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Polybrominated Diphenylethers (PBDEs) in the Canadian Marine Environment: An Emerging Health Risk for Fish, Marine Mammals and their Habitat

Les polybromodiphényléthers (PBDE) dans le milieu marin canadien : un risque émergent pour la santé des poissons, des mammifères marins et pour leur habitat

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* La présente série documente les bases scientifiques des évaluations des ressources halieutiques du Canada. Elle traite des problèmes courants selon les échéanciers dictés. Les documents qu'elle contient ne doivent pas être considérés comme des énoncés définitifs sur les sujets traités, mais plutôt comme des rapports d'étape sur les études en cours.

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Abstract

Of the three forms (penta, octa and deca) of polybrominated diphenylethers (PBDEs) that have been widely used in textiles, furniture upholstery, plastics, and electronics, only deca-BDE remains on the market in Canada. DFO and other researchers have documented the rapid emergence of PBDEs, including deca-BDE, as a priority concern in the marine and freshwater environments in Canada. In many matrices, BDE-209, the main ingredient in deca-BDE, has surpassed PCBs and DDT as the number one contaminant. PBDEs are being introduced to the marine environment by sewage discharge and atmospheric deposition. Recent DFO research shows that BDE-209 dominates the PBDEs profile in abiotic components of the marine environment, contributing up to 80% of the total PBDE concentration in air, water, and sediments. BDE-209 is taken up by low trophic level (e.g. shellfish and invertebrates) and terrestrial animal species, and therefore presents a risk to these species or those relying on these species for food. Although some studies have not reported results for BDE-209 because of technical difficulties in its measurement, BDE-209 has been found to biomagnify in aquatic food webs. The ready breakdown of BDE-209 into more bioaccumulative and toxic (lighter) PBDE forms in the environment presents perhaps the most insidious threat to aquatic biota. There are concerns within the scientific community about escalating risk of adverse health effects in marine biota, including invertebrates, fish and marine mammals, as well as human consumer groups including coastal First Nations communities. The endocrine-disrupting potential of PBDEs has been established in laboratory animals, fish and in seals.

Résumé

Des trois formes (penta, octa et déca) de polybromodiphényléthers (PBDE) qui ont été largement utilisés dans les textiles, le rembourrage de meubles, les plastiques et l'équipement électronique, seul le décabromodiphényléther (DeBDE) est toujours présent sur le marché au Canada. Le ministère des Pêches et des Océans (MPO) et d'autres chercheurs ont documenté l'émergence rapide des PBDE, y compris du DeBDE, comme étant une préoccupation prioritaire dans les milieux marin et d'eau douce au Canada. Dans bien des matrices, le BDE-209, ingrédient principal du DeBDE, a surpassé les diphényles polychlorés (BPC) et le dichlorodiphényltrichloroéthane (DDT) à titre de contaminant numéro un. Les PBDE sont introduits dans le milieu marin par les rejets d'eaux usées et le dépôt atmosphérique. Récemment, des travaux de recherche réalisés par le MPO ont révélé que le BDE-209 domine le profil des PBDE dans les composantes abiotiques du milieu marin, représentant jusqu'à 80 p. 100 de la concentration totale des PBDE dans l'air, l'eau et les sédiments. Le BDE-209 est absorbé par les niveaux trophiques inférieurs (p. ex., les mollusques, les crustacés et les invertébrés) et les espèces animales terrestres; par conséquent, il pose un risque pour ces espèces ou celles dépendant de ces espèces dans la chaîne alimentaire. Malgré le fait que certaines études n'ont pas présenté des résultats relatifs au BDE-209 en raison de difficultés techniques liées à la mesure de ce congénère, on a décelé une bioamplification du BDE-209 dans la chaîne trophique en milieu aquatique. Cependant, la disposition à la fragmentation du BDE-209 en des formes de PBDE (plus légers) davantage bioaccumulatifs et toxiques dans l'environnement constitue vraisemblablement la menace la plus insidieuse pour le biote aquatique. La communauté scientifique s'inquiète du risque croissant des effets nocifs pour le biote marin, entre autres les invertébrés, les poissons et les mammifères marins, ainsi que les groupes de consommateurs humains, notamment les collectivités de Premières nations établies dans les régions côtières. Les effets perturbants des PBDE pour le système endocrinien ont été établis en laboratoire pour certains animaux, poissons et le phoque commun.

Context:

Polybrominated diphenylethers (PBDEs) are flame retardants that have been used extensively in textiles, furniture upholstery, plastics, and electronics. Of the three forms (penta, octa and deca), only one (deca; consists primarily of BDE-209, but has small amounts of other BDE congeners as well as toxic impurities) remains on the market in North America. DFO researchers have documented the rapid emergence of PBDEs, including BDE-209, as a concern in the marine and freshwater environments in Canada. In many matrices, BDE-209 has surpassed PCBs and DDT as the top persistent contaminant.

PBDEs are being introduced to the marine environment by sewage discharge and atmospheric deposition. Increasing PBDE levels in marine biota has implications for DFO interests under the terms of the Fisheries Act, Oceans Act and Species at Risk Act. Evidence from DFO and international research indicates that all PBDE congeners, including BDE-209, are persistent, bioaccumulative and toxic. Contamination of some fisheries resources could lead to either perceived safety concerns or real consumption advisories or fisheries closures in the future, with negative economic implications. In addition, all PBDE congeners are readily transported through atmospheric processes to remote locations. The Government of Canada (Environment Canada) is currently reviewing the data on decaBDE under the terms of its obligations to regulate persistent, bioaccumulative and toxic substances through the Canadian Environmental Protection Act (CEPA). This CSAS document aims to provide up-to-date data and research findings from DFO in support of EC's technical review of PBDEs.

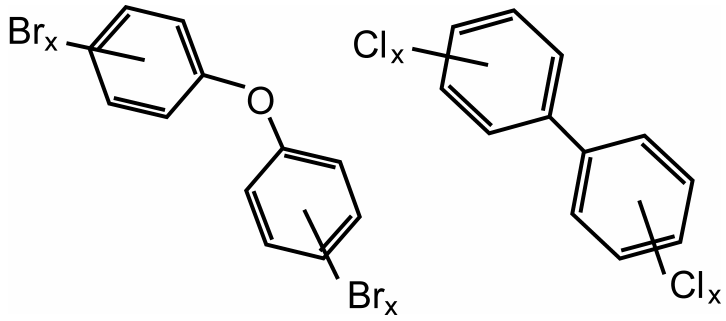

Figure 1: Polybrominated diphenylethers (PBDEs; left) have similar structural properties to the polychlorinated biphenyls (PCBs; right). Both consist of two phenyl rings, have ten carbon sites available for binding by halogens, and have up to 209 permutations. Differences between the two chemicals include the halogen found at C binding sites (bromine for PBDEs and chlorine for PCBs), a higher overall range of molecular weight and solubility in fat for PBDEs, and lower persistence of parent congeners for PBDEs. PCBs were banned in Canada in 1977, while PBDEs remain in use.

Background

Polybrominated diphenylethers (PBDEs) are widely used chemical flame retardants. PBDEs consist of two phenyl rings (12 carbon atoms) with an ether bridge (oxygen) and up to 10 bromine atoms on available C binding sites (see Figure 1). Depending on the number and position of Br atoms, up to 209 PBDE congeners are theoretically possible, although only about 40 are routinely found in the commercial products. Three commercial formulations (penta, octa and deca) were available until two of these products (penta and octa) were removed from the European marketplace in 1998 and from the North American marketplace in 2004 because of concerns about health risks in humans and wildlife. DecaBDE remains on the market, with its sales increasing exponentially.

