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Partitioning and Bioaccumulation of PBDEs and PCBs in Lake Michigan†

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Water from Lake Michigan and fish from all five Great Lakes have been sampled and analyzed for a suite of six polybrominated diphenyl ether (PBDE) congeners and 110 polychlorinated biphenyl congeners (PCBs). The Lake Michigan dissolved phase PBDE congener concentrations (0.2 to 10 pg/L) are similar to dissolved phase PCB congener concentrations (nondetected to 13 pg/L). Partitioning of PBDEs between the particulate and dissolved phases exhibits behavior similar to that of PCBs. Organic-carbon-normalized water−particle partition coefficients (log K_{OC}s) ranged from 6.2 to 6.5. Lake trout are depleted in BDE-99 relative to dissolved phase concentrations, and in contrast to what is expected from the PCB congener patterns. This reflects suspected debromination of BDE-99 in the food web of Lake Michigan. A regression of the log of the bioaccumulation factor (BAF) and the log of the octanol−water partition coefficent (K_{OW}) indicated a positive relationship for both PCB congeners and PBDE congeners. BDE-99 does not appear to follow the same trend, a further indication that it is subject to biotransformation. Using the PBDE BAFs for Lake Michigan and the PBDE fish concentrations from the other Great Lakes it is expected that the dissolved phase concentrations of congeners in the other lakes would range from 0.04 to approximately 3 pg/L.

Introduction

Polybrominated diphenyl ethers (PBDEs) are currently used as additives to retard or prevent combustion in many commercial products including plastics, foam products, textiles, and printed circuit boards (*1*). Although production of the penta- and octa-BDE products has been largely phased out in North America and Europe (*2*), PBDEs are still present in consumer products (*2*). PBDEs can enter the environment through a number of pathways including atmospheric emissions during manufacture, recycling of wastes containing PBDEs, volatilization from consumer products, and leaching from disposal sites (*3*). Once in the environment, their physical−chemical properties predict that they would undergo long-range atmospheric transport to even remote regions of the world (*4*). PBDEs may exhibit toxicity to wildlife and humans through various mechanisms including neurobehavioral development, thyroid hormone levels, fetal toxicity/teratogenicity, and liver and kidney morphology (*5*). As a result of their historic and continued use, tendency for long-range atmospheric transport, and hydrophobicity, they have been found in many environmental media and throughout the globe, including the Great Lakes. To date, PBDEs have been reported in air (*6*), fish (*7*, *8*), and sediments (*9*) of many of the Great Lakes and throughout North America (*10*).

The dominant exposure pathways to humans are expected to be through the inhalation of house dust (*11*) and through the consumption of contaminated fish (*3*). This concern has led to a number of studies that have investigated the bioaccumulation and potential for biomagnification of PBDEs in several fish species in the laboratory including carp (*12*), rainbow trout (*13*), zebra fish (*14*), pike (*15*), and lake trout (*16*). Although several field studies of biomagnification in aquatic food webs (*15*, *17*−*20*) have been reported, none of these measured PBDEs in water. Burreau et al. (*21*) investigated the concentration of PBDEs in various trophic levels as defined by δ^{15}N, and Alaee et al. (*17*) investigated biomagnification in the Lake Ontario pelagic foodweb. None of these studies measured PBDEs in water. In fact, very few data for water concentrations have been reported in the literature thus far (*10*, *22*). To best compare fish concentration data among different water bodies or to develop models of PBDE fate, transport, and bioaccumulation, it is necessary to know the bioaccumulation factor (BAF), which we define as the field-observed ratio of the fish concentration of a given compound to the water concentration, expressed in equivalent units. The objective of this study was to calculate BAFs from measured concentrations of a suite of PBDEs in fish and dissolved water samples from Lake Michigan. These data were used to further investigate the potential for biotransformation of PBDE congeners in the foodweb, explore the water−particle partitioning behavior of PBDE congeners, and estimate the dissolved phase concentrations of the other Great Lakes. This paper provides the first reported bioaccumulation factors for PBDEs in an aquatic foodweb.

Materials and Methods

Field Sampling. Water was sampled during April and July, 2004 aboard the US Environmental Protection Agency's (USEPA's) R/V *Lake Guardian* at five locations along the north−south transect of Lake Michigan (Figure 1). This sampling was conducted as part of the USEPA's Great Lakes Aquatic Contaminant Survey (GLACS) water monitoring program. Surface water samples from all five sites were collected in April and samples from sites 6 and 27 were collected in July for a total of 7 samples.

Fish were collected as part of the Great Lakes Fish Monitoring Program (GLFMP) during 2000, 2001, and 2002. The GLFMP has monitored the time trends of certain contaminants in lake trout since the 1970s (*23*−*25*), and recently added PBDEs to the list of monitored contaminants. Lake trout of standard size (600−700 mm) were collected from master sites in each lake (walleye of 500−600 mm were collected in Lake Erie, and are not discussed further). The fish from 2000 and 2002 were collected from the Apostle Islands National Lakeshore in Lake Superior, off Saugatuck in Lake Michigan, off of Rockport in Lake Huron, and off of Oswego in Lake Ontario. The fish from 2001 were collected off Keweenaw Point in Lake Superior, from Sturgeon Bay in Lake Michigan, off of Port Austin in Lake Huron, and off of North Hamlin in Lake Ontario.

Water was sampled via submersible pump from a depth of 5 m below the surface using methods described by Pearson et al. (*26*). Approximately 800 L of water was pumped through

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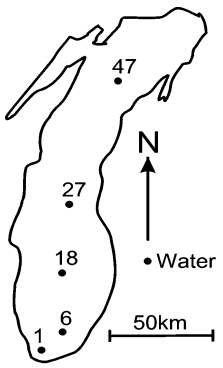

FIGURE 1. Lake Michigan water sampling sites.

five glass fiber filters (Whatman 293 mm GF/F, Florham Park, NJ) in parallel and into four 125-L, covered, stainless steel holding tanks. It was subsequently passed through a glass column (5 cm × 30 cm) filled with pre-cleaned XAD-2 microreticular resin (Supelco, Bellefonte, PA). Resin was pre-cleaned with a four solvent sequential extraction following the procedure of Achman et al. (*27*). After sampling, the XAD was transferred with methanol to pre-cleaned (combusted at 450 °C) amber jars and stored at 4 °C until extraction. This water-sampling procedure has been widely used by this lab as well as in past studies (*26*).

