various supporting information and develop conclusions based on a weight of evidence approach as required under Section 76.1 of CEPA 1999. Particular consideration was given to risk quotient analyses and persistence, bioaccumulation, chemical transformation and trends in environmental concentrations.

This assessment has used data corresponding to commercial products, individual congeners and homologues/isomer groups. The presentation of data and the risk quotient analyses have been structured around the PBDE commercial products since a great deal of empirical data which are central to this assessment (e.g., relevant to environmental toxicity) have been determined using the commercial products. Nonetheless, the risk analysis and scientific evidence presented in this report relate to all congeners found in the commercial products, PeBDE, OBDE and DBDE.

The risk determined for each commercial product is a result of the combined activity of the various co-occurring PBDEs, adding complexity to the interpretation of the results. Due to these reasons, their common chemical structure, and due to issues relating to their chemical transformation, PeBDE, OBDE, DBDE and their brominated constituents are assessed as a group.

Risk quotient analyses, integrating known or potential exposures with known or potential adverse environmental effects, were performed for each of the commercial PBDE products subject to this assessment. An analysis of exposure pathways and subsequent identification of sensitive receptors were used to select environmental assessment endpoints (e.g., adverse reproductive effects on sensitive fish species in a community). For each endpoint, a conservative Estimated Exposure Value (EEV) was selected based on empirical data from monitoring studies. Where monitoring data were not available, the EEVs were based on simple calculation procedures taking into account some degree of local environmental conditions, but largely relying on generic environmental parameters. Chemical concentrations from the Canadian and North American environment were used preferentially for EEVs; however, data from other regions in the world were used in the absence of sufficient Canadian data of satisfactory quality or to provide a weight of evidence. EEVs usually represented worse-case scenarios, as an indication of the potential for these substances to reach concentrations of concern and to identify areas where those concerns would be most likely.

An Estimated No-Effects Value (ENEV) was also determined by dividing a Critical Toxicity Value (CTV) by an application factor. CTVs typically represented the lowest ecotoxicity value from an available and acceptable data set. Preference was generally for chronic toxicity data, as long-term exposure was a concern. Where these data were not available, the following were used in order of preference: acute data, analogue data, quantitative structure—activity relationship (QSAR) data and data derived from equilibrium partitioning methods.

Application factors were derived using a multiplicative approach, which uses 10-fold factors to account for various sources of uncertainty associated with making extrapolations and inferences related to the following: intra- and interspecies variations; differently sensitive biological endpoints; laboratory-to-field impact extrapolation required to extrapolate from single-species tests to ecosystems; and potential effects from concurrent presence of other substances. For substances that meet both the persistence and bioaccumulation criteria as outlined in the CEPA 1999 Regulations (see Table 5), an additional application factor of 10 is applied to the CTV.

Risk quotients derived for PBDEs are summarized in Table 7. Exposure data used as EEVs can be found in Tables 3 and 4 or are summarized in the notes to Table 7. Toxicity data used to determine CTVs and ENEVs are summarized in Table 6.

The risk quotient analysis indicates that the greatest potential for risk from PBDEs in the Canadian environment is due to the secondary poisoning of wildlife from the consumption of prey containing elevated PeBDE and OBDE congener concentrations. Elevated concentrations of components of PeBDE in sediments may present risk to benthic organisms. HexaBDE is a component of both PeBDE and OBDE and could be a product of heptaBDE, octaBDE, nonaBDE or decaBDE transformation. Therefore, risk associated with components of PeBDE may be due to the use of OBDE or debromination of highly brominated PBDEs, in addition to the use of PeBDE itself. The risk analysis for soil organisms indicates that risk quotients were below 1 for PeBDE, OBDE and DBDE; however, the lack of data characterizing PBDE concentrations in soil and sewage sludge applied to soil indicates the need for further research. PeBDE, OBDE and DBDE would present low potential for risk as a result of direct toxicity to pelagic organisms due to their very low water solubility. In the water column, risk associated with components of PeBDE and OBDE (tetra-, penta- and hexaBDE congeners) may be due to bioaccumulation and toxicity to secondary consumers.

There is a lack of data characterizing the toxicity of PBDEs to wildlife. Recent studies using rodents provide evidence that exposure to PBDEs may lead to behavioural disturbances, disruptions in normal thyroid hormone activity and liver effects (e.g., Eriksson et al. 2002, Zhou et al. 2001 and 2002, Great Lakes Chemical Corporation 1984). The relationship of these studies to potential effects from accumulation in the wild requires further study.

There are a variety of data indicating that all PBDE congeners subject to this assessment are highly persistent and each satisfies the requirements for persistence as defined by CEPA 1999 Persistence and Bioaccumulation Regulations.