The subject of PBDEs is relevant to two of three departmental mission statements for Fisheries and Oceans Canada (DFO), namely i) *Healthy and Productive Aquatic Ecosystems*, and ii) *Sustainable Fisheries and Aquaculture*. At elevated concentrations, PBDEs have been associated with adverse health effects, including reproductive impairment, immunotoxicity, and developmental anomalies. Because chemicals that are considered Persistent, Bioaccumulative and Toxic (PBT chemicals), such as PBDEs, biomagnify in aquatic food webs, high trophic level fish and marine mammals are considered at heightened risk for adverse effects. DFO is therefore an important steward for these species that are particularly vulnerable to accumulating PBT chemicals. Other PBT chemicals, including polychlorinated biphenyls (PCBs) and the organochlorine pesticide DDT, were banned or restricted in Canada and the US in the mid 1970s. Science in the late 20th Century, in part generated through DFO researchers, formed a significant basis for advice to governments, which ultimately led to the ratification of the Stockholm Convention in 2004. This Convention aims to eliminate 12 priority POPs on a global scale, including PCBs and DDT. The PBDEs are not included in the Stockholm list, but two formulations are considered ‘candidates’ for eventual inclusion under the terms of this treaty.

While the point source release of particular chemicals into water bodies is typically regulated by Environment Canada and provincial agencies, the accumulation of PBDEs and other persistent contaminants in the marine environment is of concern to DFO. Understanding the complex mixture to which aquatic organisms are exposed represents an important facet of DFO research, and provides evidence that may be considered by risk assessors, chemical regulators, and those dealing with source control.

Analysis and response

Are PBDEs toxic to aquatic biota?

While further research will help to elucidate the mechanisms of action and the vulnerable health endpoints in biota, a gathering ‘weight of evidence’ clearly indicates that PBDEs are endocrine-disrupting and present a health risk to aquatic invertebrates, fish and marine mammals in Canada. In addition, the entry of PBDEs into the aquatic environment adds to an already complex mixture of contaminants. The risks associated with PBDEs in the environment should therefore not be considered in isolation, and attention should be paid to toxic risks associated with impurities found in PBDE products, breakdown products of parent PBDEs in the environment, and co-occurring contaminants of structurally-related compounds (e.g. PCBs) in aquatic biota.

Direct biological effects of decaBDE (or BDE-209):

- Clams injected with decaBDE (BDE-209; 1 µg per clam) had altered steroid hormone concentrations and delayed sexual maturation, but no change in condition (Pellerin *et al.* 2003).
- Some physiological or morphological effects have been reported in fish exposed to PBDEs. For example, an increase in liver weight was reported in rainbow trout after a 120-day dietary exposure to decaBDE at a dose of 7.5-10 mg BDE-209/kg body weight/day (Kierkegaard *et al.* 1999), whereas a reduction in liver weight was observed in Atlantic tomcod (*Microgadus tomcod*) injected intraperitoneally (IP) with DecaBDE at a dose of 400 ng BDE-209/g wet wt fish (Lebeuf *et al.* 2006).

Effects of lighter congeners (from commercial mixtures other than deca-BDE, or produced via debromination of BDE-209, or present as an impurity in deca-BDE):

- Only a limited number of experimental studies have been carried out on the toxicity of PBDEs in aquatic species. The mechanisms of action for resultant toxicities are generally not well understood, though the literature is expanding rapidly.
- PBDEs appear to cause similar effects in both fish and mammals, although some differences have been observed. Vulnerable biological systems include neurological development, thyroid function and reproduction.
- Developmental alterations and neurobehavioural toxicity of PBDEs have been reported in two model fish species. In killifish (*Fundulus heteroclitus)* embryos incubated in aqueous solutions of the industrial PentaBDE mixture DE-71, behavioural changes were observed at concentrations as low as 0.001 µg/L , suggesting endocrine disruption (Timme-Laragy *et al.* 2006). In zebrafish (*Danio rerio*) embryos exposed to aqueous solutions of 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), retarded growth and altered cardiac function were observed at ≥500 µg/L (78 mg/g wet weight in fish), delayed hatching at ≥2000 µg/L, and altered cerebrospinal fluid movement and dorsal curvature at ≥5000 µg/L (Kuiper *et al.* 2006).
- Endocrine disruption and reproductive disturbances have been observed in fish and invertebrates exposed to PBDEs. Oral exposure to BDE-47 reduced condition and the production of mature sperm in male fathead minnows (*Pimephales promelas*) but no effects on condition or oocyte development in females (Muirhead *et al.* 2006). Complete cessation of spawning was observed at body concentrations of 15 µg/g in males and 50-60 µg/g in females, which are much greater than the highest PBDE concentrations reported for wild fish.
- In juvenile rainbow trout (*Salvelinus namaycush*) exposed to a dietary mixture of 13 PBDE congeners (3-10 Br atoms; 2.5 and 25 ng/g dry weight in food for each of 13 BDE congeners), plasma thyroxine declined at the end of the 56-day exposure period, and thyroxine was still reduced after a 112-day depuration period (Tomy *et al.* 2004).
- *In vitro* tests using a *Drosophilia* cell line revealed that BDE-99 and BDE-100 were potential endocrine disruptors in invertebrates (ecdysterioid antagonists) (Wollenberger *et al.* 2005).
- Chemical impurities found in PBDE mixtures (thought to include polybrominated dioxins and furans) may elicit adverse effects, including those found in the commercial PeBDE product (DE-71) that were responsible for CYP1A induction in zebrafish exposed to water-borne PBDEs (Kuiper et al. 2006).
- PBDEs are highly toxic to crustaceans. Significant effects on larval development in the copepod *Nitocra spinipes* have been observed at 13 µg/L BDE-47, a concentration 338-times lower than the corresponding LC50 (4.4 mg/L) (Breitholz and Wollenberger 2003). The 5-day EC50 for larval development in the marine copepod *Acartia tona* was 1.2 µg/L

for BDE-100, 4.2 µg/L for BDE-99, and 13 µg/L for BDE-28 and BDE-47 (Wollenberger, Dinan, and Breitholz 2005).

- While there exists limited information on the health effects of PBDEs and marine mammals, two lines of evidence are available. Firstly, POP-related effects largely due to the structurally-related PCBs have been documented in captive and free-ranging seals (Tabuchi *et al.* 2006;Ross *et al.* 1996;Mos *et al.* 2007;Mos *et al.* 2006). Secondly, some evidence in support of PBDE effects in seals is available (Hall *et al.* 2003).
- A number of laboratory rodent studies demonstrate some of the effects of PBDEs (Darnerud *et al.* 2007;Hallgren *et al.* 2001). Altered thyroid function, delayed puberty, and altered liver enzymes were reported in rats exposed to PBDEs (reviewed by (Birnbaum and Staskal 2004)). Developmental alterations and neurobehavioural effects of PBDEs have been observed in rodents and related to altered thyroid hormone function and cholinergic pathways in the central nervous system (reviewed by (Costa and Giordano 2007)).
- Captive bird studies demonstrate that PBDEs alter thyroid hormone and vitamin A levels, and glutathione metabolism and oxidative stress (Fernie *et al.* 2005).
- PBDEs are structurally related to PCBs, co-occur with PCBs in the tissues of aquatic biota and in aquatic food webs, and likely cause additive, synergistic and/or antagonistic toxicities.
- PBDE and PCB congeners appear to bind to the same cellular receptors in biota (Luthe *et al.* 2008). PBDEs therefore are adding to an already complex mixture in the aquatic environment, and should not be considered in isolation. Synergistic interactions on free thyroxine (T4) in plasma and hepatic EROD activity have been demonstrated in rats exposed orally to a mixture of BDE-47 and the PCB product Aroclor 1254 (Hallgren and Darnerud 2002). A recent study demonstrates that PBDEs can interact with PCBs by enhancing neuro-behavioural defects. In ten-day-old male mice, a single oral dose of PCB 52 + PBDE 99 (1.4 + 1.4 µmol/kg bw) caused more pronounced neurobehavioural defects than a high dose of PCB 52 (14 µmol/kg bw) whereas low dose of each compound did not affect behaviour. These results suggest that the interaction is more than additive (Eriksson *et al.* 2008).
- A 'weight of evidence' suggests that PBDEs are emerging as a conservation threat to marine mammals (Ross 2006).

