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Comparing Polybrominated Diphenyl Ether and Polychlorinated Biphenyl Bioaccumulation in a Food Web in Grand Traverse Bay, Lake Michigan

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Abstract. Levels of polybrominated diphenyl ethers (BDEs) in Great Lakes salmonids and ambient air have been recently reported, but few studies worldwide have examined the accumulation of BDEs within aquatic food webs. Here we report some of the first measurements of six BDE congeners that are common components of the pentaBDE commercial mixture within an entire Lake Michigan food web. BDEs were detected in all samples and the dominant BDE congener was 2,2′,4,4′-tetrabromodiphenyl ether (BDE 47). BDE 47 levels were consistently greater than those of the 2,2′,4,4′,5-pentabromodiphenyl ether (BDE 99), despite similar levels of these two compounds in commercial mixtures, suggesting differences in the bioavailability of the BDE congeners or differences in their ability to be metabolized. Additionally, congener composition was significantly different among deepwater sculpin, bloater chub, and lake trout, indicating differences in exposure or differences in biotransformation capacities. Total BDE concentrations in this food web were positively correlated ($r = 0.94$) with levels of PCBs previously measured in these samples (Stapleton *et al.* 2001a). Levels of BDE 47 and PCB 153, compounds with similar physicochemical properties, were compared to examine the relative exposure and bioaccumulation of these two classes of chemicals that have different environmental loading histories. Food web magnification factors calculated for these two congeners were 3.2 and 4.0 for BDE 47 and PCB 153, respectively, indicating a comparable potential for biomagnification in food webs.

Polybrominated diphenyl ethers (BDEs) are used as flame retardants on a majority of plastics, textiles and electronic equipment used today (WHO 1994). Of the global commercial BDE usage, approximately 15% is pentaBDE, a mixture containing highly bioaccumulative compounds (Darnerud *et al.* 2001). A majority of the commercial BDE demand (~80%) is for decaBDE, which is a much larger, less stable, and reportedly less bioavailable compound (WHO 1994). The United States has by far the largest market demand for pentaBDE mixtures, which was reported to be as high as 98% of the 1999 global market (Renner 2000).

Recent studies have identified and quantified components of the commercial pentaBDE mixtures in marine mammals, Great Lakes fish, and human blood and breast milk (Lindstrom *et al.* 1999; Manchester-Neesvig *et al.* 2001; Sjodin *et al.* 1999; Noren and Meironyte 2000; Luross *et al.* 2002; Alaee *et al.* 2002). Levels of BDEs measured in biosolids applied to land regions within the United States have been reported to be as high as 2,000 μg/kg dry weight and suggest that significant release of these compounds to the environment is occurring (Hale *et al.* 2001a). The presence of these compounds in Atlantic sperm whales suggests they have become ubiquitous contaminants transported on global scales with the potential to bioaccumulate in marine food webs (Watanabe *et al.* 1987; de Boer *et al.* 1998; Tuerk *et al.* 2002).

Measurements of organohalogens in human breast milk, birds, and fish have shown that there is a decreasing trend in organochlorine concentrations, such as polychlorinated biphenyls (PCBs), due to bans on their use and production. However, concentrations of BDEs in these matrices have risen in the last 20 years and levels have increased more than threefold in the last decade (Noren and Meironyte 2000; Luross *et al.* 2002; Norstrom *et al.* 2002). This is most likely due to increased use of flame retardants such as BDEs in plastic resins, textiles, and furniture as the demand for these types of products increases.

The few studies that have examined the toxicity of BDEs to wildlife have shown that exposure to BDEs can impair hematocrit and blood glucose levels, decrease glutathione reductase activity, significantly alter thyroid hormone homeostasis, and induce genetic recombination in mammalian cells (Holm *et al.* 1994; Tjarnlund *et al.* 1998; Helleday *et al.* 1999; Darnerud *et al.* 2001; Zhou *et al.* 2001). BDEs also induce estrogenic responsive genes in human breast cancer cells (Meerts *et al.* 2001). Considering their structural similarities, BDEs and PCBs may display similar toxic effects, which include carcinogenicity and reduced reproductive capacities (Birnbaum 1995; Barron *et al.* 1995). Additionally, BDEs thermally decompose to form brominated dibenzofurans and dibenzodioxins (Zelinski *et al.* 1993; Sakai *et al.* 2001).

