PBDE CONGENER PROFILES IN FISH WITH DIFFERENT FEEDING BEHAVIORS FROM MAJOR RIVERS IN MINNESOTA

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Introduction

Polybrominated diphenyl ethers (PBDEs), widely used flame retardants, have become an increasing concern to scientists and regulatory agencies, because of ubiquitous detection in the environment and bioaccumulation in humans, wildlife and aquatic organisms[1]. PBDEs are additive (non-covalently bound) flame retardants in polymers and textiles at levels ranging 5% to 30% PBDEs by weight[1-3]. These compounds can be released into the environment during production and use and from the final treated products during their use and after disposal, thus their appearance in the environment is not surprising. Three commercial formulations of PBDEs are produced for use exclusively as flame retardants. Each formulation consists of a mix of PBDE homologues with different bromination patterns and different physiochemical properties. The commercial products, penta-BDE, octa-BDE and deca-BDE, consist of a limited number of congeners[3]. Deca-BDE accounts for 75% of PBDE production, but the congener profile commonly found in biota is often similar to the penta-BDE commercial product, a mix of tetra-, penta- and some hexa-BDE. Research suggests this biotic congener profile results from a preferential uptake of lower brominated compounds[1]. Tetra- and penta-BDEs have also shown more toxic and bioaccumulative properties than higher brominated congeners[4]. While the European Union Commission has banned the production and use of penta-BDE, there are no laws or regulations on PBDE production or use in the United States.

The toxicological profile of PBDEs suggests that exposure may interfere with development, behavior, and reproduction. Experimental animal studies have shown that prenatal exposure to PBDEs can affect neurodevelopment, resulting in decreased motor function[4]. Adult animals exposed to PBDEs have exhibited decreased reproductive success and impaired immune function. PBDEs can affect the normal functioning of endocrine or hormone systems and neurotransmitters in the central nervous system, both possible mechanisms of action behind the observed health effects in experimental animals. Thyroid disruption was one of the most common and sensitive endpoints observed in animal studies[1, 4].

Monitoring and assessment of PBDEs has only begun recently in the U. S., with many of these studies focusing on PBDE contamination in fish. Contaminant profiles in fish provide important information on ecological species and human exposure and environmental fate. PBDEs have been found in lake trout and salmon from Lakes Ontario, Superior, Huron and Erie, in carp and large mouth bass from Michigan and Illinois rivers, in freshwater fish from Virginia, and in salmonids from Lake Michigan and Wisconsin rivers[5-7]. Our research has detected PBDEs in carp, white suckers, walleye, northern pikes and redhorse from rivers in Minnesota. These studies indicate varied levels and patterns of PBDE congeners in different fish species collected from different sites.

Little is known about the uptake and metabolism of PBDEs by different fish species. A few studies have found that carp displayed unusual patterns of PBDE accumulation in which BDE-99 was significantly depleted in carp tissues relative to other fish collected from the same area, indicating that carp may metabolize or assimilate certain congeners[8, 9]. The aim of this study is to better understand the uptake, accumulation, and elimination of PBDE congeners in fish species from different trophic levels in the aquatic food chain. PBDE congener profiles are compared between five fish species: common carp, white sucker, redhorse, walleye and northern pike, with two different feeding behaviors, omnivorous and piscivorous, collected from major rivers in Minnesota. Congener profiles in fish are also compared to those in sediment.

Materials and Methods

During the summer of 2001, sediment samples and fish were collected from the Rainy, Red River of the North, St. Louis, Mississippi, St. Croix and Minnesota Rivers at targeted locations downstream of wastewater treatment plant discharges. PBDE analysis of the samples included quantification of current concentrations and determination of congener profiles. A composite of surficial sediments from five individual sampling locations consisting of the top 5 cm from each core was prepared. Fish species representing two different feeding behaviors (omnivorous and piscivorous) were collected from the same locations as the sediment samples. Composite samples consisted of three fish of the same species and the same size ($\pm$10 cm). Omnivorous species included the common carp (*Cyprinus carpio*), white sucker (*Catostomus commersoni*) and redhorse (a species of *Moxostoma* genera), while walleye (*Sander vitreus*), and northern pike (*Esox lucius)*, represented the piscivorous species.

Samples of sediment were placed in solvent-rinsed amber glass jars with Teflon lined lids and stored at -20°C. Fish samples were wrapped in solvent-rinsed aluminum foil and stored at -20°C. All samples were sent for homogenization and PBDE analysis to AXYS Analytical Services Ltd., located in British Columbia, Canada. AXYS continued to maintain samples at -20°C until analysis. Fish homogenates consisted of three whole fish processed through a size-appropriate homogenization apparatus. Aliquots of up to 10 grams from the composite samples were taken for analysis. Briefly, extraction, clean-up and high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) analysis was similar to EPA 1600 series methods (1668A)[10]. Samples were spiked with a suite of $^{13}C_{12}$-labeled PBDE internal standards prior to extraction, followed by soxhlet extraction and liquid chromatography clean-up. Calibration steps included use of a set of labeled standards and 41 non-labeled PBDE congeners (mono- to deca-BDEs). PBDEs were quantified against $^{13}C_{12}$-labeled internal standards and individual response factors were determined for each reported congener. Data were recovery-corrected for losses in extraction and clean-up.