Although all PBDEs subject to this assessment are considered to be persistent, evidence shows that PBDEs are susceptible to some degree of degradation. Studies have shown the transformation of higher brominated PBDEs (e.g., hepta- to decaBDEs) to lower brominated congeners (e.g., tetra- to hexaBDEs) which are associated with high levels of bioaccumulation.

DBDE has become the prevalent commercial PBDE product used in North America and the world. In North America and Europe, it is often found in concentrations which exceed those of other PBDEs in sewage sludge and sediments. Concentrations of DBDE are now reaching mg/kg dw levels in North American sewage sludge. High accumulation of DBDE in the environment and evidence of debromination has led researchers to note that even slight and very long term degradation to lower brominated diphenyl ethers could have serious ecological consequences over periods spanning several decades. Thus, while current concentrations measured in the environment for homologues found in commercial DBDE do not appear to exceed known effect thresholds, their overall persistence and potential transformation to bioaccumulative forms, and observed commercial and environmental trends, indicate environmental concerns.

Measured data indicate that tetra-, penta- and hexaBDE are highly bioaccumulative and satisfy the criteria for bioaccumulation in the CEPA 1999 regulations. Concentrations of PBDEs in herring gull eggs have increased exponentially between 1981 and 2000 at Lake Ontario, Huron and Michigan sampling sites. Concentrations of PBDEs (predominantly tetra- and pentaBDE congeners) have also increased exponentially between 1981 and 2000 in Arctic male ringed seals. There is a weight of evidence showing that highly brominated PBDEs are precursors of bioaccumulative and persistent PBDEs. While it is not known the degree to which this phenomenon adds to the overall risk presented to organisms from the tetra- to hexaBDE congeners, there is sufficient evidence for concern. The Government of Canada Toxic Substances Management Policy (TSMP) notes that "where a Track 1 substance results from the degradation or transformation of a parent substance in the environment, the parent substance may also be considered for Track 1."

Pyrolysis and extreme heating can cause all PBDEs to form brominated dibenzo-*p*-dioxins and dibenzofurans (European Communities 2000, 2002a,b). These transformation products are considered brominated analogues of the TSMP Track 1 polychlorinated dibenzo-*p*-dioxins and dibenzofurans.

The PBDEs subject to this assessment have low vapour pressures and low Henry's Law constants (see Table 2) and are not expected to partition significantly into the atmosphere. As such, they are considered to present a negligible risk with respect to atmospheric processes such as global warming,

stratospheric ozone depletion and ground-level ozone formation; however, they do reside in the atmosphere adsorbed to suspended particulates and can be transported over long distances.

It is therefore concluded that tetraBDE, pentaBDE, hexaBDE, heptaBDE, octaBDE, nonaBDE and decaBDE, which are found in commercial PeBDE, OBDE and DBDE, are entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity and thus satisfy the definition of "toxic" under Paragraph 64(a) of CEPA 1999. Based on considerations of potential contribution to atmospheric processes, it is concluded that PBDEs are not entering the environment in a quantity or concentrations or under conditions that constitute or may constitute a danger to the environment on which life depends, and thus do not satisfy the definition of "toxic" under Paragraph 64(b) of CEPA 1999.

The available data regarding persistence and bioaccumulation of tetraBDE, pentaBDE, hexaBDE indicated that they satisfy the criteria outlined in the Persistence and Bioaccumulation Regulations of CEPA 1999. Their presence in the environment results primarily from human activity, and they are not naturally occurring radionuclides or naturally occurring inorganic substances. Data regarding the potential debromination of higher brominated forms of PBDEs to bioaccumulative forms indicate that they may also be considered as Track 1 substances under the Toxic Substances Management Policy.

# Proposed recommendation to the Ministers of the Environment and Health

It is proposed that PBDEs, including tetraBDE, pentaBDE, hexaBDE, heptaBDE, octaBDE, nonaBDE and decaBDE, which are found in commercial PeBDE, OBDE and DBDE, be considered "toxic" as defined in section 64 of CEPA 1999.

It is proposed that consideration be given to adding tetraBDE, pentaBDE, and hexaBDE, which are found in commercial PeBDE and OBDE, to the Virtual Elimination List under CEPA 1999 and that PBDEs, including tetraBDE, pentaBDE, hexaBDE, heptaBDE, octaBDE, nonaBDE and decaBDE, which are found in commercial PeBDE, OBDE and DBDE, be considered as Track 1 substances under the Toxic Substances Management Policy.