To what extent have PBDEs been documented in the abiotic aquatic environment in Canada?

PBDEs enter the marine environment through municipal wastewater outfalls and atmospheric deposition from multiple sources. PBDEs now rival PCBs in multiple matrices in the coastal environment, and are readily transported through the movement of air, water, particles and biota. The 'heavy' BDE-209, the main constituent of decaBDE, is a significant component of total PBDEs in air, water and sediments. Concentrations of PBDEs, particularly BDE-209, are increasing rapidly in Canada, as evidenced by sediment cores.

- *Water*: In Strait of Georgia (British Columbia) marine water samples collected in 2005-06, PBDEs are found in similar concentration to PCBs in the particle-bound phase (8.51 pg/L vs. 8.50 pg/L respectively in surface water) and are in lower concentration than PCBs in the dissolved phase (14.9 pg/L vs. 35.0 pg/L in surface water)(Dangerfield *et al.* 2007);
- BDE-209 dominated PBDE profiles in water, accounting for 42% of total PBDE concentration in the particle-bound fraction and 17% in the dissolved (Dangerfield *et al.* 2007).

- *Air*: in Strait of Georgia air samples (Saturna Island) collected in 2004-05, the concentration of PBDEs is lower than that of PCBs in the gas + particulate phase (13 pg/m^3 vs. 25 pg/m^3) but much higher than PCBs in rainfall (14 pg/m^3 vs 4.2 pg/m^3);
- BDE-209 dominates the PBDE signal in rainfall, accounting for over 80% of the total PBDE concentration; Estimates place the 'local' contribution (i.e. Canada and adjacent US regions) for BDE-209 at 87% (Noël *et al.* 2007).

- *Surficial sediments*: surface sediment concentrations of PBDEs in 2006 ranged from 87 to 12,730 pg/g (dry weight, dw) at 20 coastal sites around the Strait of Georgia (mean = 2,385 pg/g dw), with highest concentrations in harbours and near municipal sources (Grant and Ross, *unpublished*)(Johannessen *et al.* 2007;Hale *et al.* 2006).Similarly, PBDE levels in seven sediment samples from the St Lawrence Estuary (Quebec) ranged from 8 pg/g dw to 6,000 pg/g dw and were strongly correlated to the average particle size of the sediments (Lebeuf 2004).
- BDE-209 contributes 12.2 – 76.2% (mean = 39.0%) of the total PBDEs measured at the Strait of Georgia sites (Grant and Ross, *unpublished*). In the St Lawrence sediments, BDE-209 contribution varies considerably, but was found to represent up to 90% of total PBDE concentrations at Baie St Metis, a site close to a small municipality but without a direct industrial zone (Lebeuf 2004).

- *Sediment cores*: The concentration of polybrominated diphenyl ethers (PBDEs) in sediments of the Strait of Georgia has increased rapidly since their first appearance in about 1983 (Johannessen et al. 2007)(Figure 2);
- BDE-209 makes up 56-80% of the total PBDEs in surface sediments of the Strait of Georgia (Figure 3; (Johannessen *et al.* 2007)). BDE-209 has also been increasing steadily in St Lawrence sediment cores, reaching 5-6 pg/g dw (Alaee et al, TSRI report 2002). These levels are at least ten times higher than the BDE-209 concentrations reported for the Strait of Georgia sediment samples, but approximately three times lower than the PCB levels reported for the St Lawrence (Lebeuf and Nunes 2005).

- *Sewage outfalls*: Municipal wastewater appears to be a major pathway of these contaminants into the Strait of Georgia; the concentration of deca-BDE in surface sediments collected near the Iona Island outfall is much higher than it is elsewhere in the open Strait (13-60 times as high). The surface sediments of Vancouver and Victoria harbour have concentrations almost as high as those measured near the outfall (Johannessen et al. 2007). PBDEs are not readily eliminated by advanced treatment processes (Rayne and Ikonomou 2005). High levels of PBDEs have been noted at North American outfall sites, in effluent (Song *et al.* 2006), and in sewage sludge (Hale et al. 2006). In the Strait of Georgia, a preliminary mass balance budget suggests that about 30% of the BDE-209 enters the Strait through municipal wastewater outfalls (Macdonald *et al.* 2007).

- *A preliminary mass – balance* reveals that the introduction of PBDEs to BC's Strait of Georgia (53 kg per year) has surpassed PCBs (19 kg per year) by several times, underscoring the importance of this relatively new marine contaminant (these figures exclude particle-bound entry via riverine sources) (Macdonald *et al.* 2007).

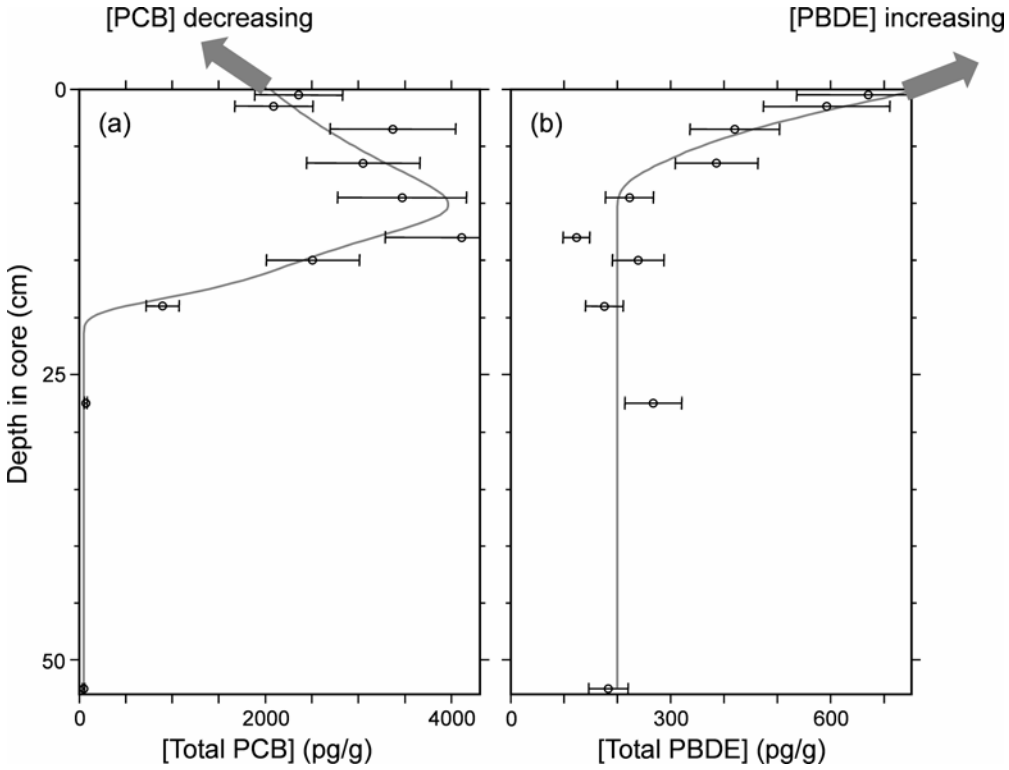

Figure 2. Depth profile of total PCB (left) and PBDE (right) concentrations measured in a sediment core collected in the Strait of Georgia (west of Texada Island) in 2003. While PCBs are still declining as a result of regulatory action in the 1970s, PBDEs are increasing rapidly. Dots represent measurements; the line is a model fit to the data which indicates that PBDEs first appeared in local sediments in about 1978. BDE-209 contributes about 80% of the total PBDEs at this site. The six other cores collected during this study show the same pattern with time (Johannessen et al. 2007).

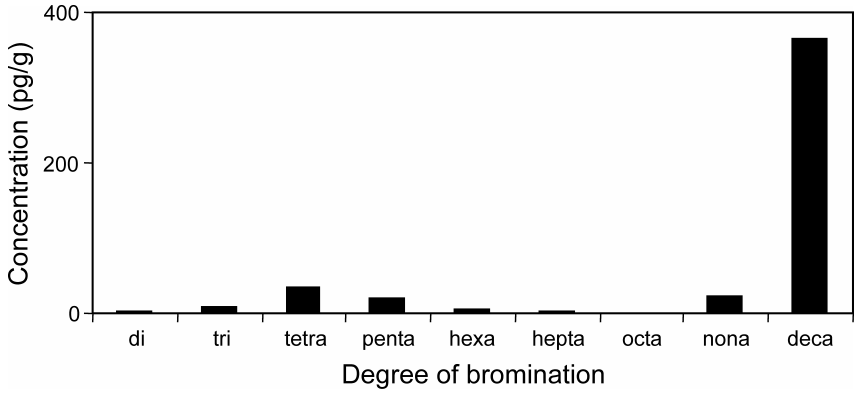

Figure 3. BDE-209 dominates PBDE profiles in sediments in the Strait of Georgia, as evidenced by homologue groups (Johannessen et al. 2007).

To what extent have PBDEs been found in aquatic biota in Canada?

PBDEs are found in all marine fish and marine mammals examined, and are poised to overtake the two long-standing major persistent contaminants in Canadian aquatic food webs, namely the PCBs and DDT. BDE-209 has been reported in aquatic food webs, although the PBDE profile observed in aquatic biota is dominated by less brominated congeners including BDE-47, 99 and 100, which in addition to their direct discharge into the environment, can be derived from the breakdown of BDE-209. PBDE concentrations are increasing exponentially in fish and marine mammals in Canada's three oceans, and in some areas/species, are doubling every 3-4 years. The dominance of BDE-209 in abiotic matrices and its relatively rapid breakdown position this congener as a risk to lower trophic level species, to terrestrial food webs, and as a precursor to more bioaccumulative and toxic break down products.

- *High trophic level biota*: exponential increases of total PBDEs have been observed in marine biota in Canada's three oceans. These include Columbia River whitefish (Rayne *et al.* 2003a), Pacific harbour seals (Ross *et al.* 2007), Arctic ringed seals (Ikonomou *et al.* 2002a), Arctic belugas, and St Lawrence beluga whales (Lebeuf *et al.* 2004)(see Figures 4, 5 and 6). They have also been found in British Columbia's endangered resident killer whales (Rayne *et al.* 2004). BDE-209 is not generally found at high levels at the top of aquatic food webs today, although trace levels of BDE-209 (<1000 pg/g lw) were found in the blubber of ringed seal and the adipose tissue of polar bears in Svalbard, Norway (Sormo *et al.* 2006). Factors explaining the relatively low levels of BDE-209 at the top of the food chain may include its very large molecular size, its relatively short half-life in the body, rapid partitioning to the particle-bound phase in the environment and to sediments, its more limited apparent uptake across the gastrointestinal tract as a result of its very high Log $K_{o/w}$, and its metabolic breakdown into lighter PBDE congeners (Thuresson *et al.* 2006). However, an alternative explanation is that BDE-209 simply has not yet had time to reach the highest trophic level. PBDEs are still new enough that, unlike PCBs, they have not reached equilibrium in the environment (e.g. Johannessen et al., 2008), and the same may be true in the biota. A recent study showed that BDE-209 was detected in 2006, but not before, in eggs of some herring gull colonies in the Great Lakes (Gauthier *et al.* 2007).

- *Low trophic level biota*: Filter-feeders and organisms that are in regular contact with marine sediments are more exposed to, and more prone to accumulate PBDEs, including the heavy BDE-209. A survey of blue mussels in the Strait of Georgia revealed that BDE-209 accounted for an average of 7.8% of total PBDEs; 8% of total PBDEs in Dungeness crabs around Vancouver Island; and 44% of total PBDEs in butter clams, *Saxidomus giganteus* (Ross et al., unpublished). PBDEs, mostly BDE 47, 99 and 100, were systematically detected in fish and shellfish from the St Lawrence estuary (Law *et al.* 2003). Ruling out the presence of BDE-209 in gastrointestinal tract or on the external surface of the organism is an important consideration in study design and the interpretation of results (Sormo et al. 2006). Controlled studies have documented the uptake of PBDEs from sediments by oligochaetes, although BDE-209 was less bioaccumulative than BDEs 47 and 99 (Ciparis and Hale 2005).

- *Terrestrial biota*: Contrary to what is typically found in aquatic biota, terrestrial food items appear to be an important source of BDE-209 to terrestrial wildlife, including Vancouver Island marmots (Lichota *et al.* 2004) and grizzly bears (Christensen *et al.* 2005); this suggests ready partitioning into plant materials, and subsequent uptake by mammals. However, the relative roles of uptake via food vs uptake via air, soil and dust remains to be more fully elucidated (Voorspoels *et al.* 2007).

- *Synthesis:* PBDEs have emerged as an environmental contaminant of concern in compartments around the world (see Figure 7). Efforts to regulate two (penta and octa) of the three products in Europe in 1998 led to a rapid downward response in human breast milk. Trends in the Canadian marine environment are likely to continue upward, although the voluntary withdrawal of the penta and octa formulations by the sole North American manufacturer in 2004 may result in short term declines in environmental concentrations of lighter PBDE congeners. A recent study of PCBs projects this class of (banned) chemical to remain a health threat to British Columbia resident killer whales until the year 2089 (Hickie *et al.* 2007), highlighting concerns about the contamination of the aquatic environment by persistent, bioaccumulative and toxic chemicals including the PBDEs.

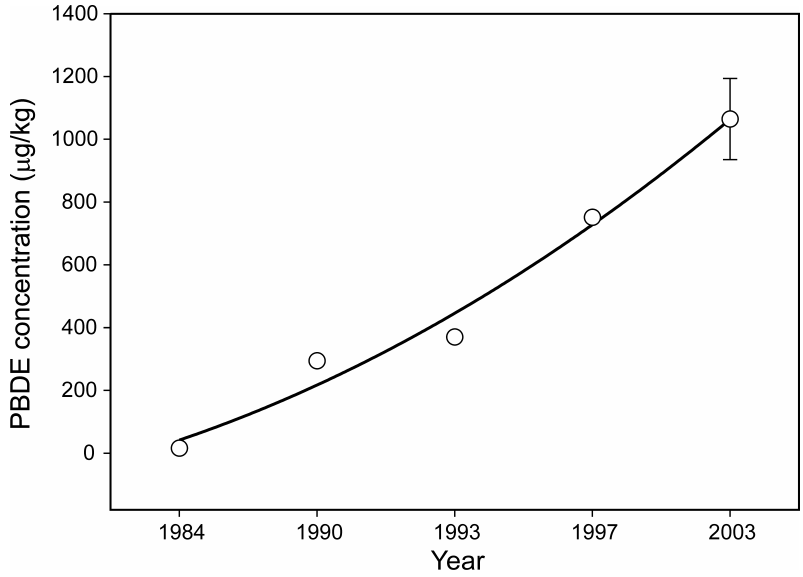

Figure 4: Total PBDE concentrations are increasing rapidly in harbour seals sampled on Gertrude Island in Puget Sound. These non-migratory animals consume fish such as herring and hake and integrate contaminant signals from coastal food webs. Doubling time is estimated at 3.5 years (Ross et al. 2007).

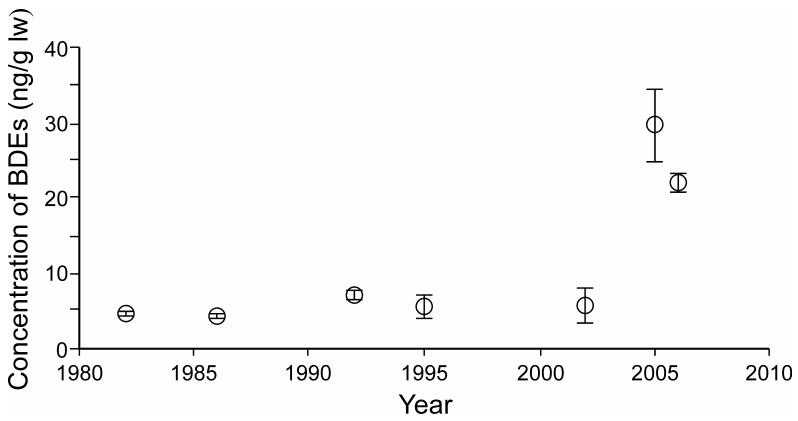

Figure 5: Change in ΣPBDE concentrations (ng/g, lipid weight) in Pangnirtung beluga blubber. Each data point represents the geometric mean (n=10) ± 1 standard error except the 2006 data point where only 5 animals were available. There was a clear exponential increase in ΣBDE concentrations in animals between 1982 and 2005 (r2=0.539, p<0.05) with a calculated doubling time of 11.6 years. After 2005, there is a statistically significant decrease in BDE concentrations.

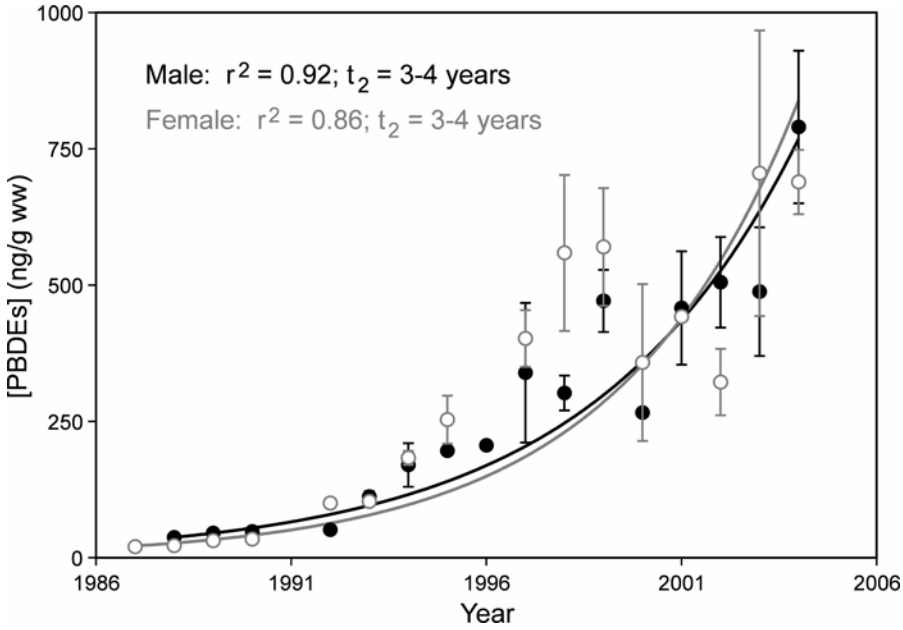

Figure 6: Change in ΣPBDE concentrations (ng/g, lipid weight) in St. Lawrence estuary beluga blubber. There was a clear exponential increase in ΣPBDE concentrations in both males and females between 1986 and 2004 with a calculated doubling time of 3-4 years (from Lebeuf et al. 2004 and unpublished data).

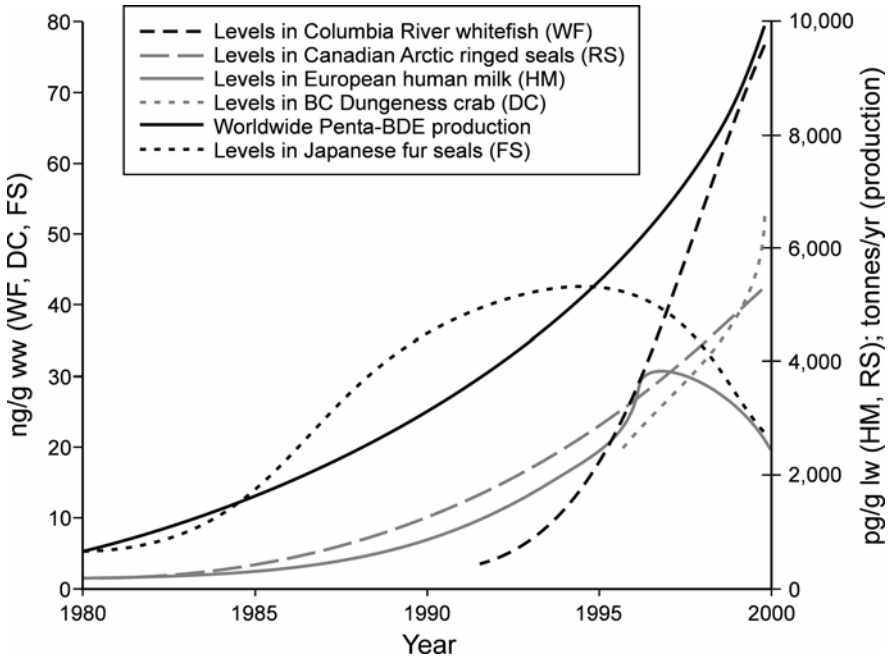

Figure 7: A history of PBDE production and trends in wildlife and humans reveal the emergence of PBDEs as a contaminant of concern. Adapted from (Ikonomou et al. 2002b;Rayne, Ikonomou, and Antcliffe 2003a;Ikonomou et al. 2006).

What do we know about the behaviour of PBDEs in the aquatic environment in Canada?

While total PBDE concentrations magnify in aquatic food webs, the biomagnification varies among different congeners. PBDEs are 'heavier' and have a higher range of octanol-water partitioning coefficients (Log $K_{o/w}$) than PCBs. The 'lighter' PBDEs bioaccumulate and biomagnify in the same manner as most PCBs. The 'heavier' PBDEs, such as BDE-209, appear less bioaccumulative, but have been shown to biomagnify in some food web studies. Some of the conflicting signals for BDE-209 can be explained by 1) its exclusion from analyses in earlier papers, 2) the 'sticky' nature of BDE-209 which predisposes it to particle binding in air, water and sediments 3) its debromination under abiotic conditions and 4) its metabolism in biota. In the latter two cases, lighter, more bioavailable and more toxic PBDE congeners result.

- We can apply lessons learned from PCBs. PCBs present a well documented health risk to high trophic level biota, including many marine mammals and seabirds, and to subsistence-oriented humans. This reflects their propensity to accumulate in organisms and their invulnerability to metabolic processes. PCBs therefore typify contaminants that biomagnify with increasing trophic level. However, it is clear that within the PCBs, there exists variation that can be attributed to their physicochemical properties (exemplified by Log $K_{o/w}$). This "optimal range" for aquatic food web – based bioaccumulation lies between Log $K_{o/w}$ ~5.8 – 7.4 (Fisk *et al.* 1998)(see Figure 8).

- It is therefore not surprising to find that PBDE congeners within this "optimal range" also bioaccumulate, as observed in salmon-eating grizzly bears in British Columbia (Christensen et al. 2005)(see Figure 9). The ready accumulation of those PBDE

congeners found within the Log $K_{o/w}$ range of ~5.8 – 7.4 in aquatic food webs represents a health risk to biota, particularly high trophic level marine mammals.

- Despite the optimal range of physicochemical properties that underlie the environmental partitioning, bioaccumulation and biomagnification in aquatic food webs (i.e. Log $K_{o/w}$ 5-8 – 7.4), even the heavier POPs are retained within an organism (i.e. increasing Log $K_{o/w}$; see Figure 10). The heavier PCB and PBDE congeners are therefore taken up from prey, and retained by predators, whereas the 'optimal range' reflects the integration of multiple environmental and biological processes.