Fifty whole lake trout were ground and combined into 10 homogeneous, equally weighted composites of five fish each. There were a total of 10 composites per lake per year. All composites were frozen until analysis.

Fish Extraction and Cleanup. Fish composites (approximately 3.5 g wet weight) were mixed with 30 g of ashed anhydrous sodium sulfate and extracted in a Soxhlet apparatus with acetone for 4 h followed by dichloromethane for 18 h. The acetone extract was exchanged to hexane and reduced to approximately 2 mL. Surrogate standards (compounds having structures similar to those of the analytes of interest, but not found in the environment) were added to the sample prior to extraction to measure losses due to sample processing. Surrogate compounds for PCBs were added to all samples and blanks and included 15 ng of PCB-65 (2,3,5,6-tetrachlorobiphenyl) and 10 ng of PCB-188 (2,2′,3,4,5,6,6′-heptachlorobiphenyl). These were chosen because they are not present in technical PCB mixtures and have not been identified in the environment. No authentic surrogate compounds for PBDEs were used (see QA/QC section below; no PBDE surrogates were used due a delay in availability at that time from the manufacturer).

The acetone fraction was reduced in volume, combined with the dichloromethane fraction, solvent exchanged to hexane, and reduced to approximately 2 mL.

Fish lipids were removed by passing the extract through a column (1 × 50 cm) containing 1 g of ashed sodium sulfate, 15 g of 10% deactivated neutral alumina, and topped with 1 g of ashed sodium sulfate that was rinsed with 3 × 50 mL of hexane. The sample was eluted with 3 × 50 mL hexane and reduced in volume to approximately 2 mL. This method removes all lipid in a 4 g wet weight sample of lake trout.

The extract was then passed through a column (1 × 50 cm) containing 1 g of ashed sodium sulfate, 6 g of 2% deactivated neutral alumina, 1 g of ashed sodium sulfate, 4.5 g of 0% deactivated silica, and topped with 3 g of ashed sodium sulfate. The columns were rinsed before use with 3 × 33 mL of 15% DCM/hexane, 3 × 33 mL of 40% DCM/hexane, and 3 × 40 mL of 100% hexane. The extracts were quantitatively transferred to the column and eluted with 3 × 33 mLof hexane (F1). The F1 fraction contained the PCBs and nonaromatic hydrocarbons. The column was then eluted with 3 × 33 mL of 40% DCM in hexane (F2). This fraction (F2) contained PBDEs and other more polar analytes of interest outside the scope of this study. Both fractions were reduced to approximately 2 mL. The internal standard, PCB 204 (2,2′3,4,4′,5,6,6′-octachlorobiphenyl), was added to F1. The F1 fraction was analyzed for PCBs, and then recombined with the F2 fraction to analyze for PBDEs.

Water Sample Extraction and Cleanup. The XAD-2 resin was transferred to a Soxhlet extractor apparatus and extracted for 4 h with methanol. The methanol was removed to a separatory funnel, and 150 mL of NaCl saturated organic free water was added. This was extracted with 3 × 50 mL of hexane. These hexane fractions were combined and held until the final XAD-2 extract was complete. The Soxhlet extractor containing the XAD was then spiked with surrogate standards (PCB 65 and PCB 188) and extracted with dichloromethane for 24 h. The extract was combined with the hexane extract and reduced to approximately 1 mL.

The water extracts underwent the same column chromatographic separation described above for the fish extracts to remove interferences.

Instrumental Analysis. Six PBDE congeners (BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, and BDE-154) were analyzed by gas chromatography/mass spectrometry in electron capture negative ionization mode (GC/MS−ECNI) equipped with a 60 m DB-5 capillary column, helium carrier gas, and methane reaction gas. The GC/MS was operated in selective ion monitoring mode for the bromine ions m/z 79 and 81, and for the internal standard using m/z 428 and 430. The GC temperature program was as follows: 110 °C for 1.90 min, 15 °C/min to 210 °C, 2 °C/min to 270 °C, 5 °C/min to 305 °C, and held at 305 °C for 20 min. Peak areas for quantitation and confirmation m/z from the ion chromatograms were integrated and were checked for acceptable ratios and retention times based on standards of known congeners. Analyte concentrations were determined by internal standard method using PCB 204 as the internal standard. This method is used to correct for injection error, but is not used to correct for losses during sample preparation and analysis.

PCB congeners (110 chromatographic peaks containing individual or groups of coeluting congeners) were analyzed by a Hewlett-Packard 5890 gas chromatograph equipped with a ^{63}Ni electron capture detector, 60 m DB-5 column (J&W Scientific, Folsom, CA), and HP ChemStation data acquisition software. The method is described elsewhere (*26*). Operating conditions of the GC were as follows: splitless mode with 1 μL sample injections, injection port 225 °C, detector 325 °C, variable oven temperature program from 100 to 280 °C over 2 h. The carrier gas was hydrogen and the makeup gas was 5% methane/95% argon. Chromatograms were carefully reviewed and baselines were set manually to ensure correct peak identification and quantitation. PCB congeners were identified based on column retention time relative to the calibration standard and quantified by the internal standard method.

Particulate organic carbon (POC) was determined by passing a known volume of water through ashed 47-mm glass fiber filters with a 0.7-μm nominal pore size and drying at 100 °C to constant weight. POC was measured by combustion of the dry filters using a Costech Analytical Elemental Combustion System (ECS) 4010. Complete operating procedures can be found on the USEPA Great Lakes National Program Office (GLNPO) website (*28*).

