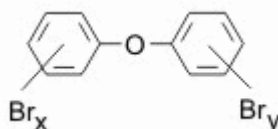




Canadian Environmental Protection Act, 1999
Ecological Screening Assessment Report on
Polybrominated Diphenyl Ethers (PBDEs)

June 2006

Environment Canada



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 Schedule 1 of CEPA 1999 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 meets the criteria as defined in section 64 of CEPA 1999. This ecological 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 represent 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 organisms.

Data relevant to the ecological 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. Information obtained as of October 2004 was considered for inclusion into this document, while that received between November 2004 and October 2005 was reviewed, but not generally added. The information obtained between November 2004 and October 2005 was found to support the conclusions of this report determined with information received up to October 2004. 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 2003). Toxicological studies were also submitted by industry under Section 70 of CEPA 1999.

This ecological 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 material in this report has been subjected to external review by Canadian and international experts selected from government and academia, including M. Alaei (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) and D. Stewart (Environment Canada, Ontario Region).

The ecological and human health screening assessment reports were approved by the joint Environment Canada/Health Canada CEPA Management Committee. The supporting working documentation for the ecological assessment is available upon request by e-mail from ESB.DSE@ec.gc.ca. Information on ecological 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, present on the Domestic Substances list (DSL), 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 2001; 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 2003). 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 2002).

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 2001 (BSEF 2003)

Commercial product	Americas ^a		Europe ^b		Asia ^c	
	Market demand	Estimated consumption (tonnes)	Market demand	Estimated consumption (tonnes)	Market demand	Estimated consumption (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

^a All countries in North, South and Central America were included.

^b All countries in Eastern and Western Europe were included.

^c Australia, New Zealand and the Indian subcontinent 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 2003). 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.

Various initiatives have resulted in significant changes in the global use of the PBDEs since 2001. The U.S. manufacturer of PeBDE and OBDE, Great Lakes Chemical Corporation voluntarily ceased its production of PeBDE and OBDE by December 31, 2004 (U.S. EPA 2005, Great Lakes Chemical Corp. 2005). ICL Industrial Products (2005) also announced complete termination of its production and sale of its OBDE product by the end of 2004. In addition, PeBDE and OBDE have been subject to a phase-out by the European Union (EU). In response to its risk assessments, the EU passed a Directive (2003/11/EC) which requires all member states to adopt laws that prohibit the marketing or use of any product containing more than 0.1% by mass of PeBDE or OBDE effective August 15, 2004. While it is expected that these actions have resulted in significant changes in the global and Canadian use of PBDEs, many products currently in use will have been manufactured during or before 2004 using PeBDE and OBDE.

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

A summary of selected physical and chemical properties of the commercial PBDE products and their primary constituents is presented in Table 2.

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

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

With their low vapour pressures, very low water solubility and high octanol/water partition coefficient (log K_{ow}) values, it is expected that PBDEs entering the environment will tend to bind to the organic fraction of particulate matter, soils and sediments. For instance, if it is assumed that equal quantities of pentaBDE are released to air, water and soil compartments, Level III fugacity modeling (EPI v. 3.10, Syracuse Research Corporation) indicates that much of the substance would be expected to partition to sediments and soils, with very little partitioning to water or air (see Table 3). If all pentaBDE is discharged to water, Level III fugacity modeling indicates that almost all of the substance would partition to sediments with only a very small proportion staying in the water column, or partitioning into air or soil compartments. If all pentaBDE were released to soil, the substance would remain almost exclusively in this environmental compartment. Partitioning characteristics for the other PBDEs subject to this assessment are expected to be very similar.

Table 3. Predicted partitioning of PentaBDE in the environment based on Level III Fugacity Modeling.

Release scenario	Predicted partitioning (%)			
	Air	Water	Sediment	Soil
Equal quantities to air, water, soil	0.2	1.2	59	40
100% to air	1.07	0.4	21	77.5
100% to water	8×10^{-5}	1.93	98.1	0.006
100% to soil	6.1×10^{-7}	0.002	0.11	99.9

