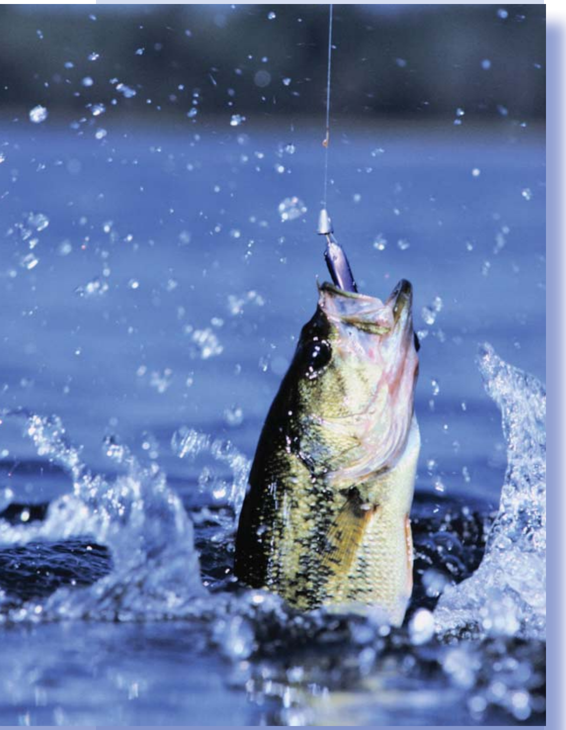
Environment Canada Environnement Canada



Environmental Monitoring and Surveillance in Support of the Chemicals Management Plan

POLYBROMINATED DIPHENYL ETHERS IN THE CANADIAN ENVIRONMENT



Polybrominated diphenyl ethers (PBDEs) are a group of chemicals that have been widely used in polyurethane foam, electronics, textiles, plastics and other materials as flame retardants since the 1970s. PBDEs are released to the environment from industrial processes, product use and waste disposal sites. They pose an environmental concern because they do not biodegrade readily, some PBDEs are found to bioaccumulate, and they may lead to hormonal disturbances or other harmful effects in animals. Currently, the use of PBDEs is declining because most commercial mixtures containing these chemicals have been either voluntarily phased out by manufacturers or subject to restrictions in Canada and other countries. However, the widespread use of PBDEs over the past several decades has led to their ubiquitous presence in the Canadian environment. In order to understand and address the risks posed by PBDEs in the environment, the Government of Canada has been monitoring PBDEs in the environment and in certain waste streams across Canada. This fact sheet summarizes the monitoring program for PBDEs and provides information on the spatial and temporal distribution of PBDEs in Canada from 1980 to 2010.

Canada

Monitoring Under the Chemicals Management Plan

Monitoring (a system of long-term standardized measurements) and surveillance (focused short-term measurements) are key elements of the Government of Canada's Chemicals Management Plan (CMP) and are essential to identifying and tracking environmental concerns and health risks. Monitoring information feeds into science-based decision-making processes, including the implementation and evaluation of control measures such as regulations.

Environment Canada scientists collect data on chemical substances in outdoor air, freshwater, sediments, aquatic biota and wildlife across Canada. Recognizing that many emerging chemicals of concern are found in products that are ultimately disposed of in waste and wastewater systems, monitoring at landfills and wastewater treatment systems is also conducted under the CMP Environmental Monitoring and Surveillance Program. Also under the CMP, Health Canada conducts human biomonitoring and monitoring in other media of concern to human health, including house dust, indoor air, drinking water and food.

Background on PBDEs

PBDEs are a group of 209 compounds (called congeners) that are classified into 10 different sub-groups, known as homologues, based on the number of bromine atoms they contain (e.g., **penta**bromodiphenyl ether or pentaBDE has five bromine atoms). Important physicochemical differences exist among the homologues, such as molecular mass (decaBDE is heavier than triBDE), which affect their toxicity and fate in the environment. PBDEs are present in three commercial mixtures known as PentaBDE, OctaBDE and DecaBDE, which contain various combinations of the homologues, but are dominated by those with 5, 8 or 10 bromine atoms, respectively.

Through risk assessment activity under the *Canadian Environmental Protection Act, 1999* (CEPA 1999), the Government of Canada has concluded that tetra- through decaBDE pose a risk to the environment but not human health. Tetra-, penta- and hexaBDE meet the persistence, bioaccumulation and inherent toxicity criteria for virtual elimination under CEPA 1999. In addition, decaBDE may accumulate to problematic levels in certain wildlife species.

In Canada, PBDEs may be released to the environment during polymer processing and product manufacturing operations, through use of products containing them, and at the end of product service life following disposal. Owing to their chemical and physical properties, PBDEs tend to bind to sediment and soil. As a result, PBDEs are generally found in soil and sediment at higher amounts than in water and air. In air, PBDEs have the potential to travel long distances and cross international boundaries before deposition to land and water. In sediment and soil, organisms such as invertebrates and earthworms may consume PBDEs, and because the tri- through hexaBDE homologues are bioaccumulative, they can build up in organisms over time. These same homologues also have the potential to biomagnify or increase in concentration moving up the food chain. Therefore, predatory fish, birds and mammals have a greater potential to suffer adverse effects from PBDEs than do animals that are lower in the food chain. In some circumstances, PBDEs may break down in the environment or within organisms from higher- (e.g., decaBDE) to less-brominated homologues (e.g., pentaBDE).

Various initiatives have resulted in significant changes in the global use of PBDEs during the 2000s. The PentaBDE and OctaBDE commercial mixtures were phased out internationally by manufacturers, and PBDEs have recently been added to agreements that prohibit their use on an international scale. Canada prohibited the manufacture, import and use of Penta and Octa commercial mixtures in 2008, and proposed in 2010 to expand this prohibition to DecaBDE as well as products containing PBDEs.

Manufacturers and importers of DecaBDE have committed to phasing out this commercial mixture voluntarily in the United States by 2013. As a result of these actions, it is anticipated that there will be fewer products containing PBDEs introduced into the Canadian market, resulting in declines in the quantity of PBDEs released to the environment. Over time, declines in PBDE levels in the environment are expected to occur.

Federal Environmental Quality Guidelines for PBDEs

Environmental monitoring can be used to measure progress towards risk management objectives and to track levels in the ambient environment over time. Environment Canada has developed Federal Environmental Quality Guidelines (FEQGs) for PBDEs to assess the ecological significance of levels of PBDEs in the environment (Table 1; Environment Canada 2010). FEQGs for PBDEs are based on studies that directly link exposure to PBDEs to adverse effects in animals. Because of uncertainties associated with a lack of data (e.g., limited number of animal species), the FEQGs include a margin of safety. When environmental concentrations of PBDEs are below the FEQGs, adverse effects on aquatic life or animals consuming aquatic life from PBDE exposure are unlikely. Concentrations above the FEQGs indicate an increased probability that adverse effects on the environment may occur. However, exceeding these concentrations does not automatically mean that adverse effects can be expected. Further investigation would be necessary to confirm whether negative impacts are actually occurring.

Table 1: Federal Environmental Quality Guidelines for Polybrominated Diphenyl Ethers

Homologue*	Congener	Water (ng/L)	Fish Tissue (ng/g ww)	Sediment** (ng/g dw)	Wildlife Diet† (ng/g ww food source)	Bird Eggs (ng/g ww)
triBDE	total	46	120	44	–	–
tetraBDE	total	24	88	39	44	–
pentaBDE	total	0.2	1	0.4	13 (birds)	29‡
pentaBDE	BDE-99	4	1	0.4	3	–
pentaBDE	BDE-100	0.2	1	0.4	–	–
hexaBDE	total	120	420	440	4	–
heptaBDE	total	17‖	–	–	64	–
octaBDE	total	17‖§	–	5600§	63§	–
nonaBDE	total	–	–	–	78	–
decaBDE	total	–	–	19§#	9	–

*FEQGs for triBDE, tetraBCD, hexaBDE, heptaBDE, nonaBDE and decaBDE are based on data for BDE-28, BDE-47, BDE-153, BDE-183, BDE-206 and BDE-209 respectively unless otherwise noted. Congener-specific FEQGs exist for BDE-99 and BDE-100; if monitoring data do not distinguish among homologues and exist only for pentaBDE, the lower of the two FEQGs for the congeners applies to the homologue.

**Values normalized to 1% organic carbon.

†Applies to mammalian wildlife unless otherwise noted.

‡Value based on the commercial formulation DE-71, which contains mostly pentaBDE and some tetraBDE.

‖Values based on a mixture of heptaBDE and octaBDE.

§Values adopted from Ecological Screening Assessment Report (SAR). Sediment guidelines for octa- and deca-BDE were adapted from the SAR by being corrected for the sediment organic carbon in the actual tests, then normalized to 1% organic carbon instead of the 4% in the SAR.

#Based on a mixture of decaBDE with some nonaBDE.

MONITORING RESULTS

Results for air, sediment, fish and wildlife monitoring are presented, with both a geographic analysis of PBDE distribution across Canada in 2008 (Figure 1) and an analysis of PBDE levels in Canada over time (within 1980–2009, Figures 2–5). Surveillance results for landfill and wastewater from 2008 to 2010 are also described. Due to the low solubility of PBDEs in water, surface water was not identified as a suitable monitoring medium for PBDEs and was therefore not included in the program.

Geographic Analysis

The spatial distribution of PBDEs in air, sediment, fish and wildlife across Canada relates largely to levels of urbanization. Higher concentrations were observed near cities, indicating that urban and industrial centres are the primary source of PBDEs in the environment. Lower levels in rural areas and northern Canada are commensurate with ambient environmental levels resulting primarily from atmospheric deposition, although minor inputs from rural populations (e.g., releases from wastewater and consumer products) may also contribute to observed levels in some of these locations. The Great Lakes and the St. Lawrence River have the highest levels of PBDEs in all media.

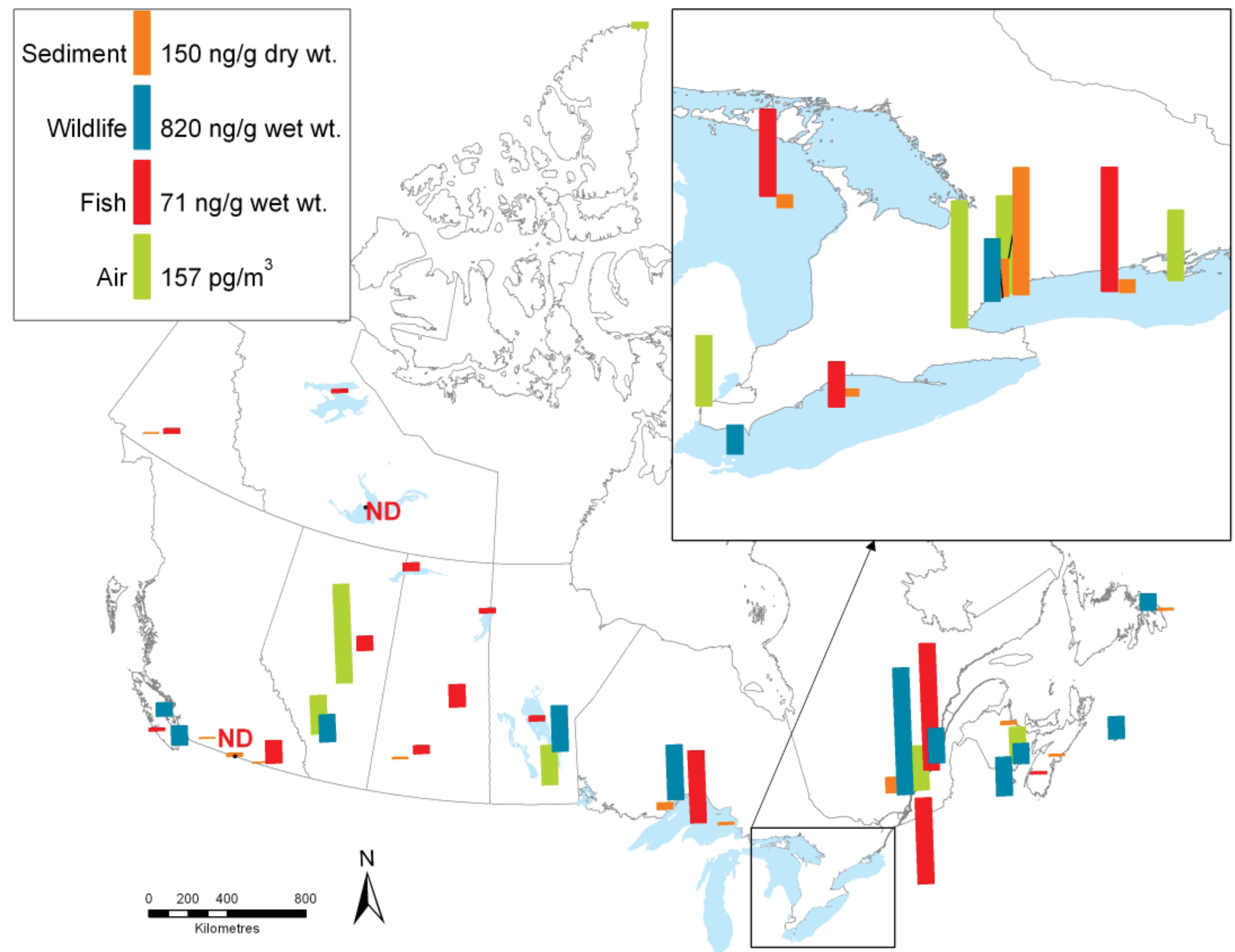


Figure 1: Total PBDEs in sediment, fish, wildlife (gull eggs) and air across Canada in 2008 (excluding the Alert site, which is for 2007). Bar heights represent the proportion of the maximum value observed for each media in that year – air: 157 pg/m^3, sediment: 130 ng/g dry weight (dw), fish: 71 ng/g wet weight (ww), and wildlife: 820 ng/g ww. Sampling sites where PBDEs were not detected (ND) in a given media are indicated in the appropriate colour.

Air:

Monitoring PBDEs in air across Canada provides information on PBDE levels within the country as well as quantities entering Canada from international sources. Total measured PBDEs were highest in Hamilton (157 pg/m^3), with similar levels observed in Toronto and Edmonton. Levels in Alert, Nunavut, for 2007 were substantially lower (7 pg/m^3). FEQGs do not exist for air.

Sediment:

PBDEs were detected in all 21 sediment locations sampled in 2008. Overall, the highest total PBDE concentrations in Canada were found in Toronto Harbour (130 ng/g dw), other areas of Lake Ontario (41 ng/g dw) and Lake Saint-Pierre on the St. Lawrence River (40 ng/g dw). Low levels were observed in B.C., Yukon, Saskatchewan and the Atlantic provinces (<4 ng/g dw). Concentrations of individual PBDE homologues were below or moderately exceeded their respective FEQGs for most regions of Canada. Exceedances in Lake Ontario and Lake Saint-Pierre were moderate; average pentaBDE concentrations were approximately twice the FEQG for pentaBDE (0.4 ng/g dw). In a few locations in Lake Ontario, however, values for pentaBDE were 10–60 times greater than the FEQG. The concentration of decaBDE exceeded the respective FEQG (19 ng/g dw) in a few locations: Toronto Harbour (70 ng/g dw) and six other locations in Lake Ontario (≤30 ng/g dw).

Fish:

Top predator fish (e.g., trout and walleye) were sampled from 19 sites across Canada in 2008. PBDE concentrations in samples collected from across Canada varied considerably, with the highest average concentrations of total PBDEs in Lake Ontario lake trout (70 ng/g ww) and St. Lawrence walleye (71 ng/g ww), and the lowest in Nova Scotia and the Northwest and Yukon Territories (<3 ng/g ww). Average concentrations of PBDEs only exceeded the FEQG for fish tissue for the pentaBDE homologue (1 ng/g ww). PentaBDE concentrations ranged from not detected to 24.5 ng/g ww, with average concentrations in 11 out of 19 sites exceeding the FEQG. When comparing concentrations in fish to the FEQGs for wildlife diet, exceedances were also observed for hexaBDE in the Great Lakes and St. Lawrence River. Average concentrations from fish in Lake Ontario (10 ng/g ww) were approximately twice the FEQG (4 ng/g ww), while other sites had just slight exceedances (e.g., average of 5 ng/g ww in Lake Huron).

Wildlife:

PBDE concentrations in pooled samples of gull eggs collected from across Canada in 2008 also varied considerably among the 13 sampling sites. Overall, average total PBDEs were highest in eggs of herring gulls from Deslauriers Island in the St. Lawrence River near Montréal (820 ng/g ww). Levels in the Great Lakes and Lake Winnipeg were next highest, with the lowest measurements in the Pacific and Atlantic colonies (≤130 ng/g ww). The average concentrations of pentaBDE were largely below or slightly above the FEQG of 29 ng/g ww. Exceptions were Toronto Harbour (Figure 5) and Deslauriers Island. At this latter site, while levels in eggs of ring-billed gulls were less than the FEQG, levels in herring gull eggs were three times above, but still within the margin of safety.

Temporal Analysis

Levels of PBDEs in sediment, fish and wildlife from Lake Ontario showed a marked increase beginning in the early 1980s. However, in recent years, they show a decreasing trend that seems to coincide with the voluntary and regulatory phase-out of the use of PentaBDE and OctaBDE commercial formulations. Tetra-, penta- and hexaBDE are the dominant homologues in fish and wildlife over the entire period, while tetra-, penta- and decaBDE congeners are dominant in air, reflecting the influence of penta-BDE and deca-BDE technical mixtures. Tetra- and pentaBDE had the highest concentrations in sediment in the beginning of the period, but by the late 1980s, levels of decaBDE had surpassed levels of the other congeners, and it remained dominant for the rest of the period. Average concentrations of pentaBDE in Lake Ontario in sediment, fish and wildlife exceeded the pentaBDE FEQG for the entire period.

Air:

Data on the level of PBDEs in air at Point Petre, located in southern Ontario, are available starting in 2005 (Figure 2). Declines are evident in tetra- and decaBDE over the period. In contrast to the Point Petre site, most congeners in Alert, Nunavut (not shown), show increasing trends between 2002 and 2007, suggesting that global use of PBDEs and long-range transport may be influencing levels of PBDEs in northern Canada.

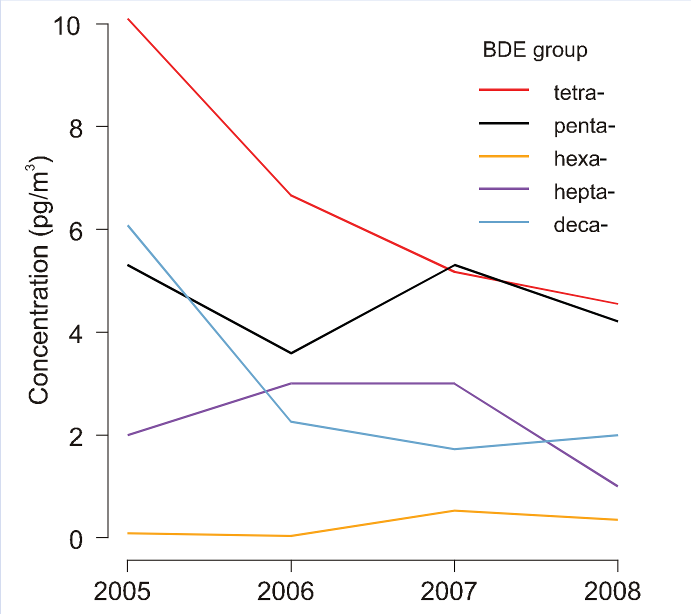


Figure 2: Average concentrations of PBDEs in air (pg/m^3) at Point Petre, Ontario, 2005 to 2008. OctaBDE and nonaBDE were not measured in air. Air data prior to 2005 are not available.

Sediment:

A sediment core taken in 2005 in Lake Ontario was sampled, dated using radioisotopic methods and analyzed for PBDEs by Environment Canada and the Ontario Ministry of the Environment. Findings show a rapid increase in accumulation of decaBDE in Lake Ontario sediment over the period between the mid-1980s and the early 2000s, with a decline starting thereafter (Figure 3). Levels of other homologues do not show evidence of a similar decline. In contrast, although total PBDEs in sediment from Lake Saint-Pierre, Quebec (not shown), decreased between 2003 and 2008, decaBDE only decreased an average of 30%, while other homologues decreased an average of 70%. In addition, some downstream sites in Lake Saint-Pierre actually showed increases in decaBDE of >10 ng/g between 2003 and 2008, while other homologues decreased at all sampling sites. These variations are correlated with particle size and total organic carbon in sediment. DecaBDE is the dominant homologue in sediment; the increased use of the DecaBDE commercial mixture in the 1990s and 2000s is likely an explanatory factor, although the biochemical characteristics of PBDEs in sediment are also important. DecaBDE is known to have both a high tendency to bind to sediment and a low tendency to degrade within sediment.

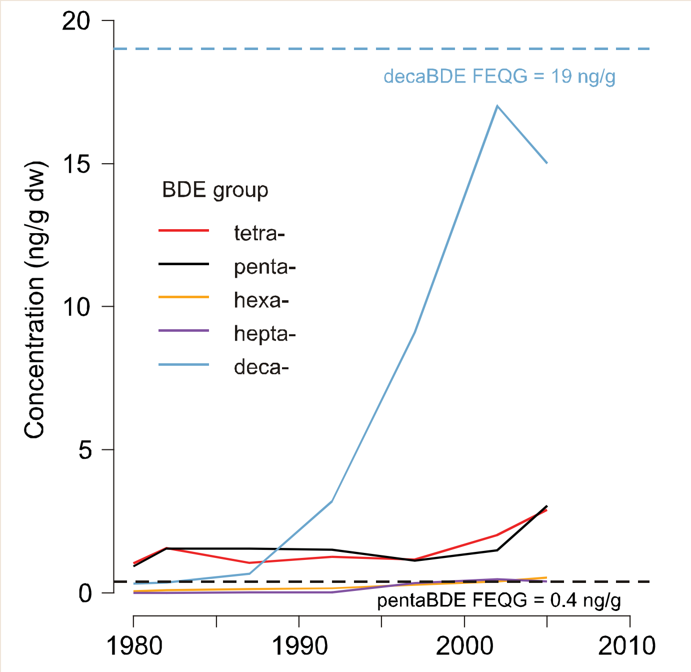


Figure 3: Average concentrations of PBDEs in sediment (ng/g dry weight) in Lake Ontario from a core sample taken in 2005. OctaBDE and nonaBDE were not measured in sediment. The FEQGs for pentaBDE and decaBDE in sediment are shown for comparison (dashed lines).

Fish:

To provide a long-term perspective for PBDEs in Lake Ontario lake trout, annual measurements made by Environment Canada (1997–2009) were combined with data gathered through the United States Environmental Protection Agency (US EPA) Great Lakes Program (1980–2000)[1]. Methodologies for the two studies differ slightly but the average concentrations can be compared[2]. The dominanthomologues throughout the period are tetra, penta- and hexaBDE (Figure 4). Tetra- and pentaBDE show an overall increase over the period of 1980 to 2000, with a decreasing trend beginning thereafter. HexaBDE shows a similar trend with stabilization and decrease beginning slightly earlier, around 1995. The heavier homologues (hepta- through decaBDE) are not found in fish in substantial quantities due to their lower bioaccumulation potential; however, biotransformation or the breakdown from heavier to lighter homologues within organisms may occur to a limited extent and contribute to the relative dominance of tetra- through hexaBDE. Levels of pentaBDE in fish tissue were 20–30-fold higher than the FEQG, but did not exceed the margin of safety built into the FEQG.

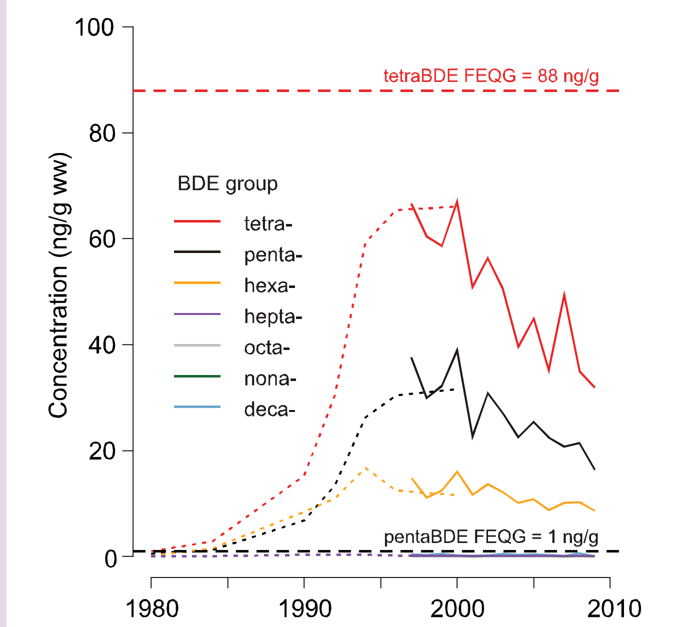


Figure 4: Average concentrations of PBDEs in lake trout (ng/g wet weight) from Lake Ontario, 1980 to 2009 (dotted lines represent data gathered through the US EPA Great Lakes Program and solid lines represent Environment Canada data). The FEQGs for tetraBDE and pentaBDE in fish are shown for comparison (dashed lines).

Wildlife:

Eggs of herring gulls have been collected annually from monitored colonies across the Great Lakes since the early 1970s by Environment Canada staff. Archived pooled samples from 1982, 1987, 1992, 1995–2006 and 2008 were analyzed to obtain long-term trend information on PBDEs in wildlife. As observed in fish, tetra-, penta- and hexaBDE are the dominant homologues because of their higher bioaccumulation potential (Figure 5). Although concentrations of tetra-, penta- and hexaBDE in wildlife are more variable from year to year than the other media, they appear to show a similar temporal trend of increase and subsequent decline to that in fish; however, the peak years and decline occur several years later. In addition, decaBDE concentrations, although relatively low, increased over the entire period. Maximum average values for pentaBDE were up to 20-fold higher than the FEQG, thus exceeding the margin of safety. While herring gull populations have been declining on the Great Lakes over the last decade, this is a basin-wide phenomenon and not specific to sites with high PBDEs. It is likely that this species may be less susceptible to the effects of PBDEs than is the American kestrel, upon which the FEQG is based.

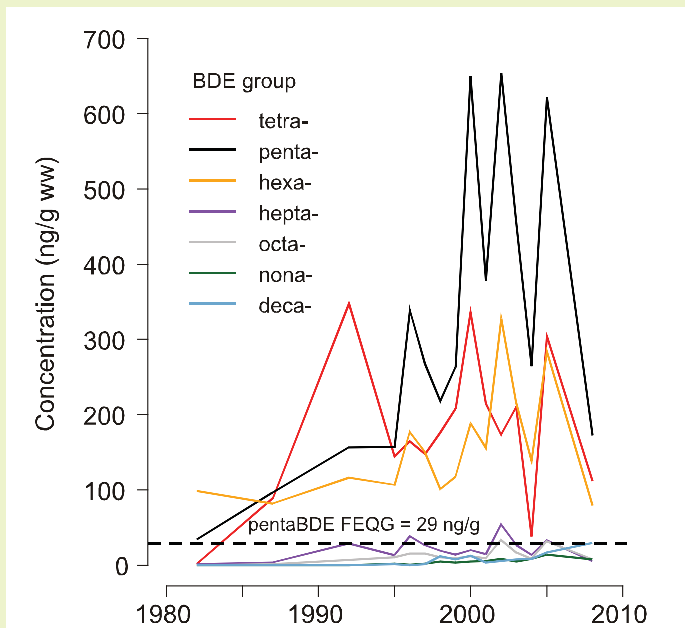


Figure 5: Average concentrations of PBDEs in herring gull eggs (ng/g wet weight) in Toronto Harbour, 1982 to 2008. The FEQG for pentaBDE in bird eggs is shown for comparison (dashed lines).

[1] Zhu, L.Z. and R.A. Hites. 2004. Temporal Trends and Spatial Distributions of Brominated Flame Retardants in Archived Fishes from the Great Lakes. Environ. Sci. Technol. 38: 2779–2784.

[2] Environment Canada concentrations were determined on individual fish (n=4–24), while the US EPA used composite samples (n=1–3) consisting of five fish. The methods used to determine the concentrations were also different; the US EPA used Gas Chromatography/Mass Spectrometry (GC/MS) while Environment Canada used high-resolution GC/MS.

Landfill and Wastewater Monitoring

In order to monitor the potential release of PBDEs from the solid waste sector between 2008 and the spring of 2010, landfill leachate (untreated and treated) was collected, during three separate sampling events, from 10 Canadian municipal solid waste landfill sites equipped with leachate collection systems. The landfills all receive municipal waste. Some also receive construction waste, industrial waste and biosolids. Although PBDEs were not expected to be found in landfill leachate due to very low solubility and their hydrophobic nature, they were detected in all leachate samples. Concentrations of total PBDEs were variable across the 10 landfills and ranged from 0.2 ng/L to 2476 ng/L in untreated leachate, with a median value of 58 ng/L (n=30). Concentrations of total PBDEs in treated leachate ranged from 0.75 ng/L to 77 ng/L, with a median value of 9 ng/L (n=5). TetraBDE, pentaBDE and hexaBDE were the dominant homologues across the majority of landfills and sampling periods.

In general, very low concentrations of PBDEs were found in leachate, and analytical data supports that treatment of leachate decreases the concentration of total PBDEs.

The wastewater component of the CMP monitoring and surveillance program provides information on the significance of wastewater effluent discharges and land application of treated biosolids as sources of PBDEs to the environment. In 2009–2010, 19 wastewater systems representing typical wastewater treatment processes in Canada were sampled in summer and winter. Municipal systems as well as systems under federal government operations or located on federal or Aboriginal lands were included in the program. Total influent PBDE concentrations across all wastewater systems ranged from 0.99 ng/L to 1010 ng/L, with a median value of 208 ng/L (n=97). Total effluent PBDE concentrations ranged from 1.2 ng/L to 270 ng/L, with a median value of 15 ng/L (n=98). Removal rates of total PBDEs during wastewater treatment were high, with a median value of 93% (n=95). Secondary biological treatment and facultative lagoons had the highest removal rates (87–98). Chemically assisted primary treatment and aerated lagoons had lower removal rates and exhibited high variability between systems (61–90% and 66–98% respectively). The most prevalent homologue groups in wastewater effluents were tetra-, penta-, nona- and decaBDE, representing approximately 26%, 27%, 9% and 28% of the total effluent PBDE concentrations respectively. Results from wastewater solids analysis showed median total PBDE concentrations of 1060 ng/g in primary sludge (n=68, concentration range 235 ng/g to 6010 ng/g), 1600 ng/g in waste biological sludge (n=45, concentration range 833 ng/g to 4250 ng/g) and 2340 ng/g in treated biosolids (n=63, concentration range 832 ng/g to 5050 ng/g). In general, solids concentrations are three orders of magnitude higher than wastewater concentrations, suggesting that PBDEs partition to solids during wastewater treatment rather than being removed through biodegradation. The most prevalent homologue groups in treated biosolids were tetra-, penta-, nona- and decaBDE, representing approximately 17%, 19%, 9% and 48% respectively.

Conclusion

Concentrations of PBDEs show evidence of a decline in environmental media sampled through this program that is consistent with Canadian and international risk management actions and industry phase-outs. As the remaining PBDE commercial mixture is phased out and products containing PBDEs are no longer in commerce, the quantity of new PBDEs entering the environment will decrease. However, due to their persistent nature, PBDEs will remain in the environment for many years to come.

Levels of PBDEs were higher in urban and industrialized locations across Canada than in rural or remote regions. Consistent with other studies, these data indicate that human activities, such as industrial processing, use of consumer products and waste disposal, are important sources of PBDEs in the environment. Atmospheric transport of PBDEs released in other countries may also be an important source of PBDEs to Canada. Preliminary measurements of PBDEs in wastewater treatment outputs, particularly in biosolids, suggest a need for further research on the importance of these releases as a source of PBDEs in the environment.

Through comparison to the FEQGs for PBDEs, data shown here suggest that concentrations of most homologues in most regions of Canada present a low potential for adverse effects on the organisms examined in this monitoring program. In cases where FEQGs are surpassed, further analysis may be required to determine the need for additional measures. These results provide an important piece of information to be used by the Government of Canada in evaluating its risk management strategy for PBDEs and considering how to best approach the risk management for similar substances of concern.

For More Information

Please consult the websites below:

The Chemicals Management Plan and Monitoring Program

- The Chemicals Management Plan: www.chemicalsubstanceschimiques.gc.ca/plan/index-eng.php
- Monitoring and Research under the Chemicals Management Plan: www.chemicalsubstanceschimiques.gc.ca/fact-fait/monitor-surveill-eng.php
- Chemicals Management Plan Monitoring Factsheet Website: www.ec.gc.ca/scitech/default.asp?lang=En&n=7AC5DC36-1

Risk Assessment and Management of PBDEs

- Final State of the Science report on Decabromodiphenyl ether and Final Revised Risk Management Strategy for PBDEs, published August 2010: www.chemicalsubstanceschimiques.gc.ca/fact-fait/glance-bref/pbde-eng.php

Health Canada's Activities

- Environmental Contaminants and Human Biomonitoring: www.hc-sc.gc.ca/ewh-semt/contaminants/index-eng.php
- Maternal-Infant Research on Environmental Chemicals: www.mirec-canada.ca/site/index.php

Other Environmental Monitoring Programs

- The Northern Contaminants Program: www.ainc-inac.gc.ca/nth/ct/ncp/index-eng.asp
- The National Air Pollution Surveillance Program: www.ec.gc.ca/rnspa-naps/default.asp?lang=En&n=5C0D33CF-1
- The Integrated Atmospheric Deposition Network: www.ec.gc.ca/rs-mn/default.asp?lang=En&n=BFE9D3A3-1
- The Global Atmospheric Passive Sampling Network: www.ec.gc.ca/rs-mn/default.asp?lang=En&n=22D58893-1
- Contaminants in Herring Gull Eggs from the Great Lakes: www.on.ec.gc.ca/wildlife/factsheets/fs_herring_gulls-e.html

Federal Environmental Quality Guidelines

- Environment Canada. 2010. Federal Environmental Quality Guidelines for Polybrominated Diphenyl Ethers (PBDEs). Draft for Review. National Guidelines and Standards Office, Gatineau, QC. 15 pp.

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