Quality Assurance/Quality Control. A rigorous quality assurance program was employed to ensure the quality of the data presented in this study (Quality Assurance Project Plans for both fish and water collection and analysis were approved by the USEPA Great Lakes National Program Office), including the addition of surrogate standards to quantify analytical recovery (PCBs only), field and procedural blanks

TABLE 1. Mean (Standard Error) PBDE Congener Concentrations and Total PCBs in Lake Michigan Water (pg/L) and Great Lakes Lake Trout (ng/g ww)

	n[c]	BDE−47	BDE−66	BDE−99	BDE−100	BDE−153	BDE−154	ΣPBDEs	ΣPCBs
Lake Michigan									
water, dissolved phase	7	10 (1.4)	0.13 (0.05)	6.1 (0.91)	1.3 (0.15)	nd[d]	nd[d]	18 (1.8)	$1.5 \times 10^{+2}$ (11)
water, particulate phase	6	1.3 (0.29)	nd[d]	1.4 (0.27)	0.18 (0.11)	nd[d]	nd[d]	3.1 (0.29)	28 (3.3)
SPM[a] = 0.47 (0.02) mg/L	10								
OC[b] = 0.21 (0.004)	10								
lake trout 2000	10	$2.3 \times 10^{+2}$ (26)	3.7 (0.44)	48 (5.1)	45 (4.1)	11 (1.3)	19 (2.2)	$3.5 \times 10^{+2}$ (27)	$1.6 \times 10^{+3}$ (15)
lake trout 2001	4	93 (15)	2.0 (0.50)	9.0 (1.0)	12 (1.0)	1.0 (0)	2.0 (0.50)	$1.2 \times 10^{+2}$ (18)	$1.8 \times 10^{+3}$ ($3.6 \times 10^{+2}$)
lake trout 2002	6	$2.1 \times 10^{+2}$ (44)	3.9 (0.65)	30 (4.9)	39 (7.7)	2.2 (0.36)	4.2 (1.4)	$2.9 \times 10^{+2}$ (33)	$1.9 \times 10^{+3}$ ($1.3 \times 10^{+2}$)
Lake Superior									
lake trout 2000	10	79 (6.6)	3.9 (0.47)	53 (4.4)	19 (1.4)	8.8 (0.98)	16 (1.3)	$1.8 \times 10^{+2}$ (9.5)	$7.8 \times 10^{+2}$ (23)
lake trout 2001	3	22 (6.3)	1.5 (0.54)	8.5 (3.2)	5.2 (1.7)	0.65 (0.08)	1.4 (0.49)	39 (4.7)	$2.9 \times 10^{+2}$ (78)
lake trout 2002	10	44 (5.4)	1.7 (0.18)	26 (4.1)	12 (1.2)	1.9 (0.28)	1.9 (0.25)	87 (5.4)	$8.9 \times 10^{+2}$ (53)
Lake Huron									
lake trout 1999	10	32 (2.4)	0.7 (0.08)	7.8 (0.70)	6.5 (0.60)	1.4 (0.14)	2.0 (0.28)	50 (3.8)	$9.2 \times 10^{+2}$ (44)
lake trout 2000	10	59 (4.1)	1.0 (0.21)	13 (0.54)	12 (0.92)	2.1 (0.25)	7.1 (0.44)	94 (6.9)	$7.8 \times 10^{+2}$ (17)
lake trout 2001	6	34 (4.5)	1.0 (0.41)	9.0 (2.4)	7.0 (1.2)	2.0 (0.41)	2.0 (0.41)	55 (5.3)	$1.1 \times 10^{+3}$ (68)
lake trout 2002	10	40 (4.7)	1.2 (0.14)	8.5 (1.2)	8.2 (1.1)	1.9 (0.23)	2.7 (0.14)	63 (4.7)	$9.1 \times 10^{+2}$ (26)
Lake Ontario									
lake trout 2000	10	$1.4 \times 10^{+2}$ (12)	2.4 (0.22)	34 (4.1)	24 (2.9)	10 (0.85)	13 (1.5)	$2.3 \times 10^{+2}$ (17)	$1.2 \times 10^{+3}$ (19)
lake trout 2001	5	45 (8.0)	1.2 (0.25)	6.5 (0.25)	7.7 (1.8)	1.1 (0.34)	2.3 (0.58)	64 (7.6)	$9.9 \times 10^{+2}$ ($1.3 \times 10^{+2}$)
lake trout 2002	8	55 (7.8)	0.74 (0.17)	8.3 (1.6)	8.8 (1.6)	1.9 (0.71)	6.2 (2.1)	81 (7.4)	$1.2 \times 10^{+3}$ ($1.2 \times 10^{+2}$)

[a] Suspended particulate matter, mean (standard error). [b] Fraction of organic carbon of particulate matter, mean (standard error). [c] Number of samples analyzed; water was individual samples and fish were composites of 5 fish each. [d] Values below the detection limit.

to assess contamination, replicate samples to assess precision, and spiked media to quantify accuracy.

The mean PCB surrogate recoveries (±standard error) for all Lake Michigan water samples were 85 ± 6.4% and 98 ± 9.3% for PCB-65 and PCB-188, respectively. The mean PCB surrogate recoveries (±standard deviation) for Great Lakes fish composite samples were 76 ± 1.0% and 76 ± 1.3% for PCB-65 and PCB-188, respectively. While no PBDE surrogate recoveries are available for these samples (there was a delay in availability from the manufacturer at the time of extractions), the acceptable and consistent recovery of PCB surrogates and the similarity in physical−chemical properties between PCBs and PBDEs suggests to us that the PBDE data are acceptable. Surrogate recoveries (±standard error) in 7 lake trout composites (after surrogates became available) gave 85% (8.8%) and 77% (4.4%) recovery, respectively, for BDE-77 and BDE-118. Also, subsequent analysis of PBDEs in procedural spike samples (procedural blanks, see below, that are spiked with the PBDE congeners of interest at concentrations similar to samples) gave a mean recovery of the 6 congeners of interest of 102 ± 5% (standard error).