The lower brominated PBDEs (tetra- to heptaBDEs) are slightly more soluble in water and have a greater propensity for volatilization and atmospheric transport than more highly brominated PBDEs. In the atmosphere, these homologues would tend to sorb to particulates. The higher brominated PBDEs are reported to have higher octanol-water ($\text{Log } K_{ow}$) and air-water ($\text{Log } K_{aw}$) partition coefficients and a greater propensity to remain in solid form, and thus, transport would likely be in the form of particles. Researchers have noted that the transport of the lower brominated PBDEs may be characterized by a series of deposition/re-volatilization “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 using a number of models (i.e., TaPL3-2.10, ELPOS-1.1.1, Chemrange-2 and Globo-POP-1.1) and various physical and chemical properties (i.e., solubility in water, vapour pressure, $\text{log } K_{ow}$, $\text{log } K_{oa}$, $\text{log } K_{aw}$ and estimated half-lives in different media). All models yielded comparable results, with tetraBDE showing the greatest potential for atmospheric transport and decaBDE the lowest transport potential. The researchers estimated a characteristic travel distance (CTD) ranging from 1,113 to 2,483 km for tetraBDE, 608 to 1,349 km for pentaBDE, and 480 to 735 km for decaBDE. The CTD was defined as the distance a parcel of air has traveled until 1/e or approximately 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 used models to predict 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.

PBDEs have been detected in all environmental media as well as sewage sludge (see Tables 4 and 5), 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 in North America, and high concentrations have been measured in sewage sludge. Kolic et al. (2004) determined levels of PBDEs in sediments from Lake Ontario tributaries flowing to Lake Ontario. The total PBDEs (tri-, tetra-, penta-, hexa-, hepta- and decaBDEs) measured in sediment samples taken from fourteen tributary sites (6 reported) ranged from approximately 12 to 430 µg/kg dw. Of the reported sediment results, concentrations of tetra- to hexaBDEs ranged from approximately 5 to 49 µg/kg dw. Concentrations of BDE209 ranged from 6.9 to 400 µg/kg dw. BDE 47, 99 and 209 were the predominant congeners measured in sediments. Rayne et al. (2003a) 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 south eastern 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 hexaBDEs 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 in Nunavut Territory 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.

Kolic et al. (2004) determined levels of PBDEs in biosolids from southern Ontario municipal wastewater treatment plants (Reiner pers. comm., 2004). They found total PBDEs (tri-, tetra-, penta-, hexa-, hepta- and decaBDEs) at five reported wastewater treatment facilities ranged from approximately 1,700 to 3,500 µg/kg dw. Of the reported biosolid results, total concentrations of tetra- to hexaBDEs ranged from approximately 1,350 to 1,900 µg/kg dw. BDEs 47, 99 and 209 were the

predominant congeners measured in biosolid samples. Concentrations of BDE 209 in the samples ranged from 310 to 2000 $\mu\text{g}/\text{kg dw}$. La Guardia et al. (2001) analyzed 11 sludge samples before land application from a sewage treatment facility in the Toronto area and from 10 facilities throughout the continental United States. Total PBDEs (sum of 11 tetra- to decaBDE congeners) in the samples of sewage sludge were 8280 $\mu\text{g}/\text{kg dw}$ at the Toronto site, while those in the U.S. ranged from 730 to 24,900 $\mu\text{g}/\text{kg dw}$. 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 $\mu\text{g}/\text{kg dw}$. Hale et al. (2002) measured total PBDEs (sum of BDEs 47, 99, 100 and 209) of 3005 $\mu\text{g}/\text{kg dw}$ in sludge samples 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 $\mu\text{g}/\text{kg lipid}$ in female ringed seals (*Phoca hispida*), 50.0 $\mu\text{g}/\text{kg}$ in the blubber of male ringed seals, 81.2 $\mu\text{g}/\text{kg lipid}$ in female beluga (*Delphinapterus leucus*) and 160 $\mu\text{g}/\text{kg lipid}$ in male beluga. 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 $\mu\text{g}/\text{kg lipid}$, was found in the blubber of a harbour porpoise from the Vancouver area. With a concentration of about 1200 $\mu\text{g}/\text{kg lipid}$, 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 $\mu\text{g}/\text{kg lipid}$ in 1981 to 6.0 $\mu\text{g}/\text{kg lipid}$ 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 $\mu\text{g}/\text{kg lipid}$ in 1989 to a maximum of 8325 $\mu\text{g}/\text{kg lipid}$ 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 $\mu\text{g}/\text{kg lipid}$ in 1982 and reached a maximum value of about 15 $\mu\text{g}/\text{kg lipid}$ in 1997. Total PBDE residues in the blubber of St. Lawrence estuary belugas sampled in 1997–1999 amounted to 466 (± 230) $\mu\text{g}/\text{kg wet weight (ww)}$ blubber in adult males and 665 (± 457) $\mu\text{g}/\text{kg ww}$ 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 4. 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 pg/m ³	Alaee et al. 2000
Air	Great Lakes; 1997–1999	5.5–52 pg/m ³	Strandberg et al. 2001
Air	Southern Ontario; 2000	10–1300 pg/m ³	Gouin et al. 2002
Air	Ontario; 2000	3.4–46 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. 2003a
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
Sewage sludge	Southern Ontario	1700–3500 µg/kg dw	Kolic et al. 2004

dw = dry weight; OC = organic carbon

Table 5. Measured concentrations of PBDEs in North American biota

Organism	Location; year	Total PBDEs	Reference
Dungeness crab hepatopancreas	West coast, Canada; 1993–1995	4.2–480 µg/kg lipid	Ikonomou et al. 2002b
Mountain whitefish (muscle)	Columbia River, British Columbia; 1992–2000	0.726–131 µg/kg ww	Rayne et al. 2003a
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	
Rainbow trout	Spokane River, Washington, USA; 1999	297 µg/kg ww	Johnson and Olson 2001
Mountain whitefish		1250 µg/kg ww	
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 evidence for long-range atmospheric transport of these compounds (Stern and Ikonomou 2000). Although 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.

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. 2004) show a leveling 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. 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 µg/kg ww at Lake Ontario; from 8.3 to 927.3 µg/kg ww at Lake Michigan; from 7.6 to 541.5 µg/kg ww at Lake Huron). These increases were found to be exponential at all three locations. Overall, the total PBDEs ranged from a low of 9.4 µg/kg ww in Lake Ontario to a high of 1544 µg/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.

Recent studies conducted in Europe provide evidence for the presence of decaBDE in biota. DecaBDE was detected in 18 of 21 analyzed eggs of peregrine falcons, *Falco peregrinus*, from Sweden, at concentrations from 28 to 430 µg/kg lipid (Lindberg et al. 2004). De Boer et al. (2004) conducted sampling to determine the occurrence of decaBDE in liver, muscle tissue and eggs of high trophic level bird species from the United Kingdom and The Netherlands. In total, 124 samples from 13 different species were analyzed. In addition, 10 peregrine falcon egg samples from the Swedish study by Lindberg et al. (2004) were re-analyzed. DecaBDE was detected in 10 of 28 liver samples (range < 1.5 to 181 µg/kg lipid weight), 14 of 28 muscle samples (range < 4.2 to 563 µg/kg lipid weight) and 25 of 68 eggs (range < 1.8 to 412 µg/kg lipid weight). Concentrations in the Swedish peregrine falcon eggs re-analyzed in the study were all within 30% of those originally determined by Lindberg et al. (2004). Highest concentrations of decaBDE were measured in muscle tissue samples collected from United Kingdom heron and peregrine falcon, and eggs from Swedish peregrine falcon.

Empirical and predicted data indicate that all PBDEs subject to this ecological 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 6). Tetra- to decaBDEs are predicted by AOPWIN (v1.90) to have air degradation half-lives which exceed 2 days (i.e., ranging from 7.14 to 317.53 days). Further, tetra-, penta-, hexa-, hepta- and decaBDEs 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. It has been shown that BDE 47 and DBDE are not subject to statistically significant anaerobic biodegradation over a period of 32 weeks. Neither PeBDE, OBDE nor DBDE are readily biodegradable based on short-term studies conducted under aerobic conditions

using an activated sludge inoculum. However, decaBDE is susceptible to some biodegradation under certain anaerobic conditions using sludge inoculum as described by Gerecke et al. (2005). Tetra- to decaBDEs are predicted by BIOWIN (v.4.00) to be recalcitrant with respect to biodegradation. It is reasonable to conclude that all PBDEs subject to this assessment meet the criteria for persistence as defined by CEPA 1999 based on known empirical and predicted data, as well as structural similarities.

Table 6. Persistence and bioaccumulation criteria as defined in CEPA 1999 Persistence and Bioaccumulation Regulations (Environment Canada 2000)

Persistence ^a		Bioaccumulation ^b
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} ≥ 5
Soil	≥182 days (≥6 months)	

^a A substance is persistent when at least one criterion is met in any one medium.

^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_{ow} will be considered.

