Polybrominated Diphenyl Ethers in Mississippi River Suspended Sediment

Jonathan Raff[1], Ronald Hites[1]

[1]Indiana University, Bloomington

Introduction

The Mississippi River Basin drains water from 41% of the conterminous U.S. and is a valuable resource that supplies food, transportation, and irrigation to more than 95 million people of the region. Discharge and runoff from industry, agriculture, and population centers have increased the loads of anthropogenic organic compounds in the river. There has been growing concern over the rising levels of polybrominated diphenyl ethers (PBDEs) in air, sediment, biota, and humans, [1] but there have been no studies to measure the concentrations of these chemicals in North America's largest river system. The goal of this study was to investigate the occurrence of PBDEs (15 congeners including BDE-209) and to identify possible sources within the Mississippi River Basin. We found PBDEs to be widespread throughout the region, rivaling PCBs in their extent and magnitude of contamination. We have also calculated the total amount of PBDEs released to the Gulf of Mexico in 2002.

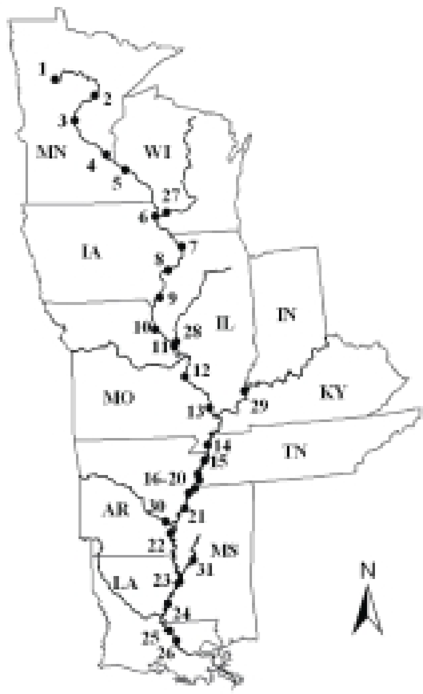

Fig. 1. Map of study area.

Methods and Materials

Sampling. Samples were collected by drawing water through aluminum tubing from a depth of 30 to 50 cm with a submersible pump and passed the water through a 60-mesh stainless steel screen and then through a 293 mm diameter glass fiber filter (Pall-Gelman A/E, 1 µm pore size) that was supported by a stainless steel filter holder. Between 60 and 300 L of water (depending on the concentration of suspended sediment) was filtered into glass vessels of a known volume. Additionally, 1 L of water was collected in a clean 1 L glass bottle to determine the suspended sediment concentration at each site.

Extraction and Cleanup. Each sample (1–30 g of sediment) was extracted was Soxhlet extracted with 1:1 (vol/vol) acetone/hexane for 24 h in the dark, exchanged to hexane, and reduced to a volume of 20 mL via evaporation (RapidVap, Labconco, MO). The remaining aqueous layer was acidified with 0.5 mL of conc. H_2SO_4, separated from the organic layer, and extracted with hexane. The combined organic extract was reduced to a volume of 1 mL under a gentle stream of dry N_2 and loaded onto a column (1.5 cm i.d. × 30 cm length) containing a 6-cm upper layer of anhydrous Na_2SO_4, a 6-cm layer of silica (40% deactivated with conc. H_2SO_4), a 2 cm layer of anhydrous Na_2SO_4, and a 1 cm bottom layer of copper beads (to remove elemental sulfur). The column was eluted with 100 mL each of hexane, 40% dichloromethane in hexane, and dichloromethane. The combined fractions were exchanged to hexane, reduced to a volume of 100 µL under a gentle stream of dry N_2, and transferred to GC autoinjector vials.

Analysis and Quantitation. Extracts were analyzed using an Agilent 5973 gas chromatographic mass spectrometer operating in the electron-capture negative-ionization, selected ion-monitoring mode (ECNI-SIM). Selected ion monitoring (SIM) of the m/z 79 and 81 was used to detect PBDEs. To ensure proper separation of all congeners, samples were analyzed twice: Once using a 60-m DB-5MS column and again on a 15-m column (to analyze BDE-209). The compounds were measured using a quantitation standard with known amounts of all the target compounds, internal standards (PCB-204), and recovery standards ($^{13}C_{10}$-γ-chlordane). Normal QC/QA precautions were followed. The average recovery of the internal standard from all samples (including procedural blanks) was 92 ± 23% (*N* = 37). Spiked recovery experiments showed that BDE-209 did not degrade under the conditions of extraction and sample workup.