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Table 6. Summary of toxicity studies used in the derivation of CTVs for the risk quotient analysis of PBDEs

Species, life stage	Composition of test material	Test duration	Test concentrations	Study design	Effect level	Reference	
Daphnia magna <24 hours old at test initiation	PeBDE: 33.7% tetraBDE 54.6% pentaBDE 11.7% hexaBDE	21 days	Nominal: 0, 1.9, 3.8, 7.5, 15 and 30 μg/L  Measured: 0, 1.4, 2.6, 5.3, 9.8 and 20 μg/L	<ul> <li>flow-through using well water</li> <li>20 ± 1°C, pH 7.9–8.3, DO ≥ 76% saturation, hardness 128–136 mg/L as CaCO<sub>3</sub>, alkalinity 174–176 mg/L as CaCO<sub>3</sub>, conductance 310–315 µmhos/cm</li> <li>40 animals per treatment</li> <li>GLP, protocol based on OECD 202, TSCA Title 40 and ASTM E1193-87</li> </ul>	<ul> <li>21-day LOEC (mortality/immobility) = 20 μg/L</li> <li>21-day NOEC (mortality/immobility) = 9.8 μg/L</li> <li>96-hour EC<sub>50</sub> (mortality/immobility) = 17 μg/L</li> <li>7- to 21-day EC<sub>50</sub> (mortality/immobility) = 14 μg/L</li> <li>21-day EC<sub>50</sub> (reproduction) = 14 μg/L</li> <li>21-day LOEC (growth) = 9.8 μg/L</li> <li>21-day NOEC (growth) = 5.3 μg/L</li> <li>LOEC (overall study) = 9.8 μg/L</li> <li>NOEC (overall study) = 5.3 μg/L</li> </ul>	CMABFRIP 1998	
Lumbriculus variegatus adult	PeBDE: 0.23% triBDE 36.02% tetraBDE 55.10% pentaBDE 8.58% hexaBDE (Great Lakes Chemical Corporation 2000c)	28 days	Nominal: 0, 3.1, 6.3, 13, 25 and 50 mg/kg dw of sediment  Analysis of test concentrations at days 0, 7 and 28 indicated they were well maintained throughout the test.  Results based on nominal concentrations.	<ul> <li>flow-through using filtered well water</li> <li>23 ± 2°C, pH 7.9–8.6, DO 6.0–8.2 mg/L, hardness 130 mg/L as CaCO<sub>3</sub></li> <li>artificial sediment: pH 6.6, water holding capacity 11%, mean organic matter &lt;2%, 83% sand, 11% clay, 6% silt</li> <li>80 animals per treatment</li> <li>GLP, protocol based on Phipps et al. (1993), ASTM E1706-95b and U.S. EPA OPPTS No. 850.1735</li> </ul>	28-day LOEC (survival/reproduction) = 6.3 mg/kg dw of sediment     28-day NOEC (survival/reproduction) = 3.1 mg/kg dw of sediment     28-day EC <sub>50</sub> (survival/reproduction) > 50 mg/kg dw of sediment     growth (dry weights) not significantly different from solvent control and not concentration-dependent	Great Lakes Chemical Corporation 2000a	
Zea mays corn	PeBDE: 0.23% triBDE 36.02% tetraBDE 55.10% pentaBDE 8.58% hexaBDE (Great Lakes Chemical Corporation 2000c)	21 days	Nominal: 0, 62.5, 125, 250, 500 and 1000 mg/kg soil dw or 0, 50.0, 100, 200, 400 and 800 mg/kg soil ww, assuming 20% soil moisture content  Analysis of test concentrations indicated they were well maintained throughout the test. Results reported based on nominal concentrations.	<ul> <li>artificial soil: 92% sand, 8% clay and 0% silt, pH 7.5, organic matter content 2.9%</li> <li>watering with well water using subirrigation, 14:10 light:dark photoperiod, 16.0–39.9°C, relative humidity 19–85%</li> <li>40 seeds per treatment</li> <li>GLP, protocol based on U.S. EPA OPPTS Nos. 850.4100 and 850.4225 and OECD 208 (based on 1998 proposed revision)</li> </ul>	<ul> <li>no apparent treatment-related effects on seedling emergence</li> <li>21-day LC<sub>25</sub>, LC<sub>50</sub> (seedling emergence) &gt; 1000 mg/kg soil dw</li> <li>mean shoot height significantly reduced at 250, 500 and 1000 mg/kg soil dw relative to controls</li> <li>21-day EC<sub>25</sub>, EC<sub>50</sub> (mean shoot height) &gt; 1000 mg/kg soil dw</li> <li>mean shoot weight significantly reduced at 62.5, 125, 250, 500 and 1000 mg/kg soil dw relative to controls</li> <li>21-day EC<sub>25</sub> (mean shoot weight) = 154 mg/kg soil dw</li> <li>21-day EC<sub>50</sub> (mean shoot weight) &gt; 1000 mg/kg soil dw</li> <li>21-day LOEC (mean shoot weight) &gt; 62.5 mg/kg soil dw</li> <li>21-day LOEC (mean shoot weight) = 62.5 mg/kg soil dw</li> <li>21-day EC<sub>05</sub> and (estimated) NOEC (mean</li> </ul>	Great Lakes Chemical Corporation 2000b	

