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Hepatic polybrominated diphenyl ether (PBDE) levels in Wisconsin river otters (*Lontra canadensis*) and Michigan bald eagles (*Haliaeetus leucocephalus*)

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Abstract

Polybrominated diphenyl ethers (PBDEs) are persistent and toxic flame-retardant chemicals widespread in the Great Lakes ecosystem. These chemicals are now being regulated and phased-out of the region; therefore it remains important to understand the extent of contamination in order to track the efficacy of recent actions. Here, Σ_4 PBDE congeners (PBDE-47, 99, 100, 153; wetweight basis unless indicated) were determined in liver tissues from Wisconsin river otters (*Lontra canadensis*; $n = 35$; 2009–2010) and Michigan bald eagles (*Haliaeetus leucocephalus*; $n = 33$; 2009–2011). In otters, Σ_4 PBDE ranged from 0.5 to 72.9 ng/g, with a mean ($\pm$ SD) and median (25th–75th percentile inter-quartile range) of 16.3 ± 16.4 ng/g and 11.3 (5.6–18.9) ng/g, respectively. The mean lipid-adjusted Σ_4 PBDE was 1377 ± 1485 ng/g. In eagles, Σ_4 PBDE ranged from 0 to 1,538.8 ng/g, with a mean and median of 74.3 ± 266.7 ng/g and 21.2 (5.7–28.9) ng/g, respectively. The mean lipid-adjusted Σ_4 PBDE was $5274.5 \pm 19,896.1$ ng/g. In both species, PBDE-47 accounted for >50% of the Σ_4 PBDE, followed by PBDE-99 and PBDE-100 (each ~17–19% of the total). The PBDE levels reported here in otters are similar to mammalian wildlife elsewhere, though the levels in eagles are among the highest worldwide across studied birds. The findings indicate that apex Great Lakes wildlife remain exposed to appreciable levels of PBDEs and more work is needed to understand whether such exposures are associated with adverse health outcomes.

Keywords

Wildlife; Biomonitoring; Tissue residues; Persistent organic pollutants; Flame retardants; Great Lakes

Introduction

Polybrominated diphenyl ethers (PBDEs) are flame-retardant chemicals that have been used in commercial products such as textiles, plastics, wood, electronic materials, and polyurethane foam (ATSDR, 2004; de Wit, 2002). At high temperatures, PBDEs release bromine radicals that inhibit the spread of flame (Hooper and McDonald, 2000). Flame-retardant chemicals are released from products and can disperse throughout the environment (Hale et al., 2003; Hites, 2004; de Wit et al., 2010). These chemicals are lipophilic and bioaccumulative, and thus they are of ecotoxicological concern (Rahman et al., 2001; Kuo et al., 2010). Exposure of humans and wildlife to PBDEs has been associated with a number of adverse health outcomes (Darnerud, 2003; Shaw et al., 2010). For example, in mammalian and avian wildlife, exposures to relevant levels of PBDEs have been linked with deleterious effects on offspring development and thyroid function (Ferne et al., 2005; Zhang et al., 2009).

A variety of PBDEs have been measured in the Great Lakes region, including in air (Melymuk et al., 2014), sediment (Zhu and Hites, 2005), and people (Anderson et al., 2008). Some of the highest concentrations of PBDEs and fastest changing levels in the region have been reported in fish and wildlife. In a study of bald eagles (*Haliaeetus leucocephalus*) sampled across the State of Michigan, several PBDE congeners (and other flame retardants) were detected in plasma samples of every bird, including many from rural regions, thus suggesting that exposures are ubiquitous (Venier et al., 2010). Potential exposures of organisms to PBDEs have increased in recent decades. Based on work by Gauthier et al (2008) using herring gull (*Larus argentatus*) eggs from Great Lakes colonies sampled between 1982 and 2006, doubling times for Σ_3 PBDE (PBDE-47, -99, -100) ranged from 4.9 to 8.7 years. Trends of PBDE levels in lake trout (*Salvelinus namaycush*) and smelt (*Osmerus mordax*) show somewhat faster doubling times (2–4 years across the Great Lakes), although the most recent data show accumulation rates are slowing (Batterman et al., 2007). In addition to accumulating in aquatic ecosystems, PBDEs are accumulating in organisms that occupy terrestrial environments within the Great Lakes, as documented in Chen et al.'s (2012) study on American kestrels (*Falco sparverius*) and European starlings (*Sturnus vulgaris*).

While appreciable PBDE levels among wildlife from the Great Lakes region have been established (Chen and Hale, 2010), important knowledge gaps remain. Beyond birds, there exists limited information on PBDE levels in mammalian wildlife across the region. For birds, a growing number of datasets exist but most investigators have studied eggs, and little is known about PBDE levels in internal organs, specifically the liver which is the major site of xenobiotic metabolism.

The goal of the current study was to increase understanding of PBDE exposures in Great Lakes wildlife, and specifically to measure key, bioaccumulative PBDE congeners in liver tissues from Wisconsin river otters (*Lontra canadensis*) and Michigan bald eagles. These apex species bioaccumulate pollutants and have served for decades as sentinel biomonitoring species. Here we focused on four PBDE congeners (PBDE-47, 99, 100, and 153) proven to be persistent, bioaccumulative, and potentially toxic to wildlife. These congeners were commercially ubiquitous in the past in the Great Lakes region, but are now being phased-out.

Methods

Sample collection

River otter carcasses ($n = 35$) were obtained throughout the State of Wisconsin during the 2009–2010 trapping season as part of the Wisconsin Department of Natural Resource's otter trapping and furbearer management program (Strom, 2008; Dornbos et al., 2013). For bald eagles ($n = 33$), liver tissues were obtained from birds collected in 2009–2011 by the Michigan Department of Natural Resources. Birds were found dead from various causes in the field. For otters and eagles, carcasses were kept frozen in -20°C freezers in regional facilities, partially thawed for tissue sampling, and then tissues were delivered to the University of Michigan School of Public Health where they were stored at -20°C until analysis.

PBDE analysis

Tissue samples (mean sample size was 8.8 g for otter and 39.5 g for eagle) were homogenized and spiked with surrogate standards (certified surrogate Mixture EO-5277; CDC persistent pesticides (PPC), PCB and PBDE calibration solutions, Cambridge Isotope Labs, MA). The calibration standard was run at concentrations of 0.01, 0.1, 1, 10, 50, 500 and 1000 ng/mL to span the expected range. Homogenates were mixed with sodium sulfate, then extracted, fractionated and cleaned by column elution methods as we have previously described (Chernyak et al., 2005). Internal standards used in each run included label compounds (CIL EO-5275 mixture of PCB 52 L and 5CB 138 L). Gas chromatography-mass spectrometry analyