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Benthic Bioaccumulation and Bioavailability of Polybrominated Diphenyl Ethers from Surficial Lake Ontario Sediments Near Rochester, New York, USA

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Abstract Polybrominated diphenyl ethers in Lake Ontario watershed sediments were assessed for benthic bioavailability through the use of biota-sediment accumulation factors. Sediments from lake and Rochester Harbor (lower Genesee River) areas were investigated. Congeners 47, 66, 85, 99 and 100 were detected in tissues of the oligochaete *Lumbriculus variegatus*. Biota-sediment accumulation factors ranged from 3.95 (congener 154) to 19.5 (congener 28) and were higher at the Lake Ontario area. The lower biota-sediment accumulation factors for the Rochester Harbor sediment may result from a higher fraction of black carbon generally expected in highly urbanized rivers. Degree of bromination may reduce bioavailability.

Keywords PDBE · Bioavailability · BSAF · Sediment

Polybrominated diphenyl ethers (PBDEs) are flame retardants widely used since the 1970s. Atmospheric deposition and fluvial transport are thought to be major contributors to PBDE loading in the Great Lakes, and PBDEs have been identified as an emerging chemical of concern in Lake Ontario. The PBDEs are a class of planar, highly hydrophobic organic bromine compounds that are structurally similar to polychlorinated biphenyls (PCBs). They are environmentally persistent and largely resist degradation, and are known to bioaccumulate and biomagnify. The PBDEs have been detected in sediment and fish in all of the Great Lakes (e.g., Zhu and Hites 2004; Stapleton and Baker 2003; Song et al. 2005). Sediments are an important repository media for PDBEs; therefore, bottom and resuspended sediments function as both a source and environmental sink. Limited information on the toxicity of PDBEs to fish (Key et al. 2009) and aquatic invertebrates (Nakari and Huhtala 2008; Wollenberger et al. 2005; Evandri et al. 2003) pertain to both technical blends and individual congeners, and effects include decreased survival, fecundity, growth and abnormal behavior.

Accumulation of PBDEs in the tissues of both marine and freshwater organisms has been reported, including bioccumulation in infaunal invertebrates from sediment (Ferguson et al. 2008; Ciparis and Hale 2005; Leppanen and Kukkonen 2004). Because of its persistency in sediment and tissues, the potential for trophic transfer from benthos to higher trophic levels vertebrates is high and has been demonstrated to occur (Law et al. 2006).

The objective of this study was to quantify and assess the bioavailability of PBDEs in surface sediments from select contaminated areas of the Lake Ontario watershed, using a standard freshwater bioaccumulation test with the aquatic oligochaete worm, *Lumbriculus variegatus*.

Materials and Methods

Sediment samples for this study were collected in 2005 in Lake Ontario watershed areas in the vicinity of Rochester, Monroe County, NY, USA. Discrete surface sediment samples were obtained via a Peterson Grab from four sites within a lake area (OL) and three sites within an area in the

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Rochester Harbor reach of the lower Genesee River area (RH) (Fig. 1). Equal volumes of the discrete samples collected within each area were combined and thoroughly mixed for obtaining OL and RH area composites for PBDE congener concentrations, total organic carbon (TOC) and grain size analyses as well as use in PBDE bioaccumulation tests.

The *L. variegatus* 28-days sediment bioaccumulation test was conducted according to USEPA/USACE (USEPA and USACE 1998). This oligochaete is a surficial sediment deposit feeder used in prescribed Great Lakes sediment bioaccumulation tests (USEPA/US Army Corps of Engineers [USACE] 1998). Twelve grams of worms were added to 4.7 L of test or control (Browns Lake, Vicksburg, MS) sediments and 10 L of water contained in 18.9-L box aquaria (40 × 21 × 25 cm), using five replicates per treatment. Experimental vessels larger than those typically used were required to generate the large mass of tissue required for PBDE analyses. The exposures were maintained under static-renewal conditions, in which two-thirds of the overlying water was renewed twice daily. Animals were not fed during the experiments. At exposure termination, worms were recovered from the sediment, placed in water for gut depuration (12–18 h), blotted dry, weighted and frozen at −20°C.

The USEPA SW-846 Method 1614 was used for PBDE sediment and tissue analyses, and SW846 Method 9060 was used for total organic carbon determination. Sediment samples including method blank, laboratory control spike/control spike duplicate and a matrix spike/matrix spike duplicate were extracted using a soxhlet apparatus with toluene and 1 g sample size. Sample extracts were concentrated by rotary evaporation following extraction, and subjected to column cleanup with silica gel/acid silica gel followed by acidic alumina. The extract volume was reduced under nitrogen and adjusted to a final volume of 20 μL for analysis. Extracts were analyzed for 11 PBDE congeners: BDE 28, 47, 66, 85, 99, 100, 138, 153, 154, 183 and 209. Concentrated extracts were analyzed for organochlorine pesticides using a Hewlett-Packard 5890 (Avondale, PA) gas chromatograph with dual capillary columns equipped with dual electron capture detectors. Average percent spike recovery for PBDE congeners was 147% (range 128%–152%) for sediments and 98% (range 74%–120%; Table 1) for tissues. Total lipid content in tissue was determined using a colorimetric method. Using the bioaccumulation experiment data, biota-sediment accumulation factors (BSAFs) were calculated as the ratio of PBDE congener concentration in the lipid compartment (whole-body concentration divided by percent lipid) to the concentration in the sediment organic carbon compartment (concentration in the sediment divided by percent total organic carbon [TOC]).

