

# POLYBROMINATED FLAME RETARDANTS

## CONCENTRATIONS AND SPATIAL VARIATIONS OF POLYBROMINATED DIPHENYL ETHERS IN FISH AND AIR FROM THE NORTHEASTERN UNITED STATES

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### Introduction

Brominated flame-retardants, such as polybrominated diphenyl ethers (PBDEs), are added, often at 10-30% by weight, to different materials such as plastics used in electronic appliances and to paints and textiles (especially those used in office buildings and in cars) to prevent them from catching fire. The annual global use of PBDEs was estimated to be 40,000 tons in 1990<sup>1</sup>. These substances can enter the environment during their production, and they can migrate from the treated products. As a consequence, PBDEs are now ubiquitous environmental pollutants.

One of the first reports of PBDE in the environment was in 1981<sup>2</sup>. PBDEs were found in pike, eel, and sea trout from a river in the western part of Sweden. Since then, PBDEs have been found in a variety of environmental samples throughout Europe, including fish<sup>2, 3, 4</sup>, birds<sup>5</sup>, sediment<sup>6</sup>, and air<sup>7</sup> and in Atlantic sperm whale tissue<sup>4</sup>, human blood<sup>8</sup>, and mothers' milk<sup>9</sup>. Reports from Europe show an increasing trend in environmental concentrations similar to that found for DDTs and PCBs a few decades ago. There are, however, only a few reports of these compounds in the environment of North America; for example, PBDE have been found in carp from the Buffalo River (New York)<sup>10</sup> and in salmon, herring, and trout from the Great Lakes<sup>11, 12</sup>.

The aim of our study was to measure PBDE concentrations in fish from a lake close to a potential point source and in fish distant from any suspected sources. We have also measured PBDE in air samples collected at an urban site and at more remote locations with the goal of understanding urban atmospheric sources and vapor-particle exchange of these compounds.

### Methods and Materials

Fish samples of white crappie and bluegill were collected from two lakes in the Midwest United States in the summer and fall of 1999. Hadley Lake (HL) is located about 1.3 km from a plant, where PBDEs are manufactured in West Lafayette, Indiana; this was considered a potential point source for these compounds. The Lake of the Ozarks (LO) was distant from any point source and is located in central Missouri (see Figure 1).

Air samples were collected from urban, rural, and remote shorelines of the Great Lakes. The sampling locations were as follows: Chicago, Illinois (CH), an urban site on Lake Michigan; Sleeping Bear Dunes, Michigan (SBD) and Sturgeon Point, New York (SP), two rural locations on Lakes Michigan and Erie, respectively; and Eagle Harbor, Michigan (EH), a remote site near Lake Superior (see Figure 1). These samples were collected as part of the Integrated Atmospheric Deposition Network (IADN).

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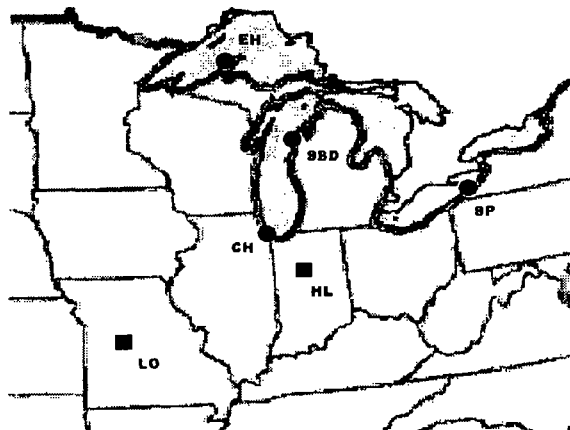


Figure 1: Air (●) and fish (■) sampling locations.

The fish from HL were pooled, with four fish in each sample, and processed in replicates ( $N = 4$ ). Four fish from LO were analyzed individually. A brief description of the clean-up procedure follows: The whole fish, including skin, intestine, and bones, was homogenized. Approximately 20 g of this homogenate was mixed with anhydrous  $\text{Na}_2\text{SO}_4$  and Soxhlet extracted with acetone/hexane (1/1). Before extraction, a surrogate standard containing  $^{13}\text{C}_{12}$ -2,3,3',4,4',5-hexachlorodiphenyl ether and  $^{13}\text{C}_{12}$ -2,2',3,3',4,4',5,5'-octachlorodiphenyl ether (Cambridge Isotope Laboratories) was spiked into the sample. Following extraction, the percent lipid was determined gravimetrically. The samples were then cleaned up using gel permeation chromatography and silica column chromatography.

Details of the sampling and analytical procedures of the air samples are described elsewhere<sup>13</sup>. In short, air samples were taken every 12 days for 24 h at each site using a high-volume air sampler equipped with a quartz fiber filter and an adsorbent to collect the particle- and gas-phase compounds, respectively. The filters and adsorbents were Soxhlet extracted for 24 h with acetone/hexane (1/1). The extract was cleaned up using silica column chromatography. In this study, four samples from 1998, taken during times when the atmospheric temperature averaged  $20^\circ\text{C} \pm 3^\circ\text{C}$ , were selected in order to compare the air concentrations at each location. Prior to analysis, a surrogate standard containing PCB#155 was spiked into the samples.