Species, life stage	Composition of test material	Test duration	Test concentrations	Study design	Effect level	Reference
					shoot weight) = 16.0 mg/kg soil dw	
Rat	PeBDE (DE-71): 45–58.1% pentaBDE 24.6–35% tetraBDE (Sjodin 2000; Zhou et al. 2001)	90 days maximum exposure with recovery periods of 6 and 24 weeks	In diet: 0, 2, 10 and 100 mg/kg bw per day (doses adjusted weekly based on mean body weight of animals)	30 male and 30 female Sprague- Dawley CD rats per treatment	decreased food consumption and body weight, increased cholesterol, increased liver and urine porphyrins at 100 mg/kg bw dose  increased absolute and relative liver weights at 10 and 100 mg/kg bw, with return to normal ranges after 24-week recovery period  compound-related microscopic changes to thyroid and liver at all dosage levels  microscopic thyroid changes reversible after 24 weeks  microscopic liver changes still evident at all dosage levels after 24-week recovery period  liver cell degeneration and necrosis evident in females at all dosage levels after 24-week recovery  LOAEL (liver cell damage) = 2 mg/kg bw  NOAEL could not be determined, as a significant effect was observed at the lowest dose tested	Great Lakes Chemical Corporation 1984
Daphnia magna <24 hours old at test initiation	OBDE: 5.5% hexaBDE 42.3% heptaBDE 36.1% octaBDE 13.9% nonaBDE 2.1% decaBDE (European Communities 2002b)	21 days	Nominal: 0, 0.13, 0.25, 0.5, 1.0 and 2.0 µg/L  Measured: 0, *, *, 0.54, 0.83 and 1.7 µg/L  * two lowest concentrations could not be measured	<ul> <li>flow-through using filtered well water</li> <li>20 ± 1°C, pH 8.2–8.5, DO ≥ 77% saturation, hardness 132–136 mg/L as CaCO<sub>3</sub></li> <li>20 animals per treatment</li> <li>GLP, protocol based on OECD 202, ASTM E1193-87 and TSCA Title 40</li> </ul>	<ul> <li>21-day LOEC (survival, reproduction, growth) &gt; 2.0 μg/L (nominal) or 1.7 μg/L (measured)</li> <li>21-day NOEC (survival, reproduction, growth) ≥ 2.0 μg/L (nominal) or 1.7 μg/L (measured)<sup>a</sup></li> <li>21-day EC<sub>50</sub> (survival, reproduction, growth) &gt; 2.0 μg/L (nominal) or 1.7 μg/L (measured)</li> </ul>	CMABFRIP 1997d
Eisenia fetida adult earthworm	OBDE (DE-79): 78.6% bromine content	56 days	Nominal: 0, 94.0, 188, 375, 750 and 1500 mg/kg dry soil Measured: 0, 84.9, 166, 361, 698 and 1470 mg/kg dry soil	<ul> <li>artificial soil: sandy loam, 69% sand, 18% silt, 13% clay, 8.0% organic matter (4.7% carbon), pH 6.0 ± 0.5</li> <li>17-21°C, 16:8 light:dark photoperiod, pH 5.9-6.8, soil moisture 22.0-33.5%</li> <li>40 animals per treatment</li> <li>GLP, protocol based on U.S. EPA OPPTS 850.6200, OECD 207 and proposed OECD (2000) guideline</li> </ul>	<ul> <li>28-day LOEC (mortality) &gt; 1470 mg/kg dry soil</li> <li>28-day NOEC (mortality) ≥ 1470 mg/kg dry soil<sup>a</sup></li> <li>28-day EC<sub>10</sub>, EC<sub>50</sub> (survival) &gt; 1470 mg/kg dry soil</li> <li>56-day LOEC (reproduction) &gt; 1470 mg/kg dry soil</li> <li>56-day NOEC (reproduction) ≥ 1470 mg/kg dry soil<sup>a</sup></li> <li>56-day EC<sub>10</sub>, EC<sub>50</sub> (reproduction) &gt; 1470 mg/kg dry soil</li> </ul>	Great Lakes Chemical Corporation 2001c
Lumbriculus variegatus adult	OBDE (DE-79): 78.6% bromine content.	28 days	Nominal: 0, 94, 188, 375, 750 and 1500 mg/kg dw of sediment	<ul> <li>80 animals per treatment</li> <li>flow-through using filtered well water, hardness 128–132 mg/L as CaCO<sub>3</sub></li> <li>Two trials with different artificial</li> </ul>	28-day LOEC (survival/reproduction, growth)     > 1340 (2% OC) or 1272 (5% OC) mg/kg dw     of sediment     28-day NOEC (survival/reproduction, growth)	Great Lakes Chemical Corporation 2001a,b