Response factors of the internal standard, PCB-204, and the relative responses to the analytes of interest were monitored over time to ensure consistency across analyses.

Field blanks and procedural blanks for XAD-2 resin and GF/F filters were used to determine sample contamination during collection and laboratory analysis. Field blanks for XAD-2 were collected by bringing pre-cleaned XAD-2 into the field, constructing a column as if preparing for sample collection, then transferring the clean XAD-2 to an ashed amber jar in the same method used for samples. The GF/F field blanks were collected by placing ashed GF/F filters in the filter head as if preparing for sample collection, and then removing the filters to ashed aluminum foil and storing in the same manner as the samples. Procedural blanks (same quantity and type of solvents used in sample extractions carried through the entire procedure but without any sample) were extracted and analyzed with every sample set. PCB surrogates were added to every blank to determine analytical recovery. Field and procedural blanks contained 16 ± 7 ng ($n = 4$; mean ± standard error) of total PCBs and 0.77 ± 0.16 ng ($n = 6$) of PBDEs (consisting of BDE-47 = 0.38 ± 0.08, BDE-99 = 0.45 ± 0.08, and BDE-100 = 0.13 ± 0.02 ng; other congeners were not detected). This corresponds to approximately 20 pg/L total PCBs and 0.48, 0.56, and 0.16 pg/L of BDE-47, -99, and -100 in a theoretical 800 L sample. We did not subtract the mass in blanks from that in samples for the quantification of samples because the actual volume sampled varied among samples. The particulate sample from July, site 27, was omitted from data analysis as it was similar to the field blank values for PBDEs. PCB congeners 1, 85, 163 + 138, and 132 + 105 were consistently high in all blanks and were omitted in sample calculations. Solvent blanks (equivalent volumes of solvent used for a sample that is reduced down to a final volume of a sample and analyzed without any Soxhlet extraction or cleanup column) contained no measurable PCBs or PBDEs. All procedural blanks for fish were less than detection limits.

Recoveries of surrogate PCBs in matrix spikes (clean XAD-2 resin spiked with surrogate compounds at the same concentrations as for samples and extracted and processed in the same manner as samples) were 91 ± 3% (mean ± standard error) for PCB-65 and 111 ± 4% for PCB-188.

Duplicate samples (10 g each) of contaminated reference fish material (EDF-2525; Cambridge Isotope Laboratories, Andover, MA) were analyzed for PBDE congeners in a similar manner as the fish from this study. Recoveries were within one standard deviation of assigned certified reference values and considered acceptable. Mean surrogate recovery ± standard error (approximately 40 ng each of BDEs 71, 118, 166) for these samples was 108 ± 25%.

Results and Discussion

Water. Concentrations of four PBDE congeners were consistently found in dissolved water samples. They include BDE-47, BDE-66, BDE-99, and BDE-100. The dissolved phase water concentrations of individual congeners ranged from 0.13 to 10 pg/L (Table 1). The dominant congeners were BDE-47 and BDE-99, followed by BDE-100, followed by BDE-66. These concentrations are similar to those for individual PCB congeners (nondetect to 22 pg/L) measured in these samples.

Three PBDE congeners (BDE-47, BDE-99, and BDE-100) were found in the particulate phase. The individual congener

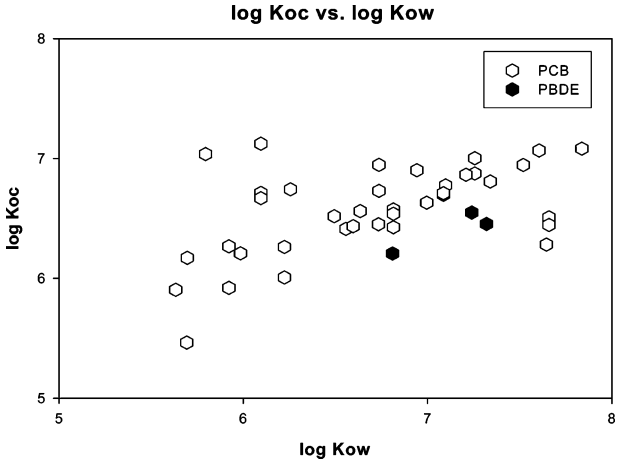

FIGURE 2. log K_{OC} vs log K_{OW} for PCB (open hexagons) and PBDE (closed hexagons) congeners. Note: log K_{OW} values are taken from Sabljic et al. (*33*) for PCBs and from Braekevelt et al. (*34*) for PBDEs.

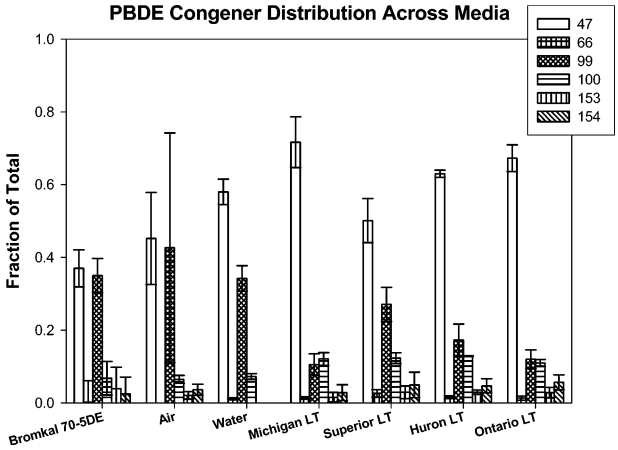

FIGURE 3. PBDE congener distribution as a fraction of total PBDEs in Lake Michigan air, water, and lake trout. Congener distributions for lake trout in lakes Superior, Huron, and Ontario are included. Congener composition of Bromkal 70-5DE was taken from Sjodin et al. (*35*). Air data were taken from Strandberg et al. (*6*).

concentrations ranged from 0.18 to 1.4 pg/L (Table 1). Hale et al. (*10*) reported total PBDE concentrations in Lake Michigan water as 31 to 158 pg/L, which are on the same order of magnitude as reported here (~18 ng/L). However, it is not clear whether the numbers reported in Hale et al. (*10*) are for dissolved phase only, or both dissolved and particulate phases. Note that while PBDE and PCB congener specific concentrations were similar, total PBDE concentrations are much less than total PCBs (Table 1) because of the number of congeners comprising the total mixture.