Although all PBDEs subject to this assessment are considered to be persistent, evidence shows that PBDEs are susceptible to some degree of abiotic and biotic transformation under certain laboratory conditions.

The predominant phototransformation pathway for decaBDE in organic solvents appears to be reductive debromination, with nona- to triBDEs and polybrominated dibenzofurans (PBDFs) identified as possible phototransformation products (e.g., Norris et al. 1973, 1974; Watanabe and Tatsukawa 1987; Eriksson et al. 2001; Palm et al. 2003; Herrmann et al. 2003; Hua et al. 2003; Peterman et al. 2003). Researchers also report the formation of other as yet unidentified photodegradation products. The relevance of these studies, which disperse PBDEs in organic solvents such as hexane and octanol, to conditions existing in the environment is still uncertain.

Studies using more environmentally relevant media have also been conducted. Söderström et al. (2004) undertook photodegradation studies in which DBDE (exact composition not provided, but contained traces of octa- and nonaBDEs) was dissolved in toluene and then applied as a thin layer to silica gel, sand, soil or sediment substrates. The toluene solvent was evaporated off in the dark prior to exposure of the substrates to ultraviolet (UV) light or natural sunlight. Prior to light exposure, a small amount of water was added to the sediment in order to more closely emulate natural conditions. DBDE applied to silica gel decayed quickly under artificial and natural lighting, with an estimated half life of less than 15 min. The half-life of DBDE on sand was 12 and 13 h under UV and natural sunlight, respectively, while that of DBDE on sediment was 40-60 and 30 h under UV and sunlight, respectively. Overall, decay proceeded slowest with DBDE on soil exposed to UV light, with a half-life of 150-200 hours. The researchers concluded from their experiments that the photodegradation of decaBDE, at least initially, seems to follow a stepwise debromination process. They noted that as decaBDE disappeared, lower brominated DEs (nona- to hexaBDEs) were formed, but that after the

maximum occurrence of hexaBDEs, only minor amounts of lesser brominated DEs (tetra- and pentaBDEs) were formed, resulting in a discontinued mass balance. This suggested that other unknown compounds were also being formed, but that these were lost during the sample clean-up. In addition to the identified PBDEs, tetra- and pentaBDFs were also detected as transformation products of DBDE adsorbed to sand, sediment and soil.

Jafvert and Hua (2001) conducted photodegradation studies of DBDE adsorbed to solid matrices (sand and quartz surfaces) with water and/or humic acid and irradiated with natural or artificial sunlight. Their studies showed that some photodegradation of DBDE occurred under natural or artificial sunlight (over time periods up to 240 h loss of decaBDE varied up to 71%). Although Jafvert and Hua (2001) did not conclude that lower brominated DEs were produced, the European Communities (2002), based on their review of the decaBDE humic acid coated sand exposure, noted that there were indications that lower brominated DEs (particularly hexaBDE) were formed. Palm et al. (2003) irradiated decaBDE adsorbed onto silicon dioxide in aqueous suspension with artificial sunlight. They also found that approximately 50% of the initial decaBDE concentration was lost after about 360 min. Details regarding the degradation products were not provided; however, Palm et al. (2004) notes that PBDFs were confirmed as short-lived trace intermediates.

Keum and Li (2005) investigated the debromination of PBDEs (including decaBDE) in contact with the reducing agents, zerovalent iron, iron sulphide and sodium sulphide. In the experiments with zerovalent iron, decaBDE was rapidly transformed to lower BDEs. Approximately 90% of the parent was converted to mono- to hexaBDEs after 40 d. During the initial reaction period (up to 5 d), BDE 209 was predominantly transformed into hexa- and heptaBDEs, but tetra and pentaBDEs were predominant after 14 d. The results demonstrated that decaBDE undergoes reductive debromination in the presence of zerovalent iron. The experiments with sodium sulphide also showed transformation of decaBDE to lower brominated DEs, but the rate was slower than that determined in the presence of zerovalent iron. A similar profile of transformation products was found to that determined in the experiment with zerovalent iron. Experiments were also conducted with BDEs 28, 47, 66 and 100 in the presence of zerovalent iron. These also showed that debromination had occurred but that the rate of reaction decreased with a decreasing number of bromines. Although the conditions of this study are not directly related to those common in the natural environment, it is possible that similar reactions maybe taking place in the environment (United Kingdom 2005).

