OCCURRENCE AND CONCENTRATIONS OF POLYBROMINSTED DIPHENYLE ETHERS (PBDEs) IN MINNESOTA ENVIRONMENT

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Introduction

In recent years unexpected and undesirable consequences from the widespread use of Polybrominated Diphenyl Ethers (PBDEs) have been observed. PBDEs are used as additive flame retardants in plastics, textiles, coatings, and electrical components in products such as computers, TVs, electrical appliances, furniture, building materials, carpets, and automobiles[1]. These chemicals have been found to persist in the environment and bioaccumulate in humans and wildlife[2, 3]. Their physiochemical properties are similar to PCBs and dioxins. So, while they have not been extensively studied, there is concern regarding their environmental occurrence and potential toxicity. They may interfere with the normal functioning of endocrine or hormone systems, central nervous systems and immune systems[3, 4]. They may cause a variety of problems with development, behavior and reproduction (i.e. birth defects in humans and/or reduced populations and altered community structures within ecosystems), and cancer[5, 6]. PBDEs have been detected globally in biotic and abiotic matrices from impacted and remote environments. They have been detected in sediment, air, wildlife, fish, human blood, and human milk [2, 3, 7, 8]. A human milk monitoring program in Sweden indicates that PBDE concentrations in breast milk are increasing exponentially, doubling every five years [9]. Similar studies of breast milk conducted in other countries confirmed that human exposure to PBDEs is increasiing[10, 11.] Monitoring and assessment of PBDEs in North America has only begun recently. In the Great Lakes, PBDE concentrations was measured in lake trout and salmon from the Lakes Erie, Huron, Superior and Ontario. Lipid-normalized concentrations were highest in Lake Ontario, followed by Superior, Huron and Erie [12, 13, 14, 15]. The relatively high level of PBDEs in Lake Superior is surprising due to the more pristine character of this lake.

In this study, we investigated the presence of PBDEs in biotic and abiotic matrices in Minnesota environment. The sampling was focused on areas most likely to be impacted by PBDEs. This focus was based on the assumption that if PBDEs are not found in these targeted areas, they are not likely to be a problem in more ambient locations in Minnesota. The targeted efforts were landfill leachates, wastewater treatment plant (WWTP) sludges and effluents as well as fish and sediment collected from rivers below WWTP effluent discharges. To ensure geographical representation, fish and sediment samples were collected from six major river basins in Minnesota (Mississippi, St. Louis, Red, Rainy, Minnesota and St. Croix). This is the first report of PBDEs being measured in different biotic and abiotic environmental matrices in Minnesota.

Methods and Material

Samples from the following environmental matrices with the potential sources and receptors of PBDEs were collected during summer of 2001.

Landfill Leachate

Five landfills were selected for sampling their leachates and the sludge of their leachates (if available) to determine the presence and concentration of PBDEs. Pine Bend Sanitary Landfill (PBSL), Burnsville Sanitary Landfill (BSL), Spruce Ridge Sanitary Landfill (SRSL); SKB Industrial Landfill (SKBIL) and SKB Demolition Landfill (SKBDL) were chosen for this study.

Sewage Sludge

Two domestic wastewater treatment facilities, MWCC-Metropolitan and Western Lake Superior Sanitary District (WLSSD), were selected for sludge sampling to assess these potential sources of PBDEs into the environment. Sample of raw or activated sludge (MWCC-Raw and WLSSD-Raw) was taken after primary/secondary treatment processes, while sample of dewatered or final sludge (MWCC-Final and WLSSD-Final) was taken after final treatment process. Sediment and fish sampling below the effluent discharges from these treatment facilities helped us to determine the presence and concentrations of PBDEs in aquatic environments impacted by wastewater effluents.

Sediment Samples

Sediments from Mississippi, St. Louis, Red, Rainy, Minnesota, and St. Croix Rivers were sampled and analyzed to quantify the current concentrations of PBDEs in the major river basins in Minnesota. From each river, a composite sediment sample represented five individual sampling locations.

Fish Samples

A high lipid species (carp or sucker) was collected from the same locations of the rivers that sediments were sampled. Three fish of the same species and the same size ($\pm$ 10 cm) were composited for PBDEs analysis.

Samples of sediment, sludge, and leachates were placed in a solvent rinsed dark glass container, and then stored in –20 °C. Fish samples were rapped in a solvent rinsed aluminum foil and stored in –4 °C. All samples were sent for PBDEs analysis to AXYS Analytical Services LTD, located at British Colombia. In short extraction and clean up for filters was the same as EPA method 1668A for PCB congeners. Filtered samples were spiked with a suit of $^{13}C_{12}$ labeled internal standards. Solvent extracted and cleaned with liquid chromatography, and further analyzed by high resolution GC/HRMS. The method was calibrated with a set of 41 PBDE congeners (mono- to deca-BDEs) based on Cambridge Isotope Labs (CIL) analytical standards. PBDEs were quantified against $^{13}C_{12}$ labeled internal standards and individual response factors were determined for each reported congener.

The AXYS Analytical Service QA/QC procedure was based on the “batch” method. Each batch consisted of maximum eight samples, plus three QA/QC samples, including spiked, blank, and duplicate samples to demonstrate accuracy of the data, absence of contamination, and precision of the method. For data acceptance, the spike recoveries for all matrices are required to be within the range of 50 to 150 %. Recoveries of the labeled surrogate compounds (added as internal standards) were required to be in an acceptable range of 40-130 %.

Results and Discussions

PBDEs were detected in all biotic and abiotic environmental matrices in Minnesota. The following figures present concentrations of dominant PBDEs congeners detected in fish, sediment, sewage sludge, and landfill leachates.

These data indicated that PBDEs are an environmental contaminant in Minnesota. We will begin creating a database of PBDE concentrations in Minnesota. The database values will be used as input for models designed to predict the transport and fate of PBDEs in aquatic ecosystems. The results of this

study will help us to better understand the environmental impacts of polybrominated diphenyl ether flame retardants. It will help establish benchmarks to guide future monitoring efforts and to track environment trends. If needed, it can form the basis of regulatory measures to reduce emissions and exposure. This «information gathering» step is essential before proceeding to the risk assessment or risk management process. Testing of fish tissue helped us to examine bioaccumulation of PBDEs in the aquatic food chain and potential exposure of humans to these chemicals through eating fish.

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POLYBROMINATED FLAMES RETARDANTS