- Given the higher range of Log $K_{o/w}$ values for the PBDE congeners, there is a consequent reduction in aquatic food web-delivered biomagnification of higher brominated congeners, although this may be due in part to a lack of steady-state in the environment and metabolism-associated debromination. The variable behaviours of different PBDE congeners in food webs is depicted in a study of Arctic biota (see Figure 12)(Kelly *et al.* 2008). While BDE-47 was found to biomagnify in Arctic food webs, BDE-209 was not (see Figure 13)(Pleskach et al*.* 2007, submitted to *Environmental Pollution*). In contrast, biomagnification of BDE-209 is apparent in the Lake Winnipeg food web (see Figure 11)(Law *et al.* 2006).

- BDE-209 readily partitions into terrestrial food webs, in part through binding to plant surfaces; terrestrial food-dependent grizzly bears had much higher BDE-209 concentrations (10.4 ug/kg lipid weight) compared to salmon-eating bears (0.5 ug/kg lw). It is therefore possible that the lack of BDE-209 in high trophic level aquatic biota does not necessarily reflect a lack of gastrointestinal uptake, but rather the partitioning features of the high Log $K_{o/w}$ BDE-209 in the marine vs terrestrial environment. In this way, nearly 100% of BDE-209 in grizzly bears comes from terrestrial foods. Terrestrial wildlife can therefore be considered at risk for exposure to BDE-209. Research is needed to better characterize the nature of BDE-209 uptake, metabolism and loss in different species.

- Marine biota that inhabit the sediment-water interface can be considered at risk for elevated exposure to all PBDE congeners, as many of these species will take up PBDEs through scavenging or filter feeding. These include crabs, lobsters, shellfish, flatfish, and scavengers. Studies in British Columbia indicate the ready accumulation of PBDEs in such species (Ikonomou *et al.* 2002c;Ikonomou, Fernandez, and Hickman 2006).

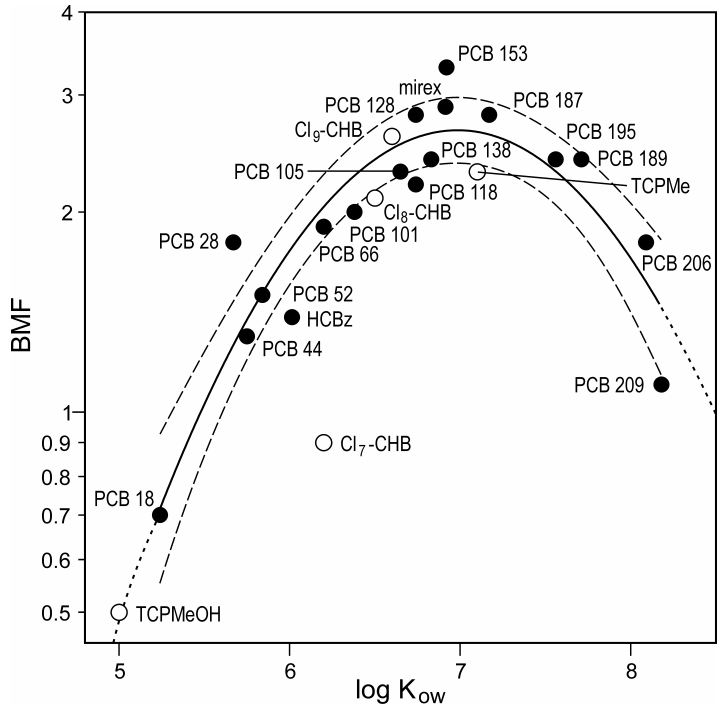

Figure 8: The biomagnification of persistent contaminants in aquatic food webs has been demonstrated in numerous aquatic systems, with abiotic and biotic factors underlying the preferential magnification within a physico-chemical window at Log $K_{o/w}$ ~ 5.8 – 7.4. From (Fisk et al. 1998).

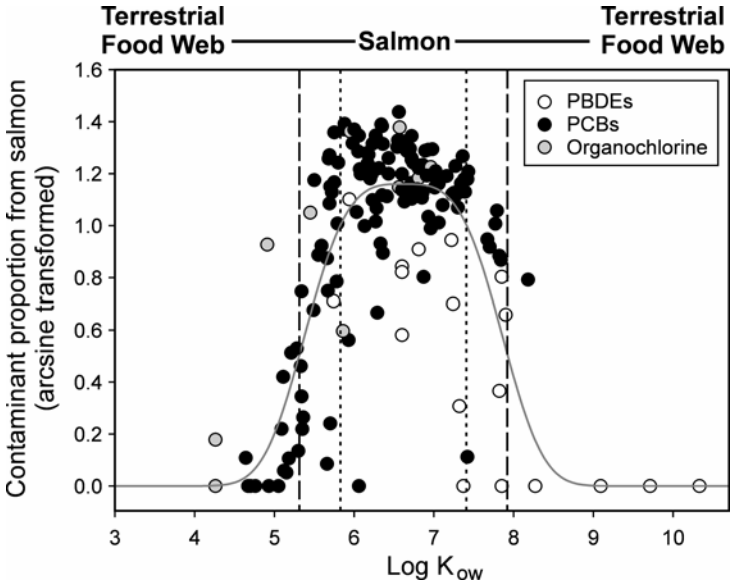

Figure 9: The proportion of different persistent contaminants in British Columbia grizzly bears that originates from salmon depends on the physico-chemical properties of the chemical in question. Up to 85 (dashed range) to 100% (dotted range) of persistent contaminants in grizzly bears can be attributed to salmon, highlighting the ready accumulation and retention of contaminants in this “optimal range” in the aquatic environment. Contaminants below (e.g. light PCBs) or above (e.g. heavy PBDEs) this window are derived increasingly from terrestrial items,

including vegetation. Symbol key: red = PBDEs, black = PCBs, blue = organochlorine pesticides. In this figure, any heavier PBDE that debrominates to a lighter counterpart would shift from one that represents a risk for terrestrial food webs to one that represents a risk to aquatic organisms at the top of the food web. In other words, debromination of BDE-209 would result in an accelerated biomagnification into high trophic species such as marine mammals (Christensen et al. 2005).

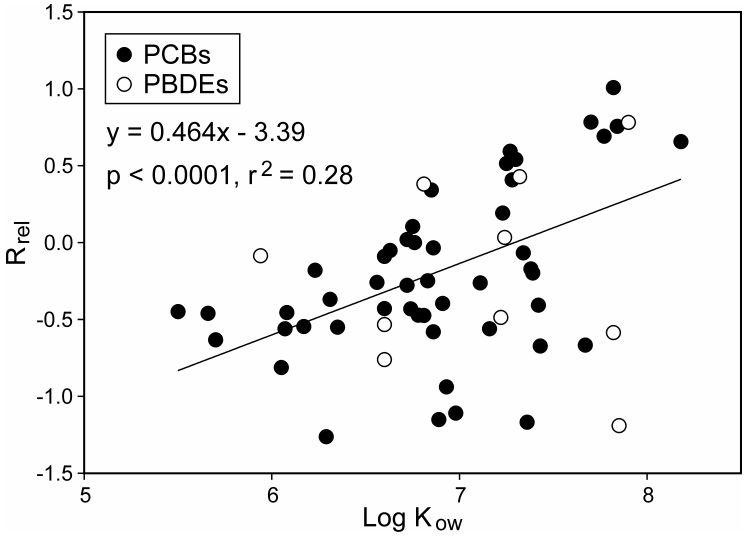

Figure 10: Despite a narrow range within which an amplified signal is observed for persistent contaminant in the marine environment, the retention of these contaminants within an animal (grizzly bear) is directly related to Log $K_{o/w}$. Persistence/retention of non-metabolizable PCBs (closed circles) and PBDEs (open circles) from prey (salmon) to predator (bear) increases with Log K_{ow}, suggesting increased retention of higher Log K_{ow} non-metabolizable PCBs and PBDEs. From: (Christensen, submitted 2008). In this way, PBDE congeners can be considered bioaccumulative unless (until) metabolism comes into play.