The Great Lakes area has been historically contaminated with PCBs (DeVault *et al.* 1996). Recently, BDE levels in Great Lakes salmonids and air have been reported (Manches-

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ter-Neesvig *et al.* 2001: Strandberg *et al.* 2001) and current data suggest that atmospheric deposition is a likely source of BDEs to the surface waters of the Great Lakes. In this paper we present BDE levels in biota measured as part of a larger study examining PCB dynamics in Grand Traverse Bay, Lake Michigan in 1997–1999 (McCusker *et al.* 1999; Stapleton *et al.* 2001a; Stapleton *et al.* 2002a; Schneider *et al.* 2001). Grand Traverse Bay is located on the northeast coast of Lake Michigan and is approximately twenty miles across from north to south. Although the samples collected may not be ideal surrogates that represent contaminant dynamics in open Lake Michigan, they do provide an adequate sample set to examine bioaccumulation. These measurements are among the first reports on BDE bioaccumulation within a freshwater system in the United States. From these results we have compared the behavior of these two classes of compounds within the food web and examined the potential for magnification between BDE and PCB congeners of similar physicochemical properties.

Materials and Methods

Sample collection and laboratory extraction methods have been reported previously for the biota samples (Stapleton *et al.* 2001a). Samples were collected from the western arm of Grand Traverse Bay (GTB), Lake Michigan between April and September of 1997 using a variety of gear, including plankton nets, benthic sleds, otter trawls, and gill nets. All samples were separated by species and month of collection and then wrapped in aluminum foil and frozen until analysis. In the laboratory, length and mass of all fish were recorded, fish were composited by size class and homogenized whole for contaminant extraction.

All biota samples were first ground with sodium sulfate with a mortar and pestle to remove water and then Soxhlet extracted with dichloromethane. The biota extracts were sub-sampled to measure lipid content gravimetrically. Gel permeation chromatography or alumina were used to remove lipid interferences and Florisil was used to clean up the samples and remove any interfering compounds. Our laboratory procedures enabled us to quantify BDEs and PCBs in the same extract. Total PCBs as reported here and in our previous publications (Stapleton *et al.* 2001a; Stapleton *et al.* 2002a; Schneider *et al.* 2001) represents a sum total of 103 individual congeners. Recoveries of the six BDE congeners in laboratory recovery experiments using sodium sulfate blanks averaged 98 ± 4%. Laboratory matrix blanks indicated that BDEs 47 and 99 were present at low levels in the laboratory and therefore blank correction was done by subtracting the average BDE levels in the blanks from all samples.

Six BDE congeners were quantified in all samples: 2,2′,4,4′-tetrabromodiphenyl ether (BDE 47), 2,2′,4,4′,5-pentabromodiphenyl ether (BDE 99), 2,2′,4,4′,6-pentabromodiphenyl ether (BDE 100), 2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE 153), 2,2′,4,4′,5,6′-hexabromodiphenyl ether (BDE 154), and 2,2′,3,4,4′,5′,6-heptabromodiphenyl ether (BDE 183). All BDE congener standards were purchased from Cambridge Isotope Laboratories, Inc., Andover, MA. BDEs were quantified using a Hewlett Packard 5890/5972A GC/MSD operated in the selected ion monitoring mode. Chromatographic conditions were as follows: injection port temperature, 260°C; detector temperature, 320°C and oven temperature ramp was initially held for two minutes at 80°C, followed by a 30°C/min ramp to 200°C and then a ramp of 5°C/min to 300°C, which was held for an additional 5 min. Helium was the GC carrier gas and the flow was maintained at 1.4 ml/min through a 30 m DB-5 column. Quantification and confirmation ions for the six BDE congeners were 486 and 326 (BDE 47); 404 and 565 (BDE 99 and 100); 484 and 644 (BDE 153 and 154); and 562 and 563 for BDE 183. PCB 204 (2,2′,3,4,4′,5,6,6′-octachlorobiphenyl) was used as the internal standard. Detection limits (in a typical biota sample) ranged from 0.4 ng/g wet weight up to 3.0 ng/g wet weight for BDE 47 and BDE 183, respectively.

Results and Discussion

The total concentration of the six BDE congeners quantified are listed in Table 1 in addition to ancillary information and previously reported values of lipid content and total PCB levels (Stapleton *et al.* 2001a). Five of the six BDE congeners were detected in a majority of the samples. However, BDE 183 (2,2′,3,4,4′,5′,6-heptabromodiphenyl ether) was not detected (<3.0 ng/g wet weight) in any of the samples quantified.

Levels of BDEs within the food web were highest in lake trout and lowest in mysid shrimp, comparable to PCB trends. Concentrations of total BDEs in lake trout ranged from 86 to 156 ng/g wet weight, which are very comparable to values recently reported by Manchester-Neesvig for the same six congeners in Lake Michigan salmon (Manchester-Neesvig *et al.* 2001). The concentration of BDE 47 ranged from 51 to 95 ng/g ww among the lake trout tissues and is as high as reported values for sperm whales (de Boer *et al.* 1998) and long-finned pilot whales (Lindstrom *et al.* 1999) from the Atlantic Ocean. BDE levels in the dominant forage fish of Lake Michigan, alewife and bloater, are higher than recently reported values of BDEs in marine forage fish (Haglund *et al.* 1997; Akutsu *et al.* 2001), indicating higher exposure in the Great Lakes. Our trends and observations are very similar to other BDE measurements recently made in Great Lakes clams, rainbow smelt, walleye, and lake trout (Hickey *et al.* 2002). Mysid shrimp displayed the lowest levels of total BDEs in their tissues, ranging from 0.29 to 3.83 ng/g ww. In our previous studies we examined seasonal differences in PCB burdens among invertebrates in our sample set, however, we observed no seasonal differences in invertebrate BDE burdens. This is most likely due to the fact that levels were too low in concentration in our sample set to observe any significant seasonal trends.

BDE Congener Patterns

Of the five BDE congeners detected, BDE 47 was the dominant component of the BDE burden in a majority of the biota samples, similar to many other studies (de Boer *et al.* 1998; Sellstrom *et al.* 1998; Allchin *et al.* 1999; Manchester-Neesvig *et al.* 2001; Hale *et al.* 2001b). BDE 47 comprised 52 ± 20% of the total BDE burden while BDE 99 contributed 34 ± 20% of the total. Figure 1A compares our Grand Traverse Bay samples with two commercial pentaBDE technical mixtures known as Bromkal 70-5DE and a DE-71 (values for Bromkal 70-5DE taken from Manchester-Neesvig *et al.* 2001). DE-71 is currently used in the U.S. and primarily applied to polyurethane foam commonly found in furniture (WHO 1994; Hale *et al.* 2001a).

The biota samples measured here are enriched in PBDE 47 relative to the commercial mixtures and suggest that BDE 47 may be more bioavailable. In a laboratory study by Burreau *et al.* (1997) pike were fed rainbow trout injected with BDEs and

Table 1. Concentrations of ΣPCBs, ΣBDEs, BDE 47, and PCB 153 (2,2′,4,4′,5,5′-hexachlorobiphenyl) in ng/g ww in composite samples

Sample	*n*	Size (mm)	% Lipid	Σ PCB	Σ BDE	BDE 47	PCB 153
lake trout	5*	533–648	14.1 ± 4.2	1200 ± 460	126 ± 33	75 ± 21	194 ± 130
salmon	1*	813	4.54	1080	95	34	130
burbot	1*	685	7.75	1700	86	43	380
whitefish	6	211–450	6.5 ± 3	280 ± 230	18 ± 12	9.8 ± 7.2	34 ± 19
deepwater sculpin	6	60–170	3.5 ± 1	120 ± 55	3 ± 1.4	2.8 ± 1.2	30 ± 13
bloater chub	9	200–250	2.4 ± 1	310 ± 97	23 ± 5	11 ± 3	80 ± 26
alewife	8	160–210	4.7 ± 3	230 ± 70	36 ± 16	16 ± 7	35 ± 17
rainbow smelt	4	60–165	2.3 ± 1	80 ± 24	11 ± 3	7 ± 2	12 ± 3
benthic amphipods	10	1–5	1.7 ± 0.7	25 ± 8	1.8 ± 1.4	0.9 ± 0.7	3.3 ± 1
mysid shrimp	5	1–5	1.4 ± 0.5	12 ± 4	1.3 ± 2.0	0.7 ± 0.7	2.1 ± 1
bulk zooplankton	5	NA	1.8 ± 0.7	20 ± 11	1.4 ± 0.9	0.8 ± 0.8	1.9 ± 1

* Samples were analyzed whole and are not composites.
NA: not available.

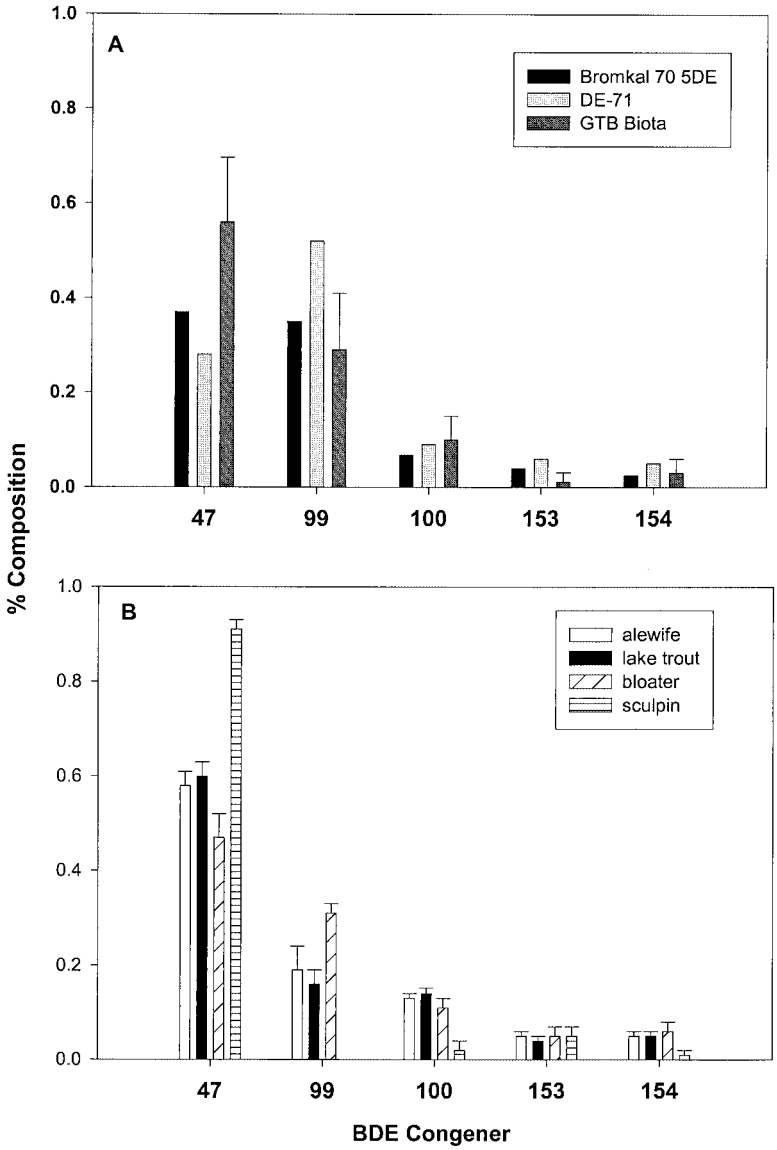

Fig. 1. Mean BDE congener pattern in Grand Traverse Bay biota compared to two commercial mixtures (data on commercial mixtures cited from Manchester-Neesvig *et al.* 2001 for Bromkal 70-5DE and Hale *et al.* 2001 for DE-71) (**A**), and the average BDE congener pattern among fish species from GTB (**B**)