Species, life stage	Composition of test material	Test duration	Test concentrations	Study design	Effect level	Reference
			Measured: (i) 2% OC: <0.354, 76.7, *, *, 755 and 1340 mg/kg dw sediment (ii) 5% OC: <12.5, 90.7, *, *, 742 and 1272 mg/kg dw sediment * concentrations were not measured	sediments: (i) 6% silt, 9% clay, 85% sand, 2% TOC, water holding capacity 9.3%, 23 ± 2°C, pH 7.6–8.4, DO ≥ 45% saturation (3.8 mg/L); (ii) 6% clay, 14% silt, 80% sand, 5% TOC, water holding capacity 13.9%, 23 ± 2°C, pH 7.5–8.3, DO ≥ 64% saturation (5.4 mg/L)  GLP, protocol based on Phipps et al. (1993), ASTM E1706-95b and U.S. EPA OPPTS 850.1735	≥ 1340 (2% OC) or 1272 (5% OC) mg/kg dw of sediment <sup>a</sup> • 28-day EC <sub>50</sub> (survival/reproduction, growth) > 1340 (2% OC) or 1272 (5% OC) mg/kg dw of sediment  For 2% TOC study:  • average individual dry weights for treatments statistically lower than in control; not considered treatment-related by authors, as average biomass in treatments comparable to control	
Rabbit	OBDE (Saytex 111): 0.2% pentaBDE 8.6% hexaBDE 45.0% heptaBDE 33.5% octaBDE 11.2% nonaBDE 1.4% decaBDE (Breslin et al. 1989)	Days 7–19 of gestation	By gavage: 0, 2.0, 5.0 and 15 mg/kg bw per day	26 New Zealand White rabbits per treatment     offspring examined on day 28 of gestation	<ul> <li>no evidence of teratogenicity</li> <li>LOAEL (maternal, increased liver weight, decreased body weight gain) = 15 mg/kg bw per day</li> <li>NOAEL (maternal) = 5.0 mg/kg bw per day</li> <li>LOAEL (fetal, delayed ossification of sternebrae) = 15 mg/kg bw per day</li> <li>NOAEL (fetal) = 5.0 mg/kg bw per day</li> </ul>	Breslin et al. 1989
Eisenia fetida adult earthworm	DBDE: 97.90% decaBDE	28 and 56 days	Nominal soil concentrations: 0, 312, 650, 1260, 2500 and 5000 mg/kg soil dw  Mean measured concentrations: <dl, 1240,="" 2480="" 320,="" 4910="" 668,="" and="" dw<="" kg="" mg="" td=""><td>artificial sandy loam soil: 69% sand, 18% silt, 13% clay, 8% TOM, 4.7% TOC, pH adjusted to 6.0 ± 0.5, 60% moisture content, 26% water holding capacity</td><td>28-day LOEC (survival) &gt; 4910 mg/kg dry soil (mean measured)     28-day NOEC (survival) ≥ 4910 mg/kg dry soil (mean measured)     28-day EC<sub>10</sub>, EC<sub>50</sub> (survival) &gt; 4910 mg/kg dry soil (mean measured)     56-day LOEC (reproduction) &gt; 4910 mg/kg dry soil (mean measured)     56-day NOEC (reproduction) ≥ 4910 mg/kg dry soil (mean measured)     56-day EC<sub>10</sub>, EC<sub>50</sub> (reproduction) &gt; 4910 mg/kg dry soil (mean measured)</td><td>ACCBFRIP 2001c</td></dl,>	artificial sandy loam soil: 69% sand, 18% silt, 13% clay, 8% TOM, 4.7% TOC, pH adjusted to 6.0 ± 0.5, 60% moisture content, 26% water holding capacity	28-day LOEC (survival) > 4910 mg/kg dry soil (mean measured)     28-day NOEC (survival) ≥ 4910 mg/kg dry soil (mean measured)     28-day EC <sub>10</sub> , EC <sub>50</sub> (survival) > 4910 mg/kg dry soil (mean measured)     56-day LOEC (reproduction) > 4910 mg/kg dry soil (mean measured)     56-day NOEC (reproduction) ≥ 4910 mg/kg dry soil (mean measured)     56-day EC <sub>10</sub> , EC <sub>50</sub> (reproduction) > 4910 mg/kg dry soil (mean measured)	ACCBFRIP 2001c
Lumbriculus variegatus adult	DBDE: 97.3% decaBDE 2.7% other (not specified) (composite from three manufacturers)	28 days	Nominal: 0, 313, 625, 1250, 2500 and 5000 mg/kg dw of sediment  Mean measured: (i) 2.4% OC: <1.16, 291, *, *, 2360 and 4536 mg/kg dw; (ii) 5.9% OC: <dl, *="" *,="" 1250="" 2034="" 258,="" 3841="" 625="" and="" dw="" kg="" kg<="" mg="" td=""><td><ul> <li>80 animals per treatment</li> <li>flow-through using filtered well water, hardness 128–132 mg/L as CaCO<sub>3</sub></li> <li>two trials with different artificial sediments: (i) 6% silt, 9% clay, 85% sand, 2.4% TOC, water holding capacity 9.3%, 23 ± 2°C, pH 7.7–8.6, DO ≥ 36% saturation (3.1 mg/L); (ii) 6% clay, 14% silt, 80% sand, 5.9% TOC, water holding capacity 13.9%, 23 ± 2°C, pH 7.7–8.6, DO ≥ 56%</li> </ul></td><td>28-day NOEC (survival/reproduction, growth) ≥ 4536 (2.4% OC) or 3841 (5.9% OC) mg/kg dw of sediment<sup>a</sup>      28-day LOEC (survival/reproduction, growth) &gt; 4536 (2.4% OC) or 3841 (5.9% OC) mg/kg dw of sediment      28-day EC₅0 (survival/reproduction, growth) &gt; 4536 (2.4% OC) or 3841 (5.9% OC) mg/kg dw of sediment</td><td>ACCBFRIP 2001a,b</td></dl,>	<ul> <li>80 animals per treatment</li> <li>flow-through using filtered well water, hardness 128–132 mg/L as CaCO<sub>3</sub></li> <li>two trials with different artificial sediments: (i) 6% silt, 9% clay, 85% sand, 2.4% TOC, water holding capacity 9.3%, 23 ± 2°C, pH 7.7–8.6, DO ≥ 36% saturation (3.1 mg/L); (ii) 6% clay, 14% silt, 80% sand, 5.9% TOC, water holding capacity 13.9%, 23 ± 2°C, pH 7.7–8.6, DO ≥ 56%</li> </ul>	28-day NOEC (survival/reproduction, growth) ≥ 4536 (2.4% OC) or 3841 (5.9% OC) mg/kg dw of sediment <sup>a</sup> 28-day LOEC (survival/reproduction, growth) > 4536 (2.4% OC) or 3841 (5.9% OC) mg/kg dw of sediment      28-day EC₅0 (survival/reproduction, growth) > 4536 (2.4% OC) or 3841 (5.9% OC) mg/kg dw of sediment	ACCBFRIP 2001a,b