Gerecke et al. (2005) conducted experiments to determine the rates of degradation of decaBDE and nonaBDEs under anaerobic conditions conducted in the dark at 37 °C using sewage sludge as inoculum. The researchers found that BDE 209 decreased by 30% within 238 d in experiments with primers added (i.e., 4-bromobenzoic acid, 2,6-dibromobiphenyl, tetrabromobisphenol A and hexabromocyclododecane) and this corresponded to a pseudo-first-order degradation rate constant of $1 \times 10^{-3} \text{ d}^{-1}$, statistically significant at the 95% confidence level. The sample with decaBDE was observed to form two nonaBDE and six octaBDE congeners. The rate of decaBDE decay without primers added was about one-half that of the experiments with primers. The study demonstrated that the debromination of decaBDE proceeded most readily by the loss of bromine from the para- and meta-positions. The United Kingdom (2005) notes that the conditions in themselves are not representative of sewage sludge treatment processes, or those typical in the natural environment. However, such conditions could occur in landfill sites which are anaerobic, methanogenic and have

high temperatures. The study provides evidence that decaBDE could be susceptible to some level of slow degradation under conditions of anaerobic biodegradation.

PBDE congener patterns found in the environment are sometimes reported to resemble those of the PeBDE and OBDE commercial products, leading some researchers (e.g., Song et al. 2004) to propose that these products are the primary sources of PBDEs into the environment. Rayne and Ikononou (2002) placed semipermeable membrane devices (SPMD) in the Fraser River, BC and analyzed the resultant SPMD samples for 36 PBDEs (mono- to hexa- congeners). They found that the congener patterns observed in the SPMD samples differed significantly from those of the commercial PeBDE and OBDE mixtures. They then applied modeling and calculation procedures and found that the reconstructed congener patterns more closely approximated those of the technical mixtures. These analyses lead the researchers to suggest that the PBDEs present in the region arose primarily from PeBDE and OBDE mixtures..

Söderström et al. (2004) also concluded that the lower brominated DEs (e.g., BDE 47, 154 and 183) found in the environment probably originate mainly as emissions from the commercial PeBDE and OBDE mixtures rather than DBDE phototransformation. In their studies they note that the most commonly found PBDEs in environmental samples (BDE 47, 99 and 100) were only formed to a very minor degree during their photolysis studies. However, it should be noted that most monitoring studies to date have only investigated PBDEs for which standards are available. These PBDEs are also the main components of the commercial products. As a result, one can expect that the results reported for environmental samples would predominantly be for PBDEs present in the commercial products. Analytical standards are not available for all congeners, and thus, it may be that studies conducted to date have not investigated all congeners present in environmental samples, including those occurring as photodegradation products of decaBDE.

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 et al. 2004b,c; 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 et al. (2004a) and Stapleton and Baker (2003), approximately 0.4% of consumed decaBDE was shown to biotransform in carp to form penta- to octaBDEs. The researchers note that while this amount may appear insignificant, high concentrations of decaBDE reported in river sediment and land-applied sludge could lead to appreciable accumulation in organisms exposed to such material (Stapleton et al. 2004a).

While conditions of laboratory experiments showing that decaBDE will transform to lesser brominated DEs are not completely representative of those in the natural environment or sewage treatment facilities, they indicate that some degree of transformation cannot be ruled out. 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 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 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 6). A BCF of about 27 400 L/kg for PeBDE was reported by European Communities (2001), 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 µg/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 1.4×10^6 was reported for PeBDE in blue mussels (*Mytilus edulis*) exposed for 44 days (Gustafsson et al. 1999). The same study reported BCFs of 1.3×10^6 for tetraBDE and 2.2×10^5 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., Alaei and Wenning 2002; de Wit 2002).

Key studies of toxicity to organisms in different environmental media are presented in Table 7. 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).

Risk Characterization

The approach taken in this ecological 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 ecological 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 the persistence and bioaccumulation criteria as outlined in the CEPA 1999 Regulations (see Table 6), an additional application factor of 10 is applied to the CTV.

Risk quotients derived for PBDEs are summarized in Table 8. Exposure data used as EEVs can be found in Tables 4 and 5 or are summarized in the notes to Table 8. Toxicity data used to determine CTVs and ENEVs are summarized in Table 7.

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 is not clear at this time.