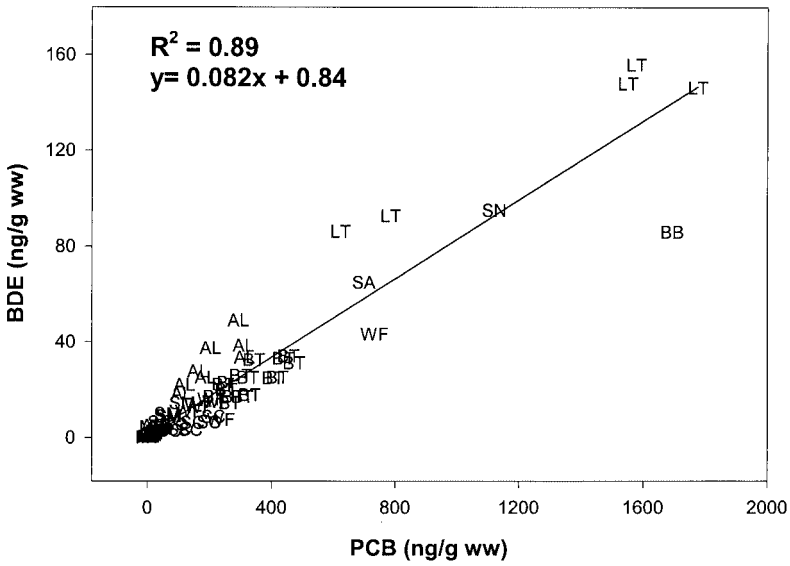

Fig. 2. Correlation between total PCB and total BDE burdens as measured in Grand Traverse Bay biota samples. [ZP = zooplankton; AP = amphipod; MY = mysid shrimp; SC = deepwater sculpin; SM = rainbow smelt; AL = alewife; BT = bloater; WF = whitefish; LT = lake trout; SA = steelhead; SN = salmon; BB = burbot]

they observed a higher uptake efficiency of BDE 47 (90%) relative to BDE 99 (60%), reinforcing this notion. However, current work now demonstrates that BDEs can be debrominated to form lower brominated BDE congeners within fish tissues (Stapleton *et al.* 2002b). Therefore, the higher contribution of BDE 47 to total BDE burdens could be a result of some debromination of BDE 99 or other BDE congeners in biota tissues.

Congener patterns differed among fish within Grand Traverse Bay. The proportion of BDE congeners in lake trout and alewife tissue are very similar (Figure 1b), which is logical considering that lake trout feed heavily upon alewife (Eck and Wells 1986). In contrast, deepwater sculpin are heavily enriched in BDE 47 and do not possess detectable levels of BDE 99. This is surprising considering that BDE congeners 100, 153, and 154 were detected in sculpin, which are typically found in biota at lower levels than BDE 99. This depletion of BDE 99 has been observed in other benthic fish, particularly carp (*Cyprinus carpio*) (Hale *et al.* 2001b; Johnson and Olson 2001; Dodder *et al.* 2002) and suggests the possibility of metabolism of BDE 99. In previous work, we have found that the deepwater sculpin is capable of metabolizing PCBs to methylsulfone derivatives (Stapleton *et al.* 2001b). Considering the similarity in structure between PCBs and BDEs, deepwater sculpin may be capable of metabolizing BDEs as well, but more work is needed to confirm this.