Partitioning. Partitioning of PBDEs between the dissolved and particulate phases exhibits behavior similar to that of PCBs (Figure 2). The organic-carbon-normalized water−particle partition coefficients (K_{OC}s) were determined by calculating the water−particle partition coefficients (K_p) and normalizing to the fraction of organic carbon of the total particulate:

$$K_p = \frac{C_{w,p}(\text{pg/L})/\text{SPM}(\text{mg/L})}{C_{w,d}(\text{pg/L})} \quad (1)$$

$$K_{OC} = \frac{K_p}{OC} \quad (2)$$

where $C_{w,p}$ is the contaminant concentration in the particulate phase; SPM is the total suspended particulate matter; $C_{w,d}$ is the contaminant concentration in the dissolved phase; and OC is the fraction of organic carbon (mass organic carbon/mass of total particulate). The mean log K_{OC}s (and standard errors) for PBDEs in Lake Michigan were 6.2 ± 0.08, 6.5 ± 0.04, and 6.4 ± 0.04 for BDE-47, BDE-99, and BDE-100, respectively. BDE-66 was not detected in the particulate phase. If partitioning between particulate and dissolved phases was in equilibrium, the organic-carbon-normalized water−particle partition coefficient (K_{OC}) and the octanol−water partition coefficient (K_{OW}) would exhibit a positive relationship with a slope of 1. There is no correlation between log K_{OC} and log K_{OW} (Figure 2; $r^2 = 0.12$, $p < 0.03$). This trend has been seen in a number of studies (*26*, *29*−*31*) and has been explained by several researchers (*26*, *29*, *32*) as due to possible partitioning to a colloidal "third" phase, or a lack of equilibrium of the contaminant between the dissolved and particulate phases.

Fish. Concentrations of six PBDE congeners were routinely found in fish samples. They include BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, and BDE-154. PBDE congener concentrations range from <1.0 to 230 ng/g wet weight in whole lake trout (Table 1). Concentrations of the PBDE congeners were in the relative order 47 > 100−99 > 153−154 > 66 in all lakes. Concentrations were greatest in lake trout from Lake Michigan, followed by those from Lake Ontario, Lake Superior, and Lake Huron. We also analyzed lake trout composites from Lake Huron collected in 1999, and there were no differences in concentrations between years. These data are comparable to those reported for fish (*8*) from the other Great Lakes.

Distribution and Biotransformation. The relative congener composition among various media is expected to elucidate source and/or biotransformation information. Figure 3 represents the PBDE congener distribution as a fraction of the total PBDEs for Lake Michigan air (*6*), lake trout, and water, along with lake trout from the other Great Lakes. The composition of a common PBDE technical mixture is included for comparison (*35*). The PBDE congener composition in Lake Michigan water is very similar to that for the overlying air, supporting the hypothesis that the atmosphere is a major source of PBDEs to the lake. It is expected that Lake Superior also receives PBDEs from atmospheric deposition with negligible contributions from point sources (*8*).

The ratio of BDE-99 to BDE-47 in lake trout in Lake Superior is about 3:5, while the ratio for lake trout from the other Great Lakes is about 1:5. This difference may be explained by the difference in lake temperatures—at the lower temperatures of Lake Superior, sorption of heavier PBDEs may be able to come closer to equilibrium conditions for phytoplankton because of their longer lifetimes in colder water, resulting in a greater proportion of heavier PBDEs in phytoplankton and the rest of the food chain (*36*). PCBs from the same lake trout show a similar enhancement (PCB 99/PCB 47 ratios of about 9:1 for lake trout from Lake Superior, but 7:2 for all other lakes) that is consistent with predictions based on a previous model (*36*).

The PBDE ratios are lower than expected, showing possible evidence of biotransformation of BDE-99. The expected behavior of PBDEs 47 and 99 can be estimated from the behavior of PCBs 47 and 99, because PCB and PBDE congeners 47 and 99 have physical properties that scale similarly to each other. The program Epi Suite (USEPA) estimated that BDE-99 has a K_{OW} about 8 times greater than that of BDE-47, and PCB 99 has a measured K_{OW} about 8 times greater than that of PCB 47 (estimates indicate PCB 99 has a K_{OW} 5 times greater than PCB 47). Likewise, the estimated Henry's law constant for BDE-99 is only about 40% of the estimated Henry's law constant for BDE-47, and

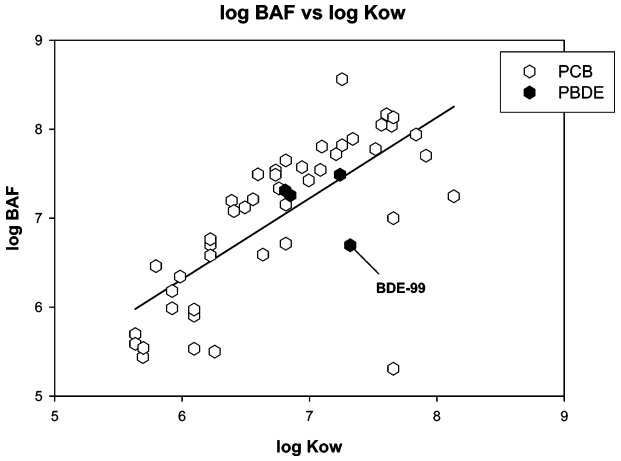

FIGURE 4. log BAF vs log K_{OW} for PCB (open hexagons) and PBDE (closed hexagons) congeners. Note: log K_{OW} values are taken from Sabljic et al. (*33*) for PCBs and from Braekevelt et al. (*34*) for PBDEs.

