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Viewpoint

Large and growing environmental reservoirs of Deca-BDE present an emerging health risk for fish and marine mammals

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) have been the subject of intense scientific and regulatory scrutiny during recent years. Of the three commercial forms (Penta, Octa and Deca) of PBDEs that have been widely used as flame retardants in textiles, furniture upholstery, plastics, and electronics, only Deca-BDE remains on the general market in North America, while a recent ruling of the European Court spells an impending end to its use in Europe. We review here highlights of aquatic research documenting the rapid emergence of PBDEs as a high priority environmental concern in Canada. PBDEs are being introduced in large quantities to the aquatic environment through sewage discharge and atmospheric deposition. In certain environmental compartments, the single congener BDE-209, the main ingredient in the Deca-BDE formulation, has surpassed the legacy PCBs and DDT as the top contaminant by concentration. Limited biomagnification of BDE-209 in aquatic food webs reflects its high log K_{ow} and preferential partitioning into the particle phase. As a result, large environmental reservoirs of BDE-209 are being created in sediments, and these may present a long-term threat to biota: BDE-209 breaks down into more persistent, more bioaccumulative, more toxic, and more mobile PBDE congeners in the environment.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used chemical flame retardants that have been sold as three formulations: Penta, Octa, and Deca. Structurally-related to the polychlorinated biphenyls (PCBs), up to 209 BDE congeners are theoretically possible, although only about 40 are routinely detected in the environment. Two of the three commercial formulations (Penta and Octa) were removed from the European (1998) and North American (2004) marketplace, because they met the definition of chemicals considered to be persistent, bioaccumulative, toxic and subject to long-range transport. Deca-BDE, of which the single congener BDE-209 makes up over 90%, is poised for a ban in Europe but remains on the national markets in Canada and the USA (some US states have regulated Deca-BDE).

In this overview, we characterize PBDE trends in the aquatic environment, with a particular focus on recent evidence from Canada. We compare the properties of PBDEs with the four characteristics considered by the Stockholm convention: persistence, bioaccumulation, toxicity, and susceptibility to long-range environmental transport. PBDEs have been generally touted as potentially congruous with the terms of the Stockholm Convention (Tanabe, 2005), but we outline here our concerns about the continued widespread use of Deca-BDE in North America and the emerging risks to aquatic biota.

1.1. Are PBDEs persistent in the environment?

Yes, but not under all conditions. They enter coastal waters through municipal and industrial wastewater outfalls, landfill leachate and atmospheric deposition from multiple sources (de Wit, 2002). PBDEs have been measured in sediments (Li et al., 2006), indicating that they do not break down completely in seawater. They are readily transported through the movement of air, water, particles and biota, and have been measured in biotic and abiotic media throughout the Arctic (de Wit et al., 2006). PBDEs now rival PCBs in multiple matrices in the coastal environment, and the ‘heavy’ BDE-209 is a significant component of total PBDEs in air, water and sediments.

PBDEs are less stable than PCBs. Laboratory studies have shown that BDE-209 can debrominate by both abiotic and biotic processes, producing the more bioaccumulative and toxic, lighter congeners (Stapleton and Dodder, 2007; Stapleton et al., 2004b).

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However, all the homologue groups appear to persist in the environment. Depth profiles measured in sediment cores illustrate a historical build-up of PBDEs in sediments that parallels the history of their discharge (Zhu and Hites, 2005). Recent research has found no evidence of their debromination in sediments (Johannessen et al., in press); they simply persist, and are therefore available to foraging organisms in the surface mixed layer, through which they may re-enter aquatic food webs.

PBDEs have been in the environment for a much shorter time than have PCBs (PBDE manufacture ~from the late 1970s to present; PCB manufacture ~from 1929 to late 1970s). Consequently, they are often in highest concentration near the immediate point of entry into a body of water, often near municipal and industrial outfalls (Law et al., 2006). However, where they have had more time to equilibrate with the environment, and at more remote sites, they seem to be distributed similarly to PCBs. Strong temperature-related gradients have been observed in the concentration of PBDEs in a remote area of the Pyrenees, compared to no such gradients near a current source of PBDEs (Gallego et al., 2007). Similarly, the relationship between the 10-year accumulation of PBDEs and sediment accumulation rate in the Strait of Georgia, Canada, implies that the distribution is controlled by environmental processes once the PBDEs travel away from the immediate point of entry, and hence, that PBDEs are conserved during transport and burial (Johannessen et al., in press). BDE-209 contributes about 80% of the total PBDE in Strait of Georgia sediments.