Metabolism of BDE congeners by fish is probable. A study by Örn and Klasson-Wehler (1998) found that rats and mice can metabolize BDE congeners to hydroxylated metabolites. PCBs can also be metabolized to hydroxylated metabolites (Letcher *et al.* 2000), but the relative efficiency by which fish metabolize PCBs and BDEs to hydroxylated metabolites is unknown. Hydroxylated metabolites of BDEs have been shown to possess greater estrogenic potency relative to the parent compounds (Meerts *et al.* 2001). Therefore there is a risk that the hydroxylated metabolites may be more toxic or detrimental than the BDEs. Fisk *et al.* (2001b), found hydroxylated BDE and PCB metabolites in lake trout plasma from the Great Lakes, indicating that metabolism does indeed occur in lake trout. And, as mentioned previously, our earlier work on sculpin indicated that they have a high capacity for metabolizing organohalogens (Stapleton *et al.* 2001b). Therefore, the reduced levels of BDE 47 relative to PCB 153 are likely affected by metabolism. However, little is known about the metabolic efficiency of alewife, bloater chub, rainbow smelt, and mysid shrimp.

The relative concentrations of BDE congeners derived from the pentaBDE commercial mixtures are altered as they cycle through aquatic environments. Biota samples are often dominated by BDE 47, similar to reports for air samples taken from the Great Lakes (Strandberg *et al.* 2001). However, sediment and some benthic organisms are dominated by BDE 99. This would suggest that the physical properties of these two specific compounds affect their ultimate fate in the environment. Bioavailability and assimilation efficiencies of hydrophobic contaminants are often correlated to their octanol-water partition coefficient, or log K_{ow}(Fisk *et al.* 1998). The log K_{ow} values for BDE 47 and BDE 99 have been reported to be 6.81 and 7.32, respectively (Braekevelt *et al.* 2003). As Fisk *et al.* (1998) showed, assimilation efficiencies and half-lives of hydrophobic contaminants increase up to a log K_{ow} value of about 7.0, and then decrease with increasing log K_{ow}. Therefore enrichment of BDE 47 relative to BDE 99 in aquatic organisms could be due to their relative assimilation and bioavailability. Further studies are needed to verify this.

Comparing PBDEs to PCBs

Among the data, total PCB and BDE levels are positively correlated (r = 0.94; Figure 2), suggesting similar routes of exposure or mechanisms of accumulation. Other investigations have observed similar correlations between total PCB and total BDE levels in environmental samples (Manchester-Neesvig *et al.* 2001; Strandberg *et al.* 2001; Loganathan *et al.* 1995; Watanabe *et al.* 1987), suggesting that these compounds cycle in the environment through similar pathways.