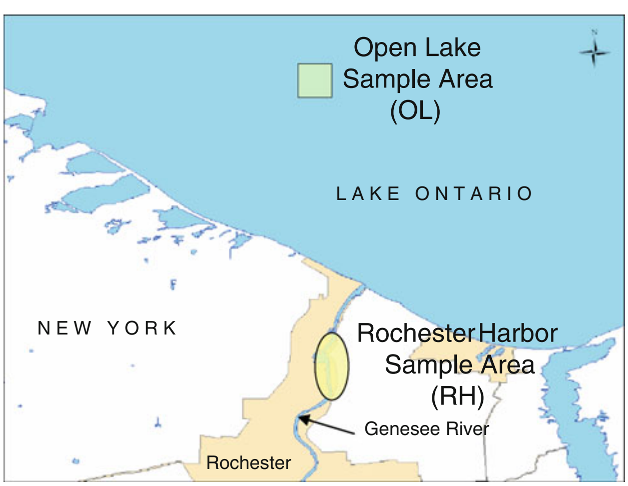

Fig. 1 Sampling areas in US Lake Ontario watershed areas near Rochester, NY

Results and Discussion

The only PBDEs detected in the sediments above the method reporting limit were BDE 153 and 154 in the OL sample, and BDE 28, 153 and 154 in the RH sample (Table 1). The method reporting limit is the lowest concentration at which an analyte can be detected in a sample and its concentration can be reported with a reasonable degree of accuracy and precision. The TOC values were 2.5% and 0.9% for the OL and RH samples, respectively.

The 28-days exposure period used in this study likely was sufficient to allow tissue concentrations of PBDEs to approach steady state in *L. variegatus,* as discussed in a related study (Pickard et al. 2005). Because of decreased worm biomass during the 28-days exposure, PBDE detection in tissue was obtained only for a limited number of replicates (Table 1). For worms exposed to RH sediment, only congeners BDE 28 and 154 were measured in tissues among some of the replicates. No PBDEs were detected in four of the five replicates in the OL exposure. In the remaining replicate, all congeners, except for BDE 138, 183 and 209 were measured above the method reporting limit. Average lipid content in *L. variegatus* tissues (±SD), as percent of wet weight, was 2.56 ± 0.20 for the OL exposure and 1.14 ± 0.19 for the RH exposure. A statistically significant linear relationship between lipid-normalized tissue PBDE concentrations and TOC-normalized sediment PBDE concentrations was obtained ($r = 0.94$; $p < 0.01$).

The PBDE BSAFs are presented in Table 2. For calculation of the BSAFs, when a congener was detected in a tissue sample but not the sediment, it was presumed to be sediment-associated and below the sediment method

Table 1 Concentrations of PBDE congeners in sediments from areas in Lake Ontario near Rochester, NY (*OL*) and Rochester Harbor on the lower Genesee River (*RH*), and in tissues of exposed *L. variegatus*

BDE	Sediment concentration (pg/g-dry weight)			Tissue concentration (pg/g-wet weight)			Tissue MS/MSD (% recovery)
	OL	RH	MRL	OL	RH	MRL	
28	BMRL	18	17	150, BMRL	230, 320, BMRL	100	102/100
47	BMRL	BMRL	870	5400, BMRL	BMRL	5,000	0.0*
66	BMRL	BMRL	17	100 BMRL	BMRL	100	9,797
85	BMRL	BMRL	21	250, BMRL	BMRL	120	105/101
99	BMRL	BMRL	870	5400, BMRL	BMRL	5,000	0.0*
100	BMRL	BMRL	270	1100, BMRL	BMRL	1,000	74/71
138	BMRL	BMRL	170	BMRL	BMRL	1,000	108/100
153	26	45	12	480, BMRL	BMRL	120	90/87
154	22	37	10	430, BMRL	120, 140, 130, 100, BMRL	100	87/84
183	BMRL	BMRL	17	BMRL	BMRL	100	99/98
209	BMRL	BMRL	8,700	BMRL	BMRL	5,000	120/101

MRL Method reporting limit, *BMRL* Below method reporting limit, *MS/MSD* Matrix spike/Matrix spike duplicate

* Sample spiked below the method reporting limit

reporting limit. In such cases, a value of one-third the method reporting limit (the method detection limit was assumed to be one-third the method reporting limit) was used to represent the sediment PBDE concentration and estimate the BSAF. All BSAFs were based on one replicate tissue sample, except for RH area values for BDE 28 (mean of 2 replicates) and BDE 154 (mean of 4 replicates).