1.2. Are PBDEs bioaccumulating in aquatic biota?

Yes, but uptake of the parent BDE-209 congener is limited by particle-binding. PBDE concentrations are increasing exponentially in fish and marine mammals in Canada's three oceans and other aquatic systems with concentrations in species from some areas doubling as rapidly as every 3–4 years (Ikonomou et al., 2002; Lebeuf et al., 2004; Rayne et al., 2003). BDE-209 has been reported in aquatic food webs, but in lower concentration than less brominated congeners like BDE-47, 99 and 100. These 'lighter' congeners can be directly discharged into the environment, or they can be introduced indirectly through the breakdown of 'heavier' PBDE congeners, including BDE-209 (Stapleton et al., 2004a). The dominance of BDE-209 in abiotic matrices such as sediments implies the accumulation of a potentially large contaminant reservoir that puts at risk lower trophic level species, especially benthos and their consumers (Ciparis and Hale, 2005). On the other hand, the breakdown products of BDE-209 are more bioaccumulative, and present risks to the upper trophic levels of aquatic food webs (Lebeuf et al., 2006).

Some of the conflicting signals for BDE-209 bioaccumulation and biomagnification in earlier papers can be explained by (1) its exclusion from analyses in earlier papers, (2) the analytical difficulties associated with its accurate determination in all environmental matrices; (3) the 'sticky' nature of BDE-209 which predisposes it to particle binding in air, water and sediments; (4) its debromination under abiotic conditions; and (5) its biotransformation by some biota. In the latter two cases, lighter, more bioavailable and more toxic PBDE congeners result.

PBDEs have been shown to biomagnify in aquatic food chains, including those in the remote Arctic (Kelly et al., 2008; Morris et al., 2007; Sormo et al., 2006; Wolkers et al., 2004). PBDE patterns in all biota were dominated by congeners 47, 99 and 100. The relative depletion of BDE-209 in upper trophic level organisms has been in part attributed to metabolism and to constraints in the uptake of particle-bound BDE-209 by biota (Tomy et al., in press).

1.3. Are PBDEs toxic to aquatic biota?

Yes, but dose–response relationships for many PBDE congeners in many aquatic species are at present not well established. PBDEs possess endocrine-disrupting properties that may predispose fish, marine mammals, and their offspring to adverse effects (Darnerud, 2008; de Wit et al., 2006). In juvenile rainbow trout (*Salvelinus namaycush*) exposed to a dietary mixture of 13 PBDE congeners (2.5 and 25 μg/kg dry weight in food), plasma thyroxine declined at the end of the 56-day exposure period (Tomy et al., 2004). In European flounder (*Platichtus flesus*) exposed to the commercial Penta-BDE mixture DE-71 in food and sediments, a dose–response model indicated that a decrease in plasma thyroxine (T4) may occur at concentrations occasionally observed in the environment (10% decrease at 51 ng BDE-47/g muscle (ww)). Oral exposure to BDE-47 reduced condition and sperm production in male fathead minnows (*Pimephales promelas*) (Muirhead et al., 2006). Increased splenic germinal center development and incidence of B-cell hyperplasia was observed in mink exposed to diets containing 10 μg/g ww of purified DE-71. The highest concentrations of PBDEs reported in freshwater fish in USA are around 1 μg total PBDE/g ww (carp, Hyco River) (Hale et al., 2008). PBDEs also negatively correlated with T4 in free-ranging harbour seals (Hall et al., 2003).

PBDEs therefore have toxic effects that are very similar to those reported for the structurally-related PCBs. PBDE and PCB congeners appear to bind to the same cellular receptors in biota (Luthe et al., 2008). Synergistic interactions on free T4 in plasma and hepatic ethoxyresorufin *O*-deethylase (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). 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 a low dose of each compound did not affect behaviour. These results suggest that the interaction is more than additive (Eriksson et al., 2006). PBDEs therefore are adding to an already complex mixture in the aquatic environment, and should not be considered in isolation.

PBDE-associated endocrine disruption may lead to effects at the whole-body level. PBDE-induced neurodevelopmental toxicity has been demonstrated in rats and mice after pre- and post-natal exposure (Costa and Giordano, 2007), and also in fish (Lema et al., in press; Timme-Laragy et al., 2006). Killifish (*Fundulus heteroclitus*) embryos incubated in aqueous solutions of as little as 0.001 μg/L of the DE-71 mixture, developed behavioural changes similar to those observed in rodents, with a J-shaped dose–response curve suggestive of endocrine disruption (Timme-Laragy et al., 2006). Effects of PBDEs on the immune system have been reported in mice and more recently in mink (Martin et al., 2007) but have not yet been fully evaluated in aquatic species.

1.4. Are PBDEs subject to long-range environmental transport?

Yes, PBDEs are found in remote regions of the world, including the Canadian Arctic, and have been shown to travel readily through air. Based solely on the physico-chemical properties of PBDE congeners, and using a multimedia model, Wania and Dugani (2003) showed that lower brominated congeners have a long-range transport potential (LRTP) similar to that of the PCBs. Conversely, the higher brominated congeners were suggested to have a lower potential to reach remote areas. In a recent review, de Wit et al. (2006) reported that concentrations of PBDEs in Arctic air were comparable to those found at monitoring sites in urban regions. Direct measurements on the atmospheric particles collected between 2002 and 2004 at Alert, Nunavut, in the Canadian High Arctic, con-

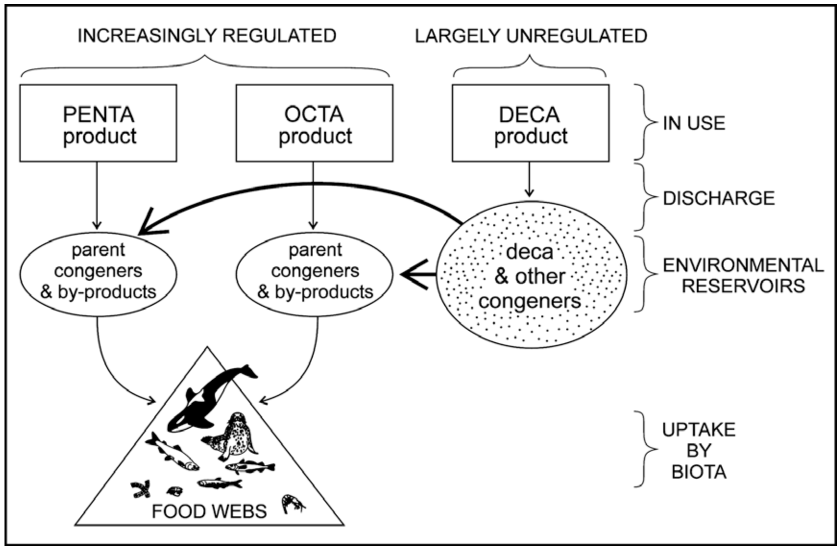

Fig. 1. Of the three commercially available formulations of polybrominated diphenyl ethers (PBDEs) available for use as flame retardants (Penta, Octa and Deca in the figure boxes) in consumer and commercial applications, the Penta and Octa products are increasingly being banned because they are persistent, bioaccumulative, toxic and subject to long-range transport. We argue here that the large and growing environmental reservoirs of the main ingredient in the Deca formulation, BDE-209, provide as ready a source of Penta- and Octa-like congeners to aquatic biota as do Penta- and Octa-containing products in homes, businesses and landfills (see bold arrows from Deca congener oval in figure).

sistently detected the PBDE congeners 28/33, 47, 99, 100, 153, 154 and 209 (Su et al., 2007).

2. Conclusions

Total PBDE concentrations are increasing rapidly in abiotic and biotic matrices in Canada, and have surpassed the structurally-related PCBs as the number one contaminant in sewage, sediments and water in near-urban parts of Canada. In extrapolating recent trends, PBDEs are projected to surpass PCBs as the top contaminant in many fish and marine mammal populations within 10 years (Ikonomou et al., 2002; Ross, 2006). Additional research is needed to answer important questions, such as a better characterization of secondary PBDE discharges via waste water treatment facilities, landfill leachates and other pathways, modes of PBDE biotransformation under abiotic and biotic conditions, and the health effects associated with exposure. However, the abundant scientific evidence available today is more than sufficient to support a precautionary approach to regulation.

Lighter and more toxic PBDE congeners biomagnify readily in aquatic food webs, and present an increasing risk to the health of fish and marine mammals. With clear scientific evidence delineating the Penta- and Octa-BDE mixtures as persistent, bioaccumulative, toxic and subject to long-range transport, a rational foundation in support of current and pending Penta- and Octa-BDE regulations has been established.

Deca-BDE presents a dilemma that perhaps explains the heterogenous responses of government regulators around the world (Ward et al., in press): BDE-209 is both persistent (when particle-bound) and non-persistent (in sunlight or in some biota), bioaccumulative (in terrestrial food webs) and non-bioaccumulative (in some aquatic food webs). We argue that this duality of properties is deeply troubling for the following reasons:

(1) the widespread presence of BDE-209 in household products ensures a continued delivery to the environment for years or decades even after production ceases;
(2) the discharge of BDE-209 to aquatic systems and coastal oceans is increasing exponentially;
(3) large and increasing reservoirs of BDE-209 exist in sediments; and
(4) the breakdown of BDE-209 into lighter PBDE congeners in such reservoirs will create products that are persistent, bioaccumulative, toxic, and subject to long-range transport.

Through its breakdown products, Deca-BDE is therefore a source of those very PBDE congener mixtures that face restrictions around the world (see Fig. 1). Should the discharge of PBDEs be reduced, our experience with PCBs over the last 40 years suggests that these largely unregulated flame retardants will continue to cycle through the environment and biota for decades or even centuries.

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