PCB 99 has a measured Henry's law constant that is about 41% that of PCB 47 (estimates indicate PCB 99 has a Henry's law constant that is about 70% that of PCB 47).

Because the physical properties of PCBs and PBDEs scale in a similar fashion, we expect PCBs and PBDEs to partition from the air to the lake and enter the food chain in a similar fashion. The PCB air data for the Great Lakes show an average PCB 99/PCB 47 ratio of about 3:2 (R.A. Hites, personal communication). The PBDE air data show a ratio of about 1:1 for BDE-99 and BDE-47 (*6*). Because the ratio of PCB 99/PCB 47 in lake trout is about 7:2 for most Great Lakes, and 9:1 for Lake Superior, the ratio of BDE-99/BDE-47 in lake trout would be expected to be around 2:1 for most Great Lakes, and 6:1 in Lake Superior (the difference being ascribed to the effect of lake temperature on partitioning, as mentioned above). However, this is far from the case; Figure 3 shows far more BDE-47 than BDE-99 is observed in lake trout.

We calculate that the amount of BDE-99 found in lake trout is about 5−15% of what we expect based on PCB behavior. Figure 3 and Table 1 show a relative decrease of BDE-99 in Lake Michigan water compared to air, but a similar decrease is also observed for PCBs (*34*), and is therefore already taken into account with our estimates. Because we see a similar enhancement of both PCB and BDE 99 compared to PCB and BDE 47 in Lake Superior (an enhancement postulated to result from the water/phytoplankton sorption step) we conclude that the majority of BDE loss (compared to expected values) must occur in the food chain where biotransformation of BDE-99 is known to occur (*16*, *37*). Stapleton et al. (*37*) demonstrated in laboratory experiments that carp are able to debrominate BDE-99 to BDE-47. Results there indicated a 10% conversion of BDE-99 to BDE-47.

Bioaccumulation Factors. Bioaccumulation factors (BAFs) are defined as the observed ratio of fish tissue concentration to dissolved water concentration expressed in equivalent units

$$\text{BAF} = \frac{\text{pg/kg wet weight}}{\text{pg/L}} \quad (3)$$

Log BAFs for PCBs ranged from 5.5 to 8.5 for whole lake trout and showed a significant positive relationship of log BAF vs log K_{OW} (Figure 4; $p < 0.01$). The best fit of the line is

$$\text{Log BAF} = 0.91 \log K_{OW} + 0.87 \quad r^2 = 0.51 \quad (4)$$

Log BAFs of PBDE congeners ranged from 6.7 to 7.5 for whole lake trout (Table 2). The low levels of dissolved organic carbon (DOC) in the Great Lakes preclude the need to adjust these BAF calculations (*38*). PBDEs exhibit behavior similar to that of PCBs, with the exception of BDE-99 which has a lower BAF (Figure 4). This further supports the conclusion that BDE-99 undergoes debromination, as a theoretical 1:1 ratio is expected based on the assumption that no transformations are occurring (*39*). A significant relationship between biomagnification potential and log K_{OW} was reported by others such as Burreau et al. (*21*) who observed biomagnification of PBDEs in fish from the Baltic Sea. The authors found that biomagnification reached a maximum with penta-BDEs. This is consistent with our data, as the congeners that we report in Lake Michigan lake trout are tetra-, penta-, and hexa-brominated diphenyl ethers which coincide with the reported maxima of Burreau et al. (*21*).

TABLE 2. Mean log Bioaccumulation Factors (BAFs) (Standard Error) of PBDE Congeners for Lake Michigan Lake Trout

congener	log BAF
BDE-47	7.3 (0.42)
BDE-66	7.3 (0.60)
BDE-99	6.7 (0.08)
BDE-100	7.5 (0.57)

TABLE 3. Calculated PCB log BAF for Great Lakes Lake Trout (*23*−*25*) and Water (*41*) from 1991 to 2000

Lake	log BAF (average)	sd	*n*[a]
Michigan	6.9	0.23	86
Huron	6.7	0.22	30
Ontario	7.1	0.07	11
Superior	7.0	0.26	22

[a] Number of fish−water data pairs. Multiple composite fish samples for a given lake were compared to one or two average lake water concentrations sampled the same year.

These data were also used to estimate the concentrations of PBDEs in the dissolved phase in the other Great Lakes, assuming that the similar foodweb lengths across the lakes would lead to similar BAFs in lake trout. Lake trout occupy a trophic position of 4.38 ± 0.02 in the Great Lakes (*40*). Because the trophic position is constant across the Great Lakes, the BAFs calculated for Lake Michigan should be applicable to the other Great Lakes. To test this idea, the BAFs for total PCBs were also calculated (Table 3). When the PCB BAF from Lake Michigan was used with the fish concentrations in other lakes to predict the concentrations of total PCBs in water, the resulting predictions were within a factor of 2 of the measured concentrations in 52 of 63 cases. Applying this method to Lake Superior for individual congeners, however, may underestimate concentrations for the most chlorinated PCBs or the most brominated PBDEs by a factor of 2−3 because of lake temperature effects on partitioning to phytoplankton (*36*). Predicted PBDE congener concentrations range from 0.04 to 2.7 pg/L in the other lakes in the order Lake Ontario > Lake Huron > Lake Superior (Table 4).