Species, life stage	Composition of test material	Test duration	Test concentrations	Study design	Effect level	Reference
a.u.g.			concentrations were not measured	saturation (4.8 mg/L) • gentle aeration from day 7 to test end • GLP, protocol based on Phipps et al. (1993), ASTM E1706-95b and U.S. EPA OPPTS 850.1735		
Rat	DBDE (Dow-FR-300-BA): 77.4% decaBDE 21.8% nonaBDE 0.8% octaBDE	30 days	In diet: 0, 0.01, 0.1 and 1.0% (nominal or measured not specified)  Dosage approximately equivalent to 0, 8, 80 and 800 mg/kg bw per day	5 male Sprague Dawley rats per treatment	<ul> <li>LOAEL (enlarged liver, thyroid hyperplasia) = 80 mg/kg bw per day</li> <li>NOAEL = 8 mg/kg bw per day</li> </ul>	Norris et al. 1974

Abbreviations used: ASTM = American Society for Testing and Materials; DL = detection limit; DO = dissolved oxygen;  $EC_{50}$  = median effective dose; EPA = Environmental Protection Agency; GLP = Good Laboratory Practice;  $LC_{50}$  = median lethal dose; LOAEL = Lowest-Observed-Adverse-Effect Level; LOEC = Lowest-Observed-Effect Concentration; LOEC = No-Observed-Effect Concentration; LOEC = No-Observed-Effect Concentration; LOEC = Organisation for Economic Co-operation and Development; LOEC = Office of Prevention, Pesticides and Toxic Substances; LOEC = total organic carbon; LOEC = total organic carbon; LOEC = L

<sup>&</sup>lt;sup>a</sup> Study identified that the highest concentration (or dose) tested did not result in statistically significant results. Since the NOEC or NOAEL could be higher, the NOEC or NOAEL are described as being greater than or equal to the highest concentration (or dose) tested.