PBDEs were analyzed using high-resolution gas chromatographic low-resolution mass spectrometry. A Hewlett Packard 6890 series gas chromatograph connected to a HP 5973 mass spectrometer was operated in the electron impact mode with selected ion monitoring. The GC column was a fused silica, DB-5-MS column (30 m  $\times$  250  $\mu\text{m}$  id, 0.25  $\mu\text{m}$  film thickness, J&W Scientific, Folsom, CA). The compounds analyzed are listed in Table 1.  $^{13}\text{C}_{12}$ -2,3,3',4,4',5-hexachlorodiphenyl ether was used to quantitate PBDE-47, and  $^{13}\text{C}_{12}$ -2,2',3,3',4,4',5,5'-octachlorodiphenyl ether was used to quantitate the other congeners. Quantitation was performed

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against an external quantification standard (Cambridge Isotope Laboratories) containing a known amount of the target compounds.

## Results and Discussion

All of our analytes were found in the samples except PBDE-190. The concentrations are given in Table 1. Air concentrations represent the average of 4 measurements at each site; crappie data are the average of three samples; and bluegill data are for a single sample.

**Table 1: PBDE concentration in air and fish. Air concentrations are in  $\text{pg}/\text{m}^3$ ; fish concentrations are in  $\text{ng}/\text{g}$  lipid**

Sample	Location	PBDE	PBDE	PBDE	PBDE	PBDE	PBDE	Total PBDE	Std dev
		47	99	100	153	154	190		
	No. Br	4	5	5	6	6	7		
Air	CH	48	25	3.0	0.66	0.55	ND	77	36
Air	SP	6.2	4.3	0.60	0.27	0.15	ND	12	2.0
Air	SBD	9.2	5.0	0.92	0.28	0.14	ND	16	4.8
Air	EH	3.7	2.6	0.33	0.21	0.11	ND	6.9	2.5
Crappie	HL	250	430	150	340	350	ND	1500	620
Bluegill	HL	420	320	240	450	430	ND	1900	--
Crappie	LO	190	78	59	7.7	8.6	ND	340	37
Bluegill	LO	200	91	59	23	14	ND	390	--

The point source near Hadley Lake (HL) may emit the PBDE technical mixtures DE-71, DE-79, and DE-81. The technical mixture DE-71, obtained from the point source, was analyzed by GC/MS according to the method described above. The congeners in this technical mixture had been previously identified by Bergman et al.<sup>14</sup>. In our measurements, the peak area profile consisted of 27% PBDE-47, 43% PBDE-99, 10% PBDE-100, 8% PBDE-153, and 9% PBDE-154. The congener profiles in the fish from HL have some similarity to that of DE-71, especially the relatively elevated concentrations of PBDE-47 and PBDE-99 compared to PBDE-100. The exception is the elevated concentrations of PBDE-153 and PBDE-154. This could be due to higher bioaccumulation factors for these two, more highly brominated, congeners. Also, an additional source of PBDE-153 could be the technical mixture DE-79, which contains 10-12 % PBDE-153<sup>1,14</sup>.

The fish from the background lake, Lake of the Ozarks (LO), had a congener profile different than the technical mixture and different than the fish from HL. In this case, PBDE-47 was the dominant congener, with a concentration at least twice that of the others. The total PBDE concentrations in the fish from HL were higher than in the fish from LO by a factor of four. The fish from LO were about twice the mass of the fish from HL; therefore, they were most likely older and may have bioaccumulated more PBDEs during their lifetimes. The average lipid percent of the fish from LO was 1.9%, but it was 3.6% for the fish from HL. This may also have led to increased bioaccumulation of PBDE in the fish from LO.

## ORGANOHALOGEN COMPOUNDS

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The air data show considerable spatial variations, with a higher concentration near the heavily populated area of Chicago (CH). The concentration at this site was approximately 5 times higher than at the other sites. Air samples consisted of predominantly PBDE-47 and PBDE-99. The particle and vapor phase concentration of PBDEs were measured separately. Typically, 70% of the total PBDE concentration was in the vapor phase and 30% was in the particle phase. The amount of PBDE on the particles changed with the homologue group. For example, in a single air sample from Chicago, 80% of PBDE-47 was in the vapor phase, but the trend was reversed for PBDE-153, which had only 20% in the vapor phase.

The vapor-particle partitioning of PBDE may explain the difference in congener profiles we observed between HL and LO. Since PBDE-47 is primarily in the atmospheric vapor phase, it could be more susceptible to long-range transport. The penta- and hexa-brominated PBDEs, due to their lower vapor pressure, spend more time on the particle phase. It is likely that these particles cannot move great distances from the source as the vapor phase molecules; thus, the more highly brominated compounds are found only relatively near a source, and the less brominated compounds are found at greater distances from a source.

PBDE-190 was not detected in any of the samples and is not known to be present in DE-71, DE-79, or DE-81. It is important to note that DE-71 is produced globally on a small scale relative to DE-81 (which consists primarily of PBDE-209). Thus, DE-71 alone may not be able to account for the observed environmental concentrations of PBDEs.

## Acknowledgements

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