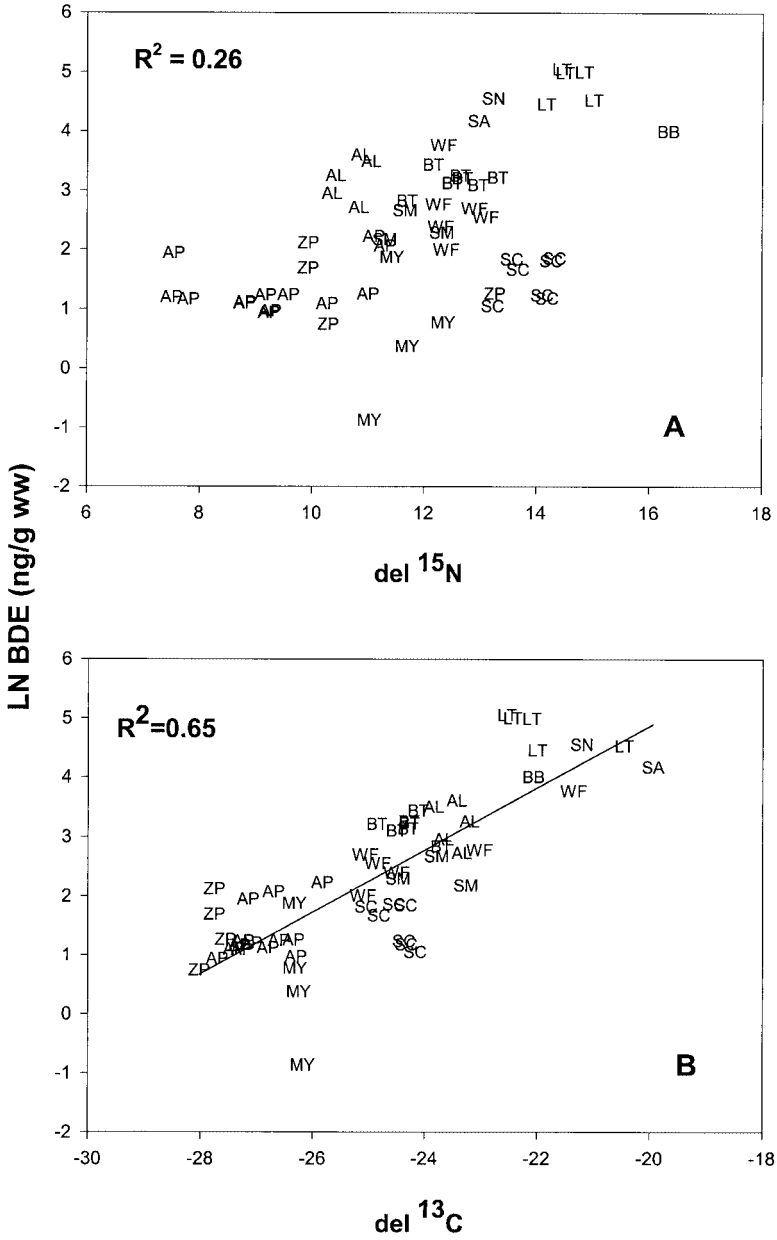

Fig. 3. Correlation between stable isotopes of nitrogen (**A**) and carbon (**B**) with total BDE concentrations in the food web. [ZP = zooplankton; AP = amphipod; MY = mysid shrimp; SC = deepwater sculpin; SM = rainbow smelt; AL = alewife; BT = bloater; WF = whitefish; LT = lake trout; SA = steelhead; SN = salmon; BB = burbot]

Laboratory studies using blue mussels have demonstrated that uptake clearance rates for BDEs are comparable or greater than corresponding PCBs of similar log K_{ow}, while both compounds displayed comparable depuration rates (Gustafsson *et al.* 1999). The log K_{ow} of PCB 153 (2,2′,4,4′,5,5′-hexachlorobiphenyl) is 6.92 (Mackay *et al.* 1992) while the value for BDE 47 has been measured at 6.81 (Braekevelt *et al.* 2003). Therefore, comparable biomagnification of BDE 47 and PCB 153 would be expected in the environment under equilibrium conditions. Another laboratory study using pike found very comparable uptake efficiencies (~90%) for both BDE 47 and PCB 153 (Burreau *et al.* 1997, 2000).

BDE levels in the GTB food web display biomagnification from lower trophic organisms, such as zooplankton and amphipods, up to higher trophic level organisms, such as lake trout, burbot, and salmon. In our previous studies we examined bioaccumulation in the food web by using stable isotopes to establish trophic positions (Stapleton *et al.* 2001a). Our analyses indicated that carbon isotopes ($\delta^{13}C$) were a better indicator of trophic level rather than nitrogen isotopes ($\delta^{15}N$) due to extreme seasonal variation in the nitrogen signals at the base of the food web. As with PCBs, BDEs displayed a positive correlation with both nitrogen and carbon isotopes (Figure 3), however, $\delta^{13}C$ again was a better variable for examining bioaccumulation among trophic levels.

In past studies (Fisk *et al.* 2001a) examined trophic transfer of organochlorine contaminants in food webs by calculating a food web magnification factor (FWMF). This calculation (shown in Equation 1) is based upon the work done by Broman *et al.* (1992), in which the natural log concentrations of the contaminant are plotted against their trophic positions (usually estimated by $\delta^{15}N$) for all food web members:

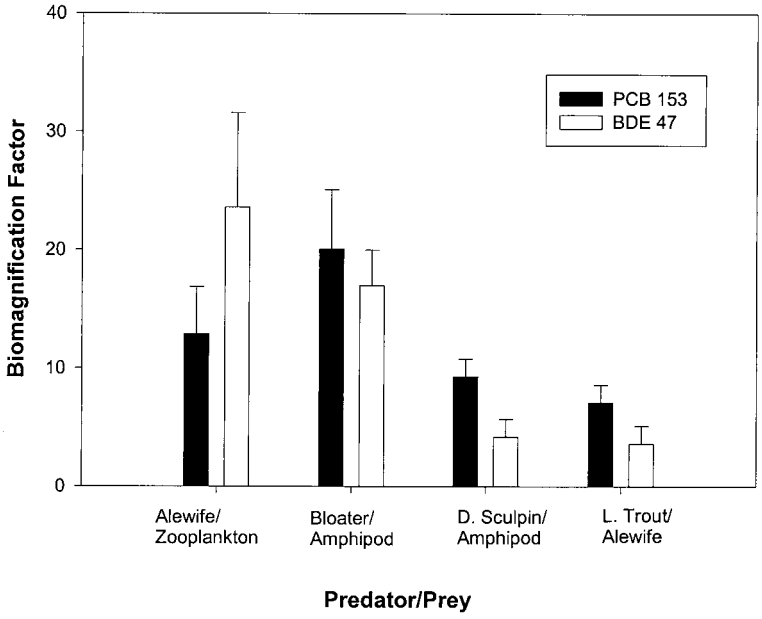

Fig. 4. Biomagnification factors calculated for PCB 153 and BDE 47 among known predators and their prey

$$\text{LN concentration} = a + (b \cdot \text{trophic level}) \quad (1)$$

The slope of the regression line (b) can be used in Equation 2:

$$\text{FWMF} = e^{b} \quad (2)$$

This provides an average assessment of the biomagnification of contaminants from one trophic level to the next. In our study, we calculated FMWFs for BDE 47 and PCB 153 using $\delta^{13}C$ as the variable for trophic level. Calculating the slope of a regression of LN BDE 47 and LN PCB 153 against $\delta^{13}C$, we obtain FWMFs of 1.8 and 2.0, respectively. However, our values here are a lower estimate compared to other studies because we have used $\delta^{13}C$ as an indicator of trophic level instead of establishing a numerical value for trophic position as Fisk *et al.* (2001) did. The food web stable analysis indicated that $\delta^{13}C$ increased in each trophic level by approximately 2.0‰ Therefore, adjusting our slopes for a 2.0 ppt increase for each trophic level, our FWMFs are 3.2 and 4.0 for BDE 47 and PCB 153, suggesting a comparable potential for biomagnificiation. Our FWMF for PCB 153 compares very well to Fisk's *et al.* (2001) value of 4.4 and Norstrom's (1994) value of 4.7, for PCB 153 and total PCBs, respectively.

Biomagnification factors (BMF, contaminant concentrations within the predator normalized to those within their prey) of BDE 47 and PCB 153 for known predators and their prey in this system have been calculated (Figure 4). BMFs are comparable for both PCBs and BDEs in the case of alewife feeding upon zooplankton and bloater feeding upon amphipods. However, BMFs calculated for deepwater sculpin/amphipods and lake trout/alewife display a higher value for PCBs relative to BDEs. In other words, sculpin and lake trout appear deficient in BDE 47 relative to other species. As we mentioned, lake trout and sculpin are the two fish most likely to be metabolizing BDEs based upon other field evidence (Fisk *et al.* 2001b; Stapleton *et al.* 2001c) and would explain this observation.

Conclusions

The similar physical and chemical properties of PCBs and lower brominated BDEs suggests that they have comparable potential to bioaccumulate in biological systems. Currently, BDE levels are lower than PCB levels in Grand Traverse Bay, Michigan. However, given that observations have demonstrated increasing concentrations of BDEs in the Great Lakes area over the past twenty years (Norstrom *et al.* 2002), it can be expected that levels will continue to increase in the near future. Additionally, we suggest that BDEs may have a greater capacity to be metabolized relative to PCBs. More work is needed to assess the efficiency by which these compounds are biotransformed and whether the resulting metabolites present a greater hazard than their parent compounds. The fact that these compounds appear to be exponentially increasing in concentration in many parts of North America suggests that BDEs and their metabolites will also increase and have potential to reach levels in fish tissue to be of some toxicological concern.

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