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 uncertainty regarding the possible transformation products of decaBDE exists, there is sufficient evidence to conclude that some level of decaBDE phototransformation likely occurs in the environment and that lower brominated PBDEs are being formed during this process. These products are likely to be more bioaccumulative than the parent compound and could be considered persistent and may be directly toxic to organisms. There is limited information available on the relative rates of lower BDE formation, and the rates by which these products subsequently degrade in the environment. In addition, results from some studies suggest that other as yet unidentified products are also being formed as well as PBDFs. It is expected that decaBDE in the environment would mainly sequester into sediment or soil and this could limit the amount available for photodegradation, but it could make some amount available for transformation via other processes such as anaerobic biodegradation or reaction with reducing agents. Overall, it is very difficult to determine the extent to which the transformation of decaBDE in the environment may contribute to the potential accumulation of lower BDEs and other products. Nevertheless, it is reasonable to consider that various transformation processes could contribute to the formation of at least some amount of lower brominated PBDEs and PBDFs. Future monitoring would help to clarify whether and the degree to which decaBDE transformation contributes to the overall risk presented by the lower brominated DEs such as tetra- to hexaBDEs.

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 exceeding 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 over periods spanning several decades could have serious ecological consequences. 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.

Pyrolysis and extreme heating can cause all PBDEs to form brominated dibenzo-*p*-dioxins and dibenzofurans (European Communities 2001, 2002, 2003). 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.

Conclusion for the Environment

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 meets the criteria 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 concentration or under conditions that constitute or may constitute a danger to the environment on which life depends, and thus do not meet the criteria under Paragraph 64(b) of CEPA 1999.

The available data regarding persistence and bioaccumulation of tetraBDE, pentaBDE and hexaBDE indicate 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.

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Table 7. 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
<i>Daphnia magna</i> <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 style="list-style-type: none"> flow-through using well water 20 ± 1°C, pH 7.9–8.3, DO ≥ 76% saturation, hardness 128–136 mg/L as CaCO₃, alkalinity 174–176 mg/L as CaCO₃, conductance 310–315 µmhos/cm 40 animals per treatment GLP, protocol based on OECD 202, TSCA Title 40 and ASTM E1193-87 	<ul style="list-style-type: none"> 21-day LOEC (mortality/immobility) = 20 µg/L 21-day NOEC (mortality/immobility) = 9.8 µg/L 96-hour EC₅₀ (mortality/immobility) = 17 µg/L 7- to 21-day EC₅₀ (mortality/immobility) = 14 µg/L 21-day EC₅₀ (reproduction) = 14 µg/L 21-day LOEC (growth) = 9.8 µg/L 21-day NOEC (growth) = 5.3 µg/L LOEC (overall study) = 9.8 µg/L NOEC (overall study) = 5.3 µg/L 	CMABFRIP 1998
<i>Lumbriculus variegatus</i> 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 style="list-style-type: none"> flow-through using filtered well water 23 ± 2°C, pH 7.9–8.6, DO 6.0–8.2 mg/L, hardness 130 mg/L as CaCO₃ artificial sediment: pH 6.6, water holding capacity 11%, mean organic matter <2%, 83% sand, 11% clay, 6% silt 80 animals per treatment GLP, protocol based on Phipps et al. (1993), ASTM E1706-95b and U.S. EPA OPPTS No. 850.1735 	<ul style="list-style-type: none"> 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 EC₅₀ (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
<i>Zea mays</i> 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 style="list-style-type: none"> artificial soil: 92% sand, 8% clay and 0% silt, pH 7.5, organic matter content 2.9% watering with well water using subirrigation, 14:10 light:dark photoperiod, 16.0–39.9°C, relative humidity 19–85% 40 seeds per treatment GLP, protocol based on U.S. EPA OPPTS Nos. 850.4100 and 850.4225 and OECD 208 (based on 1998 proposed revision) 	<ul style="list-style-type: none"> no apparent treatment-related effects on seedling emergence 21-day LC₂₅, LC₅₀ (seedling emergence) > 1000 mg/kg soil dw mean shoot height significantly reduced at 250, 500 and 1000 mg/kg soil dw relative to controls 21-day EC₂₅, EC₅₀ (mean shoot height) > 1000 mg/kg soil dw mean shoot weight significantly reduced at 62.5, 125, 250, 500 and 1000 mg/kg soil dw relative to controls 21-day EC₂₅ (mean shoot weight) = 154 mg/kg soil dw 21-day EC₅₀ (mean shoot weight) > 1000 mg/kg soil dw 21-day LOEC (mean shoot weight) = 62.5 mg/kg soil dw 21-day EC₀₅ and (estimated) NOEC (mean shoot weight) = 16.0 mg/kg soil dw 	Great Lakes Chemical Corporation 2000b