These estimates were obtained by setting congener-specific BAFs for Lake Michigan equal to the BAFs for the other Great Lakes, and then rearranging to solve for the PBDE dissolved phase concentration of the other lakes.

$$\frac{\text{pg/kg wet weight}}{\text{pg/L}}\text{Lake Michigan} = \frac{\text{pg/kg wet weight}}{\text{pg/L}}\text{other Great Lake} \quad (5)$$

TABLE 4. Estimated Dissolved Phase Concentrations (pg/L) of PBDEs (Estimated Standard Deviation) in Other Great Lakes

Congener	Superior	Huron	Ontario
47	1.0 (0.8)	2.0 (1.2)	2.7 (1.6)
66	0.08 (0.09)	0.07 (0.06)	0.04 (0.04)
99	1.7 (1.5)	1.7 (1.0)	1.8 (1.1)
100	0.2 (0.1)	0.3 (0.2)	0.3 (0.2)

Lake trout from 2002 were used to estimate dissolved phase concentrations for lakes Huron and Ontario. Lake trout from 2001 were used to estimate PBDE concentrations in Lake Superior because the fish collected in 2002 from the Apostle Islands may have different and longer foodwebs than lake trout from the Keweenaw Peninsula (*36*). It is important to note that these are first-order estimates based on a number of assumptions and with great uncertainty; they are to provide some idea of the range of concentrations that might be found.

In recent years PBDEs have emerged as a contaminant of concern potentially affecting the health of both humans and wildlife. To date, very few data have been reported regarding PBDEs in water, and this paper provides the first reported bioaccumulation factors of PBDEs in an aquatic foodweb. BAFs can be used to compare fish concentrations among different bodies of water, develop models of fate and transport, and estimate human dietary exposure to PBDEs related to the consumption of contaminated fish.

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Literature Cited

(1) Alaee, M.; Arias, P.; Sjodin, A.; Bergman, A. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ. Int.* **2003**, *29*, 683−689.

(2) Hites, R. A. Polybrominated Diphenyl Ethers in the Environment and in People: A Meta-Analysis of Concentrations. *Environ. Sci. Technol.* **2004**, *38*, 945−956.

(3) Watanabe, I.; Sakai, S.-i. Environmental release and behavior of brominated flame retardants. *Environ. Int.* **2003**, *29*, 665−682.

(4) Gouin, T.; Harner, T. Modelling the environmental fate of the polybrominated diphenyl ethers. *Environ. Int.* **2003**, *29*, 717−724.

(5) Darnerud, P. O. Toxic effects of brominated flame retardants in man and in wildlife. *Environ. Int.* **2003**, *29*, 841−853.

(6) Strandberg, B.; Dodder, N. G.; Basu, I.; Hites, R. A. Concentrations and Spatial Variations of Polybrominated Diphenyl Ethers and Other Organohalogen Compounds in Great Lakes Air. *Environ. Sci. Technol.* **2001**, *35*, 1078−1083.

(7) Zhu, L. Y.; Hites, R. A. Temporal trends and spatial distributions of brominated flame retardants in archived fishes from the Great Lakes. *Environ. Sci. Technol.* **2004**, *38*, 2779−2784.

(8) Luross, J. M.; Alaee, M.; Sergeant, D. B.; Cannon, C. M.; Michael, Whittle, D.; Solomon, K. R.; Muir, D. C. G. Spatial distribution of polybrominated diphenyl ethers and polybrominated biphenyls in lake trout from the Laurentian Great Lakes. *Chemosphere* **2002**, *46*, 665−672.

(9) Song, W.; Ford, J. C.; Li, A.; Mills, W. J.; Buckley, D. R.; Rockne, K. J. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 1. Lake Superior. *Environ. Sci. Technol.* **2004**, *38*, 3286−3293.

(10) Hale, R. C.; Alaee, M.; Manchester-Neesvig, J. B.; Stapleton, H. M.; Ikonomou, M. G. Polybrominated diphenyl ether flame retardants in the North American environment. *Environ. Int.* **2003**, *29*, 771−779.

(11) Stapleton, H. M.; Dodder, N. G.; Offenberg, J. H.; Schantz, M. M.; Wise, S. A. Polybrominated diphenyl ethers in house dust and clothes dryer lint. *Environ. Sci. Technol.* **2005**, *39*, 925−931.

(12) Stapleton, H. M.; Alaee, M.; Letcher, R. J.; Baker, J. E. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (*Cyprinus carpio*) following dietary exposure. *Environ. Sci. Technol.* **2004**, *38*, 112−119.

(13) Kierkegaard, A.; Bignert, A.; Sellstrom, U.; Olsson, M.; Asplund, L.; Jansson, B.; de Wit, C. A. Polybrominated diphenyl ethers (PBDEs) and their methoxylated derivatives in pike from Swedish waters with emphasis on temporal trends, 1967−2000. *Environ. Pollut. (Amsterdam, Netherlands)* **2004**, *130*, 187−198.

(14) Andersson, P. L.; Wagman, N.; Berg, H. A.; Olsson, P.-E.; Tysklind, M. Biomagnification of structurally matched polychlorinated and polybrominated diphenylethers (PCDE/PBDE) in zebrafish (*Danio rerio*). *Organohalogen Compd.* **1999**, *43*, 9−12.

(15) Burreau, S.; Axelman, J.; Broman, D.; Jakobsson, E. Dietary uptake in pike (*Esox lucius*) of some polychlorinated biphenyls, polychlorinated naphthalenes and polybrominated diphenyl ethers administered in natural diet. *Environ. Toxicol. Chem.* **1997**, *16*, 2508−2513.

(16) Tomy, G. T.; Palace, V. P.; Halldorson, T.; Braekevelt, E.; Danell, R.; Wautier, K.; Evans, B.; Brinkworth, L.; Fisk, A. T. Bioaccumulation, Biotransformation, and biochemical effects of brominated diphenyl ethers in juvenile lake trout (*Salvelinus namaycush*). *Environ. Sci. Technol.* **2004**, *38*, 1496−1504.

(17) Alaee, M.; Luross, J. M.; Whittle, D. M.; Sergeant, D. B. Bioaccumulation of polybrominated diphenyl ethers in the Lake Ontario pelagic food web. *Organohalogen Compd.* **2002**, *57*, 427−430.