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Table 7. Summary of data used in risk quotient (Q) analysis of PBDEs

Commercial	Pelagic organisms				Benthic organisms			Soil organisms				Wildlife consumers								
product	EEV <sup>a</sup> (µg/L)	CTV <sup>b</sup> (µg/L)	AFc	ENEV (µg/L)	Q (EEV/ ENEV)	EEV <sup>d</sup> (mg/kg dw)	CTV <sup>e</sup> (mg/kg dw)	AFc	ENEV (mg/kg dw)	Q (EEV/ ENEV)	EEV <sup>f</sup> (mg/kg dw)	CTV <sup>g</sup> (mg/kg dw)	AFc	ENEV (mg/kg dw)	Q (EEV/ ENEV)	EEV <sup>h</sup> (mg/kg ww)	CTV <sup>i</sup> (mg/kg ww food)	AF <sup>j</sup>	ENEV (mg/kg ww food)	Q (EEV/ ENEV)
PeBDE	$2 \times 10^{-4}$	5.3	100	0.053	4 × 10 <sup>-3</sup>	1.4	3.1	100	0.031	45.2	0.035- 0.070	16	100	0.27 <sup>m</sup>	0.13- 0.26	1.250	8.4	1000	0.0084	149
OBDE	$2 \times 10^{-4}$	1.7	100	0.017	0.01	3.03	1340	100	9.1 <sup>1</sup>	0.33	0.03- 0.06	1470	100	6.3 <sup>m</sup>	0.005- 0.01	0.325	62.9	1000	0.06	5.4
DBDE	NA <sup>k</sup>	NA	NA	NA	NA	3.19	4536	100	76 <sup>1</sup>	0.04	0.31- 0.62	4910	100	21 <sup>m</sup>	0.02- 0.03	0.03	336	1000	0.336	0.09

Stapleton and Baker (2001).

OBDE: PBDEs found in OBDE are very poorly characterized in North America. Therefore, measured OBDE concentrations from Europe were used as a surrogate for Canadian data. Concentrations of OBDE up to 3.03 mg/kg dw have been reported for sediments in the UK downstream of a warehouse facility. This value is used as the EEV (Environment Agency 1997; European Communities

DBDE: There has been insufficient sampling conducted to properly characterize DBDE concentrations in sediments in North America. Concentrations of DBDE in UK sediments up to 3.19 mg/kg dw were determined, with the highest concentration located near a foam manufacturer downstream of a wastewater treatment plant (Law et al. 1996; Allchin et al. 1999). As a surrogate for the Canadian environment, this value is taken as the EEV.

Great Lakes Chemical Corporation (2000a, 2001a,b); ACCBFRIP (2001a,b).

Due to the lack of measured data, the EEVs were estimated for tilled agricultural soil and pastureland based on the equation (Bonnell Environmental Consulting 2001):

$$\begin{split} EEV_{soil} &= (C_{sludge} \times AR_{sludge} \times T) \, / \, (D_{soil} \times BD_{soil}) \\ where: \end{split}$$

 $EEV_{soil}$ = EEV for soil (mg/kg);

= concentration in sludge (mg/kg);

= application rate to soils ( $kg/m^2$  per year, default value = 0.5);

= sludge is mixed in soil to a depth of 0.2 m (depth of tillage) in agricultural soils and 0.1 m in pastureland (European Communities 1994);

 $BD_{soil}$ = bulk density of soil (kg/m $^3$ , default value = 1700); and

= number of years sludge is applied to soils (assumed 10 years).

This equation assumes the following:

- no PBDE loss due to erosion;
- no PBDE transformation (including transformation of highly brominated PBDEs to tetra- to hexaBDE congeners);
- no PBDE input from atmospheric deposition; and
- no background PBDE accumulation in the soil.

In order to calculate the EEVs for PeBDE, a concentration of 2.380 mg/kg dw (total tetraBDE, pentaBDE and hexaBDE) reported in biosolids from a California wastewater treatment facility was used (La Guardia et al. 2001). The EEVs for OBDE were calculated using measured PBDE concentrations (total of hexaBDE, heptaBDE and octaBDE) of 2.08 mg/kg dw in biosolids reported by La Guardia et al. (2001). This biosolids sample was taken from a Massachusetts wastewater treatment facility. To calculate the EEVs for DBDE, a PBDE concentration of 21.22 mg/kg dw (total of nonaand decaBDE) in biosolids was used. This concentration was also reported for a Massachusetts wastewater treatment facility biosolid sample (La Guardia et al. 2001).

CMABFRIP (1997d, 1998).