Species, life stage	Composition of test material	Test duration	Test concentrations	Study design	Effect level	Reference
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)	<ul style="list-style-type: none"> 30 male and 30 female Sprague-Dawley CD rats per treatment 	<ul style="list-style-type: none"> 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
<i>Daphnia magna</i> <24 hours old at test initiation	OBDE: 5.5% hexaBDE 42.3% heptaBDE 36.1% octaBDE 13.9% nonaBDE 2.1% decaBDE (European Communities 2003)	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 style="list-style-type: none"> flow-through using filtered well water 20 ± 1°C, pH 8.2–8.5, DO ≥ 77% saturation, hardness 132–136 mg/L as CaCO₃ 20 animals per treatment GLP, protocol based on OECD 202, ASTM E1193-87 and TSCA Title 40 	<ul style="list-style-type: none"> 21-day LOEC (survival, reproduction, growth) > 2.0 µg/L (nominal) or 1.7 µg/L (measured) 21-day NOEC (survival, reproduction, growth) ≥ 2.0 µg/L (nominal) or 1.7 µg/L (measured)^a 21-day EC₅₀ (survival, reproduction, growth) > 2.0 µg/L (nominal) or 1.7 µg/L (measured) 	CMABFRIP 1997d
<i>Eisenia fetida</i> 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 style="list-style-type: none"> artificial soil: sandy loam, 69% sand, 18% silt, 13% clay, 8.0% organic matter (4.7% carbon), pH 6.0 ± 0.5 17–21°C, 16:8 light:dark photoperiod, pH 5.9–6.8, soil moisture 22.0–33.5% 40 animals per treatment GLP, protocol based on U.S. EPA OPPTS 850.6200, OECD 207 and proposed OECD (2000) guideline 	<ul style="list-style-type: none"> 28-day LOEC (mortality) > 1470 mg/kg dry soil 28-day NOEC (mortality) ≥ 1470 mg/kg dry soil^a 28-day EC₁₀, EC₅₀ (survival) > 1470 mg/kg dry soil 56-day LOEC (reproduction) > 1470 mg/kg dry soil 56-day NOEC (reproduction) ≥ 1470 mg/kg dry soil^a 56-day EC₁₀, EC₅₀ (reproduction) > 1470 mg/kg dry soil 	Great Lakes Chemical Corporation 2001c
<i>Lumbriculus variegatus</i> adult	OBDE (DE-79): 78.6% bromine content.	28 days	Nominal: 0, 94, 188, 375, 750 and 1500 mg/kg dw of sediment Measured: (i) 2% OC: <0.354, 76.7, *, *, 755 and 1340 mg/kg dw sediment	<ul style="list-style-type: none"> 80 animals per treatment flow-through using filtered well water, hardness 128–132 mg/L as CaCO₃ Two trials with different artificial sediments: (i) 6% silt, 9% clay, 85% sand, 2% TOC, water holding capacity 9.3%, 23 ± 2°C, pH 7.6–8.4, DO ≥ 	<ul style="list-style-type: none"> 28-day LOEC (survival/reproduction, growth) > 1340 (2% OC) or 1272 (5% OC) mg/kg dw of sediment 28-day NOEC (survival/reproduction, growth) ≥ 1340 (2% OC) or 1272 (5% OC) mg/kg dw of sediment^a 28-day EC₅₀ (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
			(ii) 5% OC: <12.5, 90.7, *, *, 742 and 1272 mg/kg dw sediment * concentrations were not measured	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 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	<ul style="list-style-type: none"> 26 New Zealand White rabbits per treatment offspring examined on day 28 of gestation 	<ul style="list-style-type: none"> no evidence of teratogenicity LOAEL (maternal, increased liver weight, decreased body weight gain) = 15 mg/kg bw per day NOAEL (maternal) = 5.0 mg/kg bw per day LOAEL (fetal, delayed ossification of sternebrae) = 15 mg/kg bw per day NOAEL (fetal) = 5.0 mg/kg bw per day 	Breslin et al. 1989
<i>Eisenia fetida</i> 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, 320, 668, 1240, 2480 and 4910 mg/kg dw	<ul style="list-style-type: none"> 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 	<ul style="list-style-type: none"> 28-day LOEC (survival) > 4910 mg/kg dry soil (mean measured) 28-day NOEC (survival) ≥ 4910 mg/kg dry soil (mean measured)^a 28-day EC₁₀, EC₅₀ (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)^a 56-day EC₁₀, EC₅₀ (reproduction) > 4910 mg/kg dry soil (mean measured) 	ACCBFRIP 2001c
<i>Lumbriculus variegatus</i> 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, 258, *, *, 2034 and 3841 mg/kg dw * 625 and 1250 mg/kg concentrations were not measured	<ul style="list-style-type: none"> 80 animals per treatment flow-through using filtered well water, hardness 128–132 mg/L as CaCO₃ 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% 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. 	<ul style="list-style-type: none"> 28-day NOEC (survival/reproduction, growth) ≥ 4536 (2.4% OC) or 3841 (5.9% OC) mg/kg dw of sediment^a 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
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	EPA OPPTS 850.1735 • 5 male Sprague Dawley rats per treatment	<ul style="list-style-type: none"> • LOAEL (enlarged liver, thyroid hyperplasia) = 80 mg/kg bw per day • NOAEL = 8 mg/kg bw per day 	Norris et al. 1974