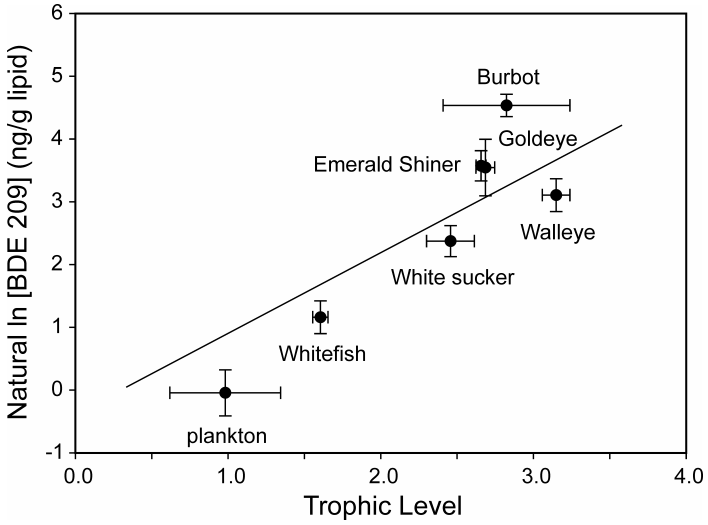

Figure 11: BDE 209 bioaccumulates in the freshwater food web in Lake Winnipeg, providing clear evidence that this heavily brominated congener is taken up readily across the G.I. tract and retained in the tissues of fish (Law et al. 2006).

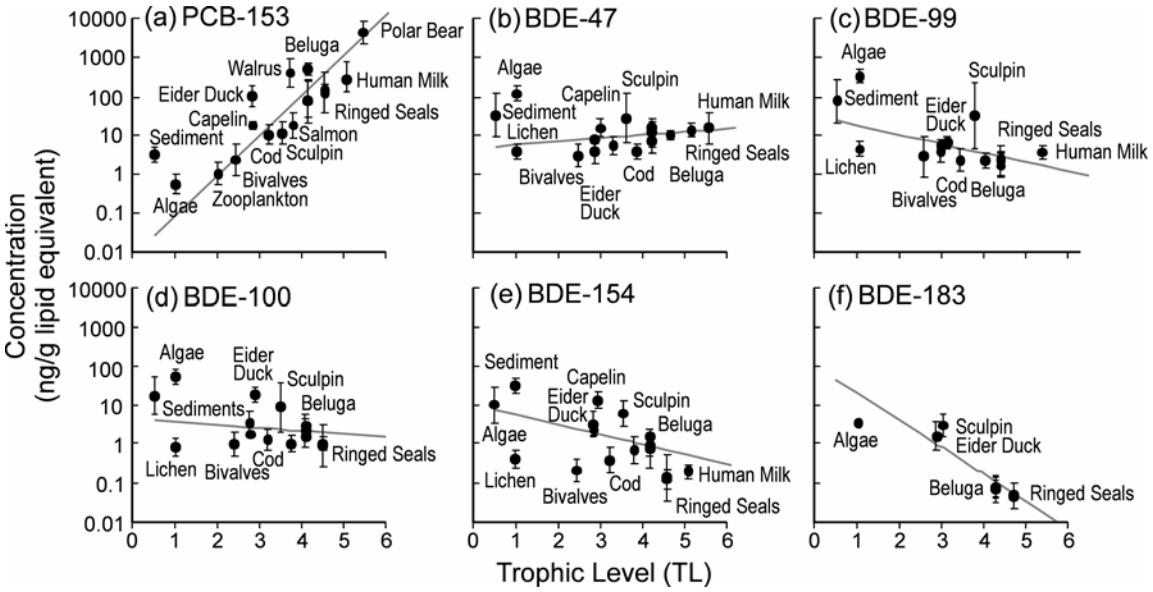

Figure 12: Chemical concentrations in organisms of the E. Hudson Bay marine food web (CB, ng·g-1 lipid equivalent) versus trophic level (TL) for (a) PCB-153, (b) BDE-47, (c) BDE-99, (d) BDE-100, (e) PBDE-154 and (f) BDE-183. Solid line represents log-linear regression of CB-TL relationship over the entire food web (Kelly et al. 2008).

How stable and/or persistent are PBDEs in the environment?

PBDEs are less stable than PCBs. They debrominate under both abiotic and biotic processes, producing the more bioaccumulative and more toxic, lighter congeners. The half-life for this conversion in biota has been calculated at 8-26 days. BDE-209 in the marine environment presents an inherent risk to biota in the future, as large environmental reservoirs are converted into persistent, bioaccumulative and toxic congeners in the future.

- DFO research on the direct issue of PBDE degradation in the environment or in biota is relatively limited, although some work has been done (Rayne *et al.* 2003b). The debromination of lower brominated PBDE congeners into metabolites has been observed in beluga whale cell lines using short term assays (<90 minutes) (McKinney *et al.* 2006). Debromination of PBDEs, including BDE-209, takes place under a number of abiotic conditions (e.g. sunlight, anaerobic conditions) (Rayne, Ikonomou, and Whale 2003b;Söderström *et al.* 2004) and in biota (He *et al.* 2006;Stapleton *et al.* 2004c;Stapleton *et al.* 2004a;Mörck *et al.* 2003;Van den Steen *et al.* 2007;Thomas *et al.* 2005;Tomy *et al.* 2004;Lebeuf *et al.* 2006), including humans (Thuresson *et al.* 2006).

- BDE-47, with a Log $K_{o/w}$ of 6.81, readily biomagnifies in an Arctic food web, while BDE-209, with a Log $K_{o/w}$ of 10.33, does not (see Figures 13a and 13b). Since BDE-209 is found at notable concentrations at lower trophic levels, this suggests that one or more of the following is taking place: 1) metabolism to less brominated forms at various trophic levels or rapid elimination rate, 2) the longer lifespan of marine mammals reflects an as-

yet non-steady state for PBDEs in the food web, and/or 3) a more limited uptake across the gastrointestinal tract of fish and marine mammals. The metabolic option is supported by published half-lives for BDE-209 of 8.5-13 days in grey seals (Thomas et al. 2005), 13 days in starlings (Van den Steen et al. 2007), and 26 days in lake trout (Tomy et al. 2004). Debromination to less brominated congeners has been documented, with some of the likely by-products including PBDE congeners 207, 208, 206, 196 and 197 (Van den Steen et al. 2007;Mörck et al. 2003). Limited uptake across the gastrointestinal tract is supported by several studies in fish (Kierkegaard *et al.* 1999;Stapleton *et al.* 2004b).

- 91.3% of BDE-209 was estimated to be metabolized in grizzly bears during their hibernation, and a complete lack of excretion by urine or feces indicates that metabolic by-products are retained by the bears (Christensen *et al.* 2007). The extent to which lower brominated PBDEs or parent congener metabolites were formed is unclear, but BDE-209 proved to be one of the least persistent relative to less brominated congeners, suggesting a progressive shift in the bears, mediated via metabolism, to a 'lighter' and more toxic PBDE profile. The extent to which such metabolic processes may be taking place in marine mammals remains to be elucidated.

- BDE-209 is broken down in the rat to less brominated PBDE metabolites (Morck *et al.* 2008).