Results and Discussion

Fish tissue primarily consisted of the tetrabromo-congeners (BDE-47, BDE-49), pentabromo-congeners (BDE-99, BDE-100), and to a lesser extent, hexabromo congeners (BDE-153, BDE-154), a pattern similar to the congener composition in the penta-BDE commercial product (Figures 1 & 2). The omnivorous species, including carp, redhorse and white sucker, displayed a distinct pattern of PBDE congeners, characterized by significantly lower concentrations of BDE-99 relative to the patterns of PBDE congeners found in the piscivorous species (walleye and northern pike) collected from the same rivers. While BDE-47 was the dominant congener in both,

omnivorous and piscivorous, BDE-100 was significantly higher than BDE-99 congener in omnivorous species. The omnivorous species may posses the ability to metabolize specific PBDE congeners or may not assimilate them because of the differences in their feeding behavior. Omnivores eat any available food item, including insects, other fish, plants, seeds and algae; the omnivorous species examined in this study are all bottom feeders. Piscivores rely primarily on small fish for food, with small quantities of insects, crayfish, worms, and clams also consumed. The high fish to sediment ratio for the lower brominated congeners indicates that these compounds are highly bioavailable. The higher brominated congeners (BDE-183, BDE-209) with considerable concentrations in the sediments (Figure 3), were not found in the fish tissues. These findings suggest that the higher brominated congeners may not be bioavailble, may be biotransformed, or may be debrominated prior to fish uptake.

Further investigation is required to better understand factors influencing the uptake and metabolisms of PBDEs in fish with different feeding behaviors.

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References

1. Darnerud PO, G. S. Eriksen, T. Johannesson, P. Larsen, and M. Viluksela. 2001. Polybrominated diphenyle ethers: Occurrence, dietry exposure, and toxicology. Environmental Health Perspective. 109 (Suppl 1): 49-68.

2. Alaee, M., and R. Wenning. 2002. The Significance of brominated flame retardants in the environment: Current understanding, issue and challenges. 2002. Chemosphere. 46: 579-582.

3. De Boer, J., P.G. Wester, A. van der Horst, and P. Leonards. 2003. PBDEs in influents, suspended particulate matter, sediments, sewage treatment plants and effluent and biota from the Netherlands. Environmental Pollution. 122: 63-74.

4. Hardy, M. L. 2002. The toxicology of the three commercial polybrominated diphenyl oxide (ether) flame retardants. Chemosphere. 46: 757-777.

5. Easton, M.D.L., D. Luszniak, and E. Von der Geest. 2002. Preliminary examination of contaminant loadings in farmed salmon, wild salmon and commercial salmon feed. Chemosphere. 46: 1053-1074.

6. Dodder, N.G., B. Strandberg and R.A. Hites. 2002. Concentrations and spatial variations of PBDEs and several organochlorine compounds in fishes from Northern United States. Environ. Sci. Technol. 36: 146-151.

7. Oliaei, F., P. King, and C. Hamilton. 2002. Occurrence and concentrations of PBDEs in Minnesota's environment. Organohalogen Compounds. 58: 185-188.

8. Boon, J., w. Lewis, M. Tjoen-A-Choy, C. Allchin, R. Law, J. De Boer, and B. Zegers. 2002. Levels of PBDEs flame retardants in animals representing different trophic levels of the North Sea food web. . Environ. Sci. Technol. 36: 4025-4032.

9. Stapleton, H., R. Letcher, and J. Baker. 2002. Uptake, metabolism and depuration of PBDEs by the common carp, (*Cyprinus Carpio*). Organohalogen Compounds. 58: 201-204.

10. U.S. EPA Method 1668: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS, Revision A. 1999. Office of Water, Washington D.C.

Figure 1

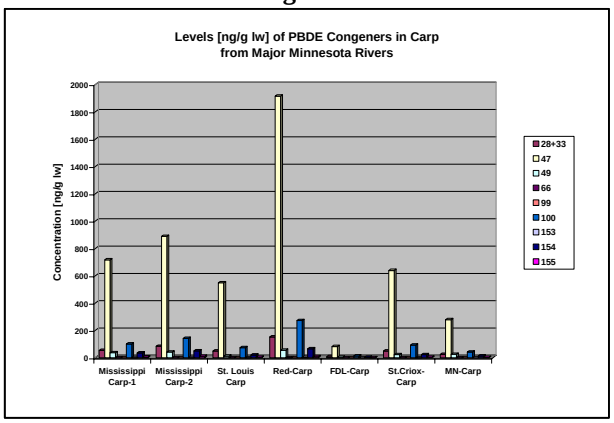

Figure 2

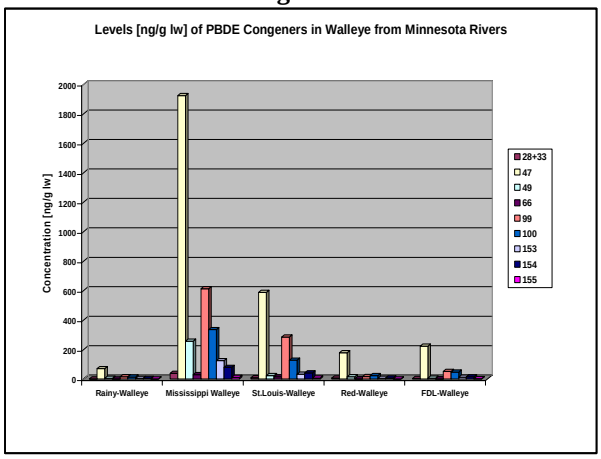

Figure 3