The BSAFs for BDE 28 and 154 could be compared among the RH and OL sediment samples. Both samples showed a lower bioavailability of BDE 154 relative to BDE 28, suggesting that bioavailability may vary with degree of bromination. For the OL sediment, the more heavily brominated (and larger) congeners (i.e., BDE 85, 99, 100, 153 and 154) did not appear to be less bioaccumulative since the BSAF range of these congeners was similar to that of the tetrabrominated BDE 28, 47 and 66. No relationship between PBDE BSAFs and log K_{ow} values (Wania and Dugani 2003) was apparent (Fig. 2). This finding for PBDEs contrasts with the decrease of bioavailability observed for highly hydrophobic PCDD/F congeners to *L. variegatus* (Lyytikainen et al. 2003; Pickard and Clarke 2008).

The PBDE BSAFs ranged from 3.95 (BDE 154 at RH) to 19.5 (BDE 28 at OL), and were higher for the OL sediment than for the RH sediment. Future studies should investigate the mechanisms influencing the high bioavailability of PBDEs in the Lake Ontario sediments. This investigation did not determine the sediment concentration

Table 2 PBDE BSAFs for *L. variegatus* exposed to sediments from areas in Lake Ontario near Rochester, NY (OL) and Rochester Harbor on the lower Genesee River (RH)

BDE	Bromination	Sample	
		OL	RH
28	Tri	19.5	11.1
47	Tetra	13.6	NC*
66		13.0	NC
85	Penta	26.0	NC
99		13.6	NC
100		14.1	NC
138	Hexa	NC	NC
153		13.5	NC
154		14.3	3.95
183	Hepta	NC	NC
209	Deca	NC	NC
MEAN BSAF		15.9	7.53

* NC = not calculated due to non-detectable concentrations in both sediment and tissue

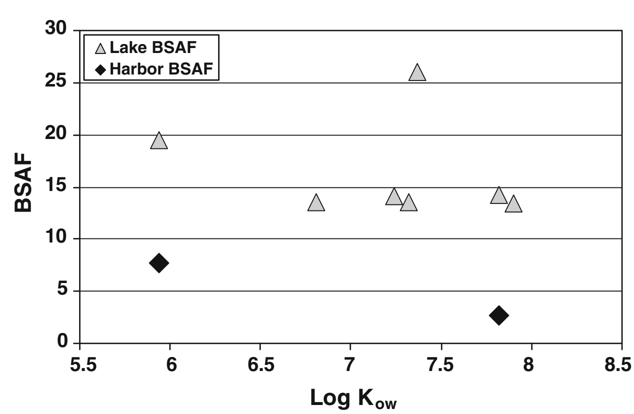

Fig. 2 Plot of PBDE BSAFs versus log K_{ow} obtained from Wania and Dugani (2003)

of black carbon (BC), which are highly condensed carbonaceous particles with inordinately high sorption strength for planar hydrophobic organic compounds. The lower BSAFs for RH sediment may be at least in part caused by the higher fraction of BC expected with the closer proximity to potential sources within the highly urbanized lower Genesee River watershed, as speculated previously for polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) in a similar study (Pickard and Clarke 2008).

Few studies have previously investigated the bioaccumulation of sediment-associated PBDEs in benthic organisms. Leppanen and Kukkonen (2004) determined that the BDE congeners 47 and 99 were bioavailable to *L. variegatus* from spiked freshwater sediments, and reported steady-state BSAFs of 3.1 and 3.5 for BDE 47, and 3.0 and 3.7 for BDE 99. More recently, Ciparis and Hale (2005) determined the temporal bioaccumulation pattern in *L. variegatus* exposed to biosolids containing PDBEs, and to sediments spiked with penta- and deca-BDE formulations. While they presented bioaccumulation factors (BAFs) for several PBDE congeners, they did not convey BSAFs, and the lipid content of the exposed oligochaetes was not reported. Use of 1% as the dry-weight-based lipid content for *L. variegatus* to estimate PBDE BSAFs from Ciparis and Hale (2005) data yields values ranging from 5.5 to 13.6 for spiked sediments, and from 1.0 to 2.2 for biosolids. The lower bioavailability of PBDEs in biosolids evidenced for Ciparis and Hale (2005) relative to the spiked sediments used in Leppanen and Kukkonen (2004) can be attributed to the much longer contact period between the sediment particles and the PBDEs, and the organic matter composition of the biosolids. Published BSAFs for hydrophobic organic compounds (including dichlorodiphenyldichloroethane [DDT], dichlorodiphenyldichloroethylene [DDE], and several PCBs and PCDD/Fs) derived using infaunal invertebrates range from 0.04 to 2.42 (US Army Engineer Research and Development Center 2006). The BDE 99 is one of the most frequently reported congeners in freshwater biota and has been shown to be toxic to invertebrates at relatively low aqueous concentrations. The BSAF of 13.6 for this congener in the OL sediment was over three to fourfold relative to other field sediments reported in the literature (i.e., Leppanen and Kukkonen 2004). The PBDE BSAFs derived for OL sediment in this investigation far exceeded empirical and theoretical values for highly hydrophobic chlorinated compounds. The reasons for this exceedance are unknown.

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