AF (application factors): 10 applied for extrapolation from laboratory to field conditions, intraspecies and interspecies variations in sensitivity; 10 applied because components of PeBDE and OBDE are bioaccumulative and persistent.

d PeBDE: Due to a lack of empirical data characterizing PeBDE sediment concentrations in Canada and due to uncertainty in concentrations throughout North America, data from Sweden were used as a surrogate for Canadian data. Concentrations of PeBDE-related components (tetraBDE and pentaBDE) totalled 1.4 mg/kg dw in sediments from Sweden in a heavily industrialized area downstream from a polymer processing site involved with the production of circuit boards (Sellström 1996). This value is used as the EEV. Although climate and local hydrological regimes may be different in the two countries, polymer processing facilities also exist in Canada. The European Union risk assessment of PeBDE also used this value to assess local risk from a polyurethane production site (European Communities 2000).

- <sup>g</sup> Great Lakes Chemical Corporation (2000b, 2001c); ACCBFRIP (2001c).
- h Johnson and Olson (2001); Allchin et al. (1999); Sellström et al. (2001); Lindberg et al. (2003).

  PeBDE: Johnson and Olson (2001) measured a total PBDE (i.e., BDEs 47, 99, 100, 153 and 154) concentration of 1250 μg/kg ww in mountain whitefish from the Spokane River in an area receiving drainage from urbanized areas. No sources other than those typically associated with urbanization (e.g., sewage discharge and urban runoff) are known to exist upstream of the sampling sites (Johnson, pers. comm. 2003). Although these data are from the United States, such a scenario could exist in Canada, and therefore, the concentration 1250 μg/kg ww in mountain whitefish is used as the EEV.

  OBDE: Due to very limited sampling for PBDEs found in OBDE in Canadian biota, the concentration of OBDE of 325 μg/kg ww in dab from the River Tees, UK, was used as the EEV (Allchin et al. 1999). Although this concentration was determined in liver tissues, it was assumed to equal the concentration of OBDE on a whole body basis.
- DBDE: There is also a similar lack of data characterizing PBDEs found in DBDE in Canadian biota. DBDE was detected in 18 of 21 analyzed eggs of peregrine falcons (*Falco peregrinus*) from Sweden, at concentrations from 28 to 430 µg/kg lipid weight (lw) (Sellström et al. 2001; Lindberg et al. 2003). The value 430 µg/kg lw (or 0.43 mg/kg lw) will be used as the EEV. Since the mean lipid content of these 21 eggs was 5.94% (de Wit 2003), the EEV is converted to 0.03 mg/kg ww.
- Studies reporting dietary or oral exposure were used for the evaluation of secondary poisoning. The results of these studies are usually expressed as a concentration in food (mg/kg) or a dose (mg/kg body weight [bw] per day) causing low or no observed effects. For derivation of a CTV<sub>food</sub> and ENEV<sub>food</sub>, the results were expressed as a concentration in food (in units mg/kg food), requiring information on the effect level (CTV<sub>total daily intake</sub>, mg/kg bw per day) in units of daily food intake (DFI, kg ww/day) and body weight (bw, kg ww) for the receptor species being considered. CTV<sub>food</sub> = (CTV<sub>total daily intake</sub> × bw) / DFI. This equation assumes that all substance is exposed via food, and that the substance is completely bioavailable for uptake by the organism. There are no available data characterizing the toxicity of PBDEs to wildlife species; therefore, data derived using rodents and rabbits were used as surrogates. Interspecies scaling using data for a typical adult mink was used to extrapolate to determine a food concentration protective of this species. This calculation involved the use of a typical adult body weight (i.e., 0.6 kg) and daily food ingestion rate (0.143 kg ww/day) of a female American mink (*Mustela vison*) (CCME 1998). References for toxicity data used in the calculation of the CTV<sub>food</sub> include Great Lakes Chemical Corporation (1984), Breslin et al. (1989) and Norris et al. (1974).
- To derive the ENEVs, the CTVs were divided by a factor of 10 to account for extrapolation from laboratory to field conditions, a factor of 10 to extrapolate from a rodent to a wildlife species and a further factor of 10 since components of PeBDE and OBDE are bioaccumulative and persistent, and DBDE congeners are persistent and there is a weight of evidence indicating debromination to bioaccumulative PBDEs
- k Not applicable. An ENEV was not derived for pelagic organisms and a risk quotient analysis was not conducted. Based on the available DBDE studies and the toxicity of other less brominated PBDEs, it was considered very unlikely that effects for DBDE will be observed in aquatic organisms up to the substance's water solubility limit.
- Adjusted to 4% organic carbon.
- <sup>m</sup> Adjusted to 2% organic carbon.