Abbreviations used: ASTM = American Society for Testing and Materials; DL = detection limit; DO = dissolved oxygen; EC₅₀ = median effective dose; EPA = Environmental Protection Agency; GLP = Good Laboratory Practice; LC₅₀ = median lethal dose; LOAEL = Lowest-Observed-Adverse-Effect Level; LOEC = Lowest-Observed-Effect Concentration; NOAEL = No-Observed-Adverse-Effect Level; NOEC = No-Observed-Effect Concentration; OC = organic carbon; OECD = Organisation for Economic Co-operation and Development; OPPTS = Office of Prevention, Pesticides and Toxic Substances; TOC = total organic carbon; TOM = total organic matter; TSCA = *Toxic Substances Control Act*

^a 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.

Table 8. Summary of data used in risk quotient (Q) analysis of PBDEs

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

^a Stapleton and Baker (2001).

^b CMABFRIP (1997d, 1998).

^c 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 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 2002, 2003).

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.

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

^f 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):

$$EEV_{soil} = (C_{sludge} \times AR_{sludge} \times T) / (D_{soil} \times BD_{soil})$$

where:

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

C_{sludge} = concentration in sludge (mg/kg);

AR_{sludge} = application rate to soils (kg/m² per year, default value = 0.5);

D_{soil} = 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/m³, default value = 1700); and

T = 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 nona- and decaBDE) in biosolids was used. This concentration was also reported for a Massachusetts wastewater treatment facility biosolid sample (La Guardia et al. 2001).

^g Great Lakes Chemical Corporation (2000b, 2001c); ACCBFRIP (2001c).

- ^h Johnson and Olson (2001); Allchin et al. (1999); Sellström et al. (2001); Lindberg et al. (2004).
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. 2004). 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.
- ⁱ 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_{food} and ENEV_{food}, the results were expressed as a concentration in food (in units mg/kg food), requiring information on the effect level (CTV_{total daily intake}, 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. $CTV_{food} = (CTV_{total\ daily\ intake} \times bw) / DFI$. 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_{food} include Great Lakes Chemical Corporation (1984), Breslin et al. (1989) and Norris et al. (1974). It is noted that Norris et al. (1974) used the product, Dow FR-300-BA, an older DBDE formulation which was composed of 77.4% decaBDE, 21.8% nonaBDE and 0.8% octaBDE. This product is no longer produced and current formulations of DBDE are composed of a much higher proportion of decaBDE (e.g., usually > 97%). The value, 80 mg DBDE/kg bw/d in food is nevertheless considered appropriate for use as a CTV for DBDE since the subject study is of acceptable quality and represents a conservative measured endpoint. Although this study used an older DBDE formulation, its constituents represent homologue groups (predominantly nonaBDEs and decaBDE) subject to this assessment. This assessment is not limited to analyses of the commercial products, but rather PBDEs in the homologue groups with four to 10 bromine atoms/molecule. Thus, this study is deemed appropriate for use in the quotient analysis, but it is noted that it reflects a mixture with a greater proportion of nonaBDE (and a small fraction of octaBDE) than current DBDE formulations.
- ^j 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.
- ^l Adjusted to 4% organic carbon.
- ^m Adjusted to 2% organic carbon.