(18) Boon, J. P.; Lewis, W. E.; Tjoen-A-Choy, M. R.; Allchin, C. R.; Law, R. J.; de Boer, J.; Ten, Hallers-Tjabbes, C. C.; Zegers, B. N. Levels of Polybrominated diphenyl ether (PBDE) flame retardants in animals representing different trophic levels of the North Sea food web. *Environ. Sci. Technol.* **2002**, *36*, 4025−4032.

(19) Johnson-Restrepo, B.; Kannan, K.; Addink, R.; Adams, D. H. Polybrominated diphenyl ethers and polychlorinated biphenyls in a marine foodweb of coastal Florida. *Environ. Sci. Technol.* **2005**, *39*, 8243−8250.

(20) Wolkers, H.; van Bavel, B.; Derocher, A. E.; Wiig, O.; Kovacs, K. M.; Lydersen, C.; Lindstroem, G. Congener-specific accumulation and food chain transfer of polybrominated diphenyl ethers in two Arctic food chains. *Environ. Sci. Technol.* **2004**, *38*, 1667−1674.

(21) Burreau, S.; Zebuhr, Y.; Broman, D.; Ishaq, R. Biomagnification of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) studied in pike (*Esox lucius*), perch (*Perca fluviatilis*) and roach (*Rutilus rutilus*) from the Baltic Sea. *Chemosphere* **2004**, *55*, 1043−1052.

(22) Litten, S.; McChesney, D. J.; Hamilton, M. C.; Fowler, B. Destruction of the World Trade Center and PCBs, PBDEs, PCDD/Fs, PBDD/Fs, and chlorinated biphenylenes in water, sediment, and sewage sludge. *Environ. Sci. Technol.* **2003**, *37*, 5502−5510.

(23) DeVault, D. S.; Clark, J. M.; Lahvis, G.; Weishaar, J. Contaminants and trends in fall run coho salmon. *J. Great Lakes Res.* **1988**, *14*, 23−33.

(24) DeVault, D. S.; Hesselberg, R.; Rodgers, P. W.; Feist, T. J. Contaminant trends in lake trout and walleye from the Laurentian Great Lakes. *J. Great Lakes Res.* **1996**, *22*, 884−895.

(25) Hickey, J. P.; Batterman, S. A.; Chernyak, S. M. Trends of chlorinated organic contaminants in Great Lakes trout and walleye from 1970 to 1998. *Arch. Environ. Contam. Toxicol.* **2006**, *50*, 97−110.

(26) Pearson, R. F.; Hornbuckle, K. C.; Eisenreich, S. J.; Swackhamer, D. L. PCBs in Lake Michigan water revisited. *Environ. Sci. Technol.* **1996**, *30*, 1429−1436.

(27) Achman, D. R.; Hornbuckle, K. C.; Eisenreich, S. J. Volatilization of polychlorinated biphenyls from Green Bay, Lake Michigan. *Environ. Sci. Technol.* **1993**, *27*, 75−87.
(28) USEPA. *Standard Operating Procedure for the Analysis of Particulate-Phase Organic Carbon*; Washington, DC, 2002; http://www.epa.gov/glnpo/monitoring/procedures/Chapter_2/LG207.pdf.
(29) Baker, J. E.; Eisenreich, S. J.; Swackhamer, D. L. In *Organic Substances in Sediments and Water*; Baker, R. A., Ed.; Lewis Publishers: Chelsea, MI, 1991; pp 79−90.
(30) Swackhamer, D. L.; Armstrong, D. E. Distribution and characterization of PCBs in Lake Michigan water. *J. Great Lakes Res.* **1987**, *13*, 24−36.
(31) Swackhamer, D. L. Studies of polychlorinated biphenyls in the Great Lakes. *Issues Environ. Sci. Technol.* **1996**, *6*, 137−153.
(32) Baker, J. E.; Eisenreich, S. J. PCBs and PAHs as tracers of particulate dynamics in large lakes. *J. Great Lakes Res.* **1989**, *15*, 84−103.
(33) Sabljic, A.; Guesten, H.; Hermens, J.; Opperhuizen, A. Modeling octanol/water partition coefficients by molecular topology: chlorinated benzenes and biphenyls. *Environ. Sci. Technol.* **1993**, *27*, 1394−1402.
(34) Braekevelt, E.; Tittlemier, S. A.; Tomy, G. T. Direct measurement of octanol-water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere* **2003**, *51*, 563−567.
(35) Sjodin, A.; Patterson, D. G.; Bergman, A. A review on human exposure to brominated flame retardants - particularly polybrominated diphenyl ethers. *Environ. Int.* **2003**, *29*, 829−839.
(36) Carlson, D. L.; Swackhamer, D. L. Results from the U.S. Great Lakes fish monitoring program and effects of lake processes on bioaccumulative contaminant concentrations. *J. Great Lakes Res.* **2006**, *32*, 370−385.
(37) Stapleton, H. M.; Letcher, R. J.; Baker, J. E. Debromination of Polybrominated Diphenyl Ether Congeners BDE 99 and BDE 183 in the Intestinal Tract of the Common Carp (*Cyprinus carpio*). *Environ. Sci. Technol.* **2004**, *38*, 1054−1061.
(38) Burkhard, L. P.; Lukasewycz, M. T. Some bioaccumulation factors and biota-sediment accumulation factors for polycyclic aromatic hydrocarbons in lake trout. *Environ. Toxicol. Chem.* **2000**, *19*, 1427−1429.
(39) Mackay, D. Correlation of bioconcentration factors. *Environ. Sci. Technol.* **1982**, *16*, 274−278.
(40) Vander Zanden, M. J.; Rasmussen, J. B. A trophic position model of pelagic food webs: impact on contaminant bioaccumulation in lake trout. *Ecol. Monogr.* **1996**, *66*, 451−477.
(41) Hornbuckle, K. C.; Carlson, D. L.; Swackhamer, D. L.; Baker, J. E.; Eisenreich, S. J. In *Persistent Organic Pollutants in the Great Lakes*; Hites, R. A., Ed.; Springer: Berlin, 2006; Vol. 5/N, pp 13−70.

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