Results and Discussion

Suspended sediment (s.s.) samples were collected from 26 sites along the Mississippi River and from 5 of its major tributaries during July 5–August 23, 2002 and March 17–20, 2003, from public access boat ramps and docked ferryboats 3–20 meters offshore. The concentration of total PBDEs (ΣPBDE; the sum of 15 congeners) in suspended sediment (in ng/g s.s.) is listed in Table 1 and shown in Figure 2 as a function of upstream distance. PBDEs were detected in all river samples and in a sample collected from Lake Itasca, MN (the source of the Mississippi River). The average distribution of the six most commonly measured BDE congeners in all (*N* = 31) our samples was 1.16, 1.26,

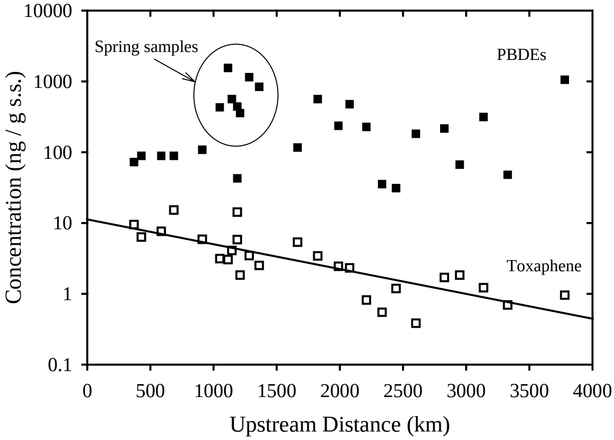

Fig. 2. Concentrations of ΣPBDEs (solid squares) as a function of upstream distance from the Gulf of Mexico. Toxaphene concentrations (open squares) determined from the same samples[4] are included for

0.26, 0.12, 0.11, and 96.8 % for BDE-47, 99, 100, 153, 154, and 209, respectively. This pattern mirrors closely that of previous studies of BDEs in bottom and suspended sediment in European rivers.[2, 3]

Concentrations along the main stem of the river ranged from 37–1053 ng/g s.s. The highest ΣPBDE concentration measured during the summer 2002 was in Lake Itasca, MN (site 1). While there is no major city nearby, this Lake is a popular summer vacation destination (500,000 annual visits). Among the tributaries, a sample from the Illinois River (site 28) showed the highest concentration of PBDEs; the Yazoo River in the state of Mississippi had the lowest concentrations. The Illinois River drains regions of the highly populated Chicago area of northern Illinois, while the Yazoo River drains mostly agricultural areas of low population density. Surprisingly, the Ohio River sample did not contain high relative levels of PBDEs despite large population centers along its length.

It is interesting to compare the concentrations of PBDEs with levels of other organic pollutants found in suspended sediment from the same trip. Pesticides such as toxaphene increase in concentration as the river flows through source areas (the cotton growing regions of the southern U.S.); see Figure 2.[4] However, no distinct concentration-source trend is evident for PBDEs; there is little correlation between PBDE concentrations and potential source areas such as large population areas. The ubiquity of these chemicals reflects their widespread use as flame retardants in commercial and household products that are not necessarily limited to use in urban areas. The variability of the data may also reflect the complexity of the river system. Differences in river bottom profiles, water flow, and sediment suspension/deposition characteristics also contribute to variability in the data.

Nonetheless, there appears to be a seasonal difference in ΣPBDE concentrations. Spring 2003 samples from sites around Memphis, TN were on average 10 times higher than samples collected in the same region of the river in the summer of 2002. In spring, the river discharge almost triples from a summer low due to increased precipitation and snowmelt. The increase in runoff is typically accompanied by a rise in anthropogenic pollutants as they are flushed from sources and enter storm drains and streams. Two of the spring samples collected from sites 15 and 16 had chromatograms that showed signs that BDE-209 had degraded to nona- and octa-brominated congeners. While we were able to detect nona- and octa-brominated congeners at all sites, those samples contained higher concentrations of BDE-206 (as verified by full scan, ECNI mode) than the deca congener. These samples also contained high levels of BDE-196 and 203. The concentrations reported in Table 1 and Figure 2 do not include these octa- and nona-congeners.

From the data presented here, we can provide an estimate of the annual amount of PBDEs discharged into the Gulf of Mexico by the Mississippi River. Based on ΣPBDE concentrations at sites 25 and 26 from Figure 2 (~90 ng/g s.s.), the average annual suspended sediment concentration measured by the USGS (NASQAN) for the year 2002 at St. Francisville, LA (190 mg/L),[5] and the annual discharge of water at Tarbert's Landing, MS obtained by integrating the average daily discharge over the year 2002 (4.7×10^{14} L/year),[6] we estimate that ~8 tons/year of BDEs were discharged into the Gulf of Mexico in 2002. This is comparable to a PCB load of 6.8 tons/year as determined by Rostad *et al.* in their 1989–1990 study.[7]

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References

1 Hites R.A. (2004) Environ. Sci. Technol. 38, 945.
2 de Boer J., Wester P.G., van der Horst A., and Leonards, P.E.G. (2003) Environ. Pollut. 122, 63.
3 Sellström U., Kierkegaard A., de Wit C., and Jansson B. (1998) Environ. Toxicol. Chem., 17, 1065.
4 Raff J. D. and Hites R. A. (2004) Environ. Sci. Technol., 38, in press.
5 Kelly V.J. The USGS National Stream Water Quality Network (NASQAN) published data for the Mississippi Basin (1996-2002): http://water.usgs.gov/nasqan/data/finaldata/miss.html, Accessed April 19, 2004.
6 Data are available from the water control pages of U.S. Army Corps of Engineers: http://www.mvd.usace.army.mil/main.php, Accessed April 19, 2004.
7 Rostad C.E., Pereira W.E., and Leiker T.J. (1999) Arch. Environ. Contam. Toxicol., 36, 248.

Tab. 1. Sampling Sites and Dates, River Location (*d*, in km), and ΣPBDE concentrations (in ng/g s.s.)

No.	Sampling Site	Date	River	*d*	ΣBDEs
1	L. Itasca, MN	8/5/02	Mississippi	3780	1053
2	Palisade, MN	8/6/02	Mississippi	3328	48
3	Little Falls, MN	8/4/02	Mississippi	3137	314
4	Minneapolis, MN	8/7/02	Mississippi	2949	67
5	Lake City, MN	8/8/02	Mississippi	2827	215
6	Prarie Du Chein, WI	8/9/02	Mississippi	2602	182
7	Savannah, IL	8/10/02	Mississippi	2445	31
8	Andalucia, IL	8/11/02	Mississippi	2334	35
9	Dallas City, IL	7/5/02	Mississippi	2210	228
10	Hannibal, MO	7/5/02	Mississippi	2077	476
11	Red Landing, IL	7/6/02	Mississippi	1988	237
12	Herculaneum, MO	7/7/02	Mississippi	1824	561
13	Cape Girardeau, MO	8/17/02	Mississippi	1665	116
14	Caruthersville, MO	3/17/03	Mississippi	1362	838
15	Ashport, TN	3/18/03	Mississippi	1282	1146
16	Shelby Forest, TN	3/18/03	Mississippi	1210	356
17	Memphis, TN	3/19/03	Mississippi	1188	441
18	Memphis, TN	8/24/02	Mississippi	1188	43
19	Norfolk, MS	3/19/03	Mississippi	1144	562
20	Peters, AR	3/20/03	Mississippi	1114	1548
21	Friars Point, MS	3/20/03	Mississippi	1049	430
22	Arkansas City, AR	8/20/02	Mississippi	911	108
23	Le Tourneau, MS	8/22/02	Mississippi	686	89
24	Natchez, MS	8/22/02	Mississippi	586	89
25	St. Francisville, LA	8/23/02	Mississippi	428	89
26	Baton Rouge, LA	8/23/02	Mississippi	370	72
27	Boscobel, WI	8/10/02	Wisconsin	2595	45
28	Kampsville, IL	7/6/02	Illinois	1930	393
29	Old Shawneetown, IL	8/16/02	Ohio	1580	91
30	Pendelton, AR	8/18/02	Arkansas	935	220
31	Yazoo City, MS	8/21/02	Yazoo	703	29