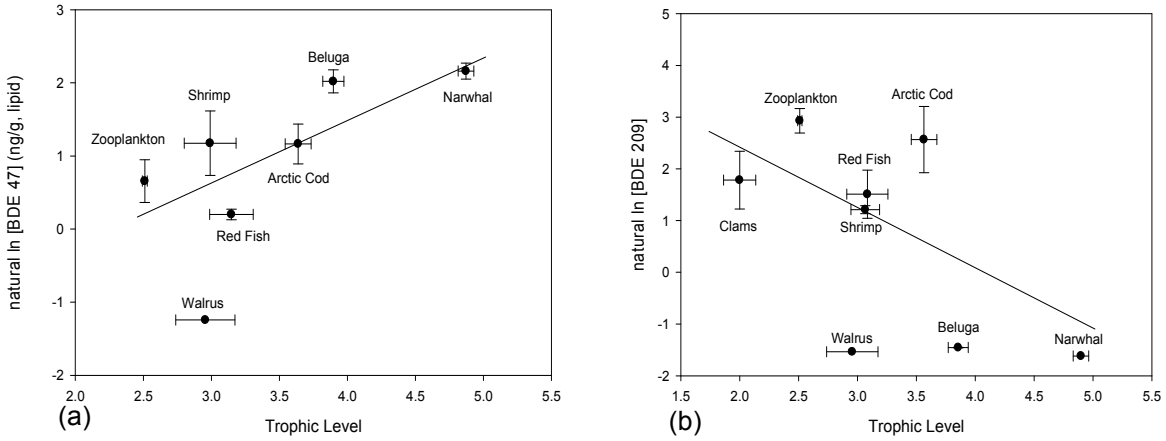

Figure 13. Bioaccumulation and biomagnification of PBDE congeners in Arctic food webs. 13a) Relationship between concentrations (ng/g, lipid weight) of BDE-47 in an Eastern Arctic marine food web. Error bars represent the standard error. Regression analysis: ln[BDE-47]= 0.9078 x TL -2.164 (r2=0.38, p=0.001). 13b) Relationship between concentrations (ng/g, lipid weight) of BDE-209 in an Eastern Arctic marine food web. Error bars represent the standard error. Regression analysis: ln[BDE-209]= -1.2109 x TL + 4.8712 (r2=0.266, p=0.001). From: (Pleskach et al. 2007, to be submitted to Environmental Pollution).

Is BDE-209 the only ingredient of concern in the decaBDE formulation?

While DecaBDE contains over 90% BDE-209, it also contains quantities of less brominated BDE congeners that are more readily taken up by biota and are considered at this time to be more toxic. In addition, the ready debromination of BDE-209 in abiotic compartments and in some biota underscores the risk of future health effects in biota, as a large reservoir of BDE-209 in the environment gradually shifts towards more bioaccumulative and more toxic forms.

- Up to 9% of the DecaBDE mixtures comprises BDE congeners other than BDE-209 (La Guardia *et al.* 2006) as well as some polybrominated biphenyl (PBB) impurities.
- In most studies that have examined DecaBDE biotransformation (Stapleton, Letcher, and Baker 2004b;Kierkegaard et al. 1999), it remained unclear as to whether the presence of 'metabolites' originated from impurities in the original mixture or resulted from the transformation of BDE-209 (Lebeuf et al. 2006). Either way, the presence of less brominated BDE congeners present a health risk to biota.
- The use of the DecaBDE mixture represents a direct source of more than just BDE-209 to the environment (mainly octa and nona-BDE congeners). Given the more rapid dispersion of such lighter congeners away from source, their increased partitioning into aquatic food webs, their increased propensity to bioaccumulate and biomagnify, and their heightened toxicity, the feature of DecaBDEs represents a significant threat to aquatic biota.

Are there research needs that would help inform managers about PBDE fate and effects in the Canadian aquatic environment?

- ❖ Research on the toxicological effects of PBDEs on aquatic species, incorporating complex mixtures found in the environment, PBDE metabolites or impurities, and chronic exposures;
- ❖ Research on health endpoints of concern to population health, including neurological development and behaviour, immune function and resistance to disease, reproductive health, and growth, reproduction and survival.
- ❖ Research on the comparative vulnerability of different aquatic species to PBDEs, and the influence of sex, age and life history parameters.
- ❖ Research on exposure, accumulation and metabolism (toxicokinetics) of PBDEs in aquatic biota.
- ❖ Research on PBDE toxicity in the context of multiple stressors in the environment, including the presence of other contaminants, changes in food web structure, and changes in climate.
- ❖ Research on the behaviour and fate of different PBDEs, especially the heavily brominated congeners found in the decaBDE formulation, in aquatic food webs and in the environment.
- ❖ Research on the persistence and stability of different PBDEs, especially the heavily brominated congeners, in the environment.
- ❖ Research on the spatial distribution of PBDE mixtures away from point sources such as sewage effluent and into areas of critical habitat or spawning habitat for aquatic biota.
- ❖ Research on PBDE concentrations and profiles in aquatic species, including commercial species, fish foods, and fish habitat.
- ❖ Model to predict PBDE discharge trends for products already in use; how long will discharge continue or continue to increase after PBDE production and import cease?

Conclusions

The lighter formulations, penta and octa-BDE have been removed from the market and are being considered for a ban under the terms of the Canadian Environmental Protection Act because they present a clear and measurable risk to biota. However, deca-BDE also possesses many properties of concern to biota. It bioaccumulates in terrestrial and marine organisms and is metabolized on a time scale of days into the congeners that are already under the proposed

ban. Its discharge to the coastal oceans is increasing exponentially. Because of its widespread presence in household and industrial products, the discharge of decaBDE is likely to continue to increase for years or decades after its production stops. Once its discharge is reduced, the experience with PCBs suggests that decaBDE and the other PBDEs will continue to cycle through the environment and biota for decades or even centuries.

While population-level impacts of PBDEs have not been detected in aquatic biota in Canada, waiting for such observations might signal a large-scale problem that would be difficult, if not impossible, to rectify. There exists an escalating risk of adverse health effects associated with PBDEs in aquatic biota, including invertebrates, fish, and marine mammals, as well as those human consumer groups that rely on these resources. The endocrine-disrupting potential of PBDEs has been established in laboratory animals, fish and in seals. Increasing PBDE levels in marine biota may have implications on DFO's responsibilities under the terms of the Fisheries Act, the Oceans Act, and the Species at Risk Act. The contamination of aquatic food webs by PBDEs and the risk to biota posed by this chemical should be considered under the terms of Integrated Ecosystem Management. Should PBDE concentrations continue to increase, there is a distinct possibility that fisheries closures (such as occurred with pulp mill-derived dioxins and furans in crab and prawns in 1200 ha of BC coastal waters; mercury in Saguenay shrimp) or consumption advisories (e.g. mercury and PCBs in tuna, swordfish, and fish from many inland lakes) could be enacted, with negative socio-economic implications.

Evidence from DFO and other research groups indicates that all PBDE congeners, including BDE-209, are persistent, bioaccumulative and toxic. In addition, all PBDE congeners are readily transported through atmospheric processes to remote locations. Given the structural similarity of PBDEs to the PCBs that were banned by Canada in 1977 with only very cursory data on its toxicity, Canada should apply lessons learned from the past to the case of PBDEs. In this regard, the additive, synergistic and/or antagonistic effects of PBDEs in the environment as they interact in complex mixtures in the environment with other compounds such as the PCBs, dioxins and furans, must also be considered. There is a growing body of scientific evidence that the aquatic environment in Canada faces increasing risks associated with PBDEs.

A summary of findings follows:

- PBDEs are persistent, bioaccumulative and toxic contaminants, and thereby pose a risk to aquatic food webs in Canada.
- The continued Canadian practices for penta, octa, deca PBDE uses will lead to increased contamination of aquatic biota.
- PBDEs have surpassed the structurally-related PCBs (banned in 1977) as the number one contaminant in sewage, sediments and water in many parts of Canada, and under current use trends are projected to surpass PCBs as the top contaminant in marine mammals within 10-15 years.
- Further inputs/releases of PBDEs into the Canadian aquatic environment will increase the likelihood, extent and significance of population-level health effects in aquatic invertebrates, fish and marine mammals.
- The breakdown of BDE-209 in the Canadian aquatic environment will lead to increasing levels of the less brominated, more mobile, more bioaccumulative, and more toxic forms of PBDEs over time.
- Additional research on the fate and effects of PBDE constituents will provide better mechanistic insight into the possible consequences for this class of chemical at the population and/or ecosystem levels.
- Experience gained from the PCBs suggests that PBDEs may remain a threat to aquatic biota for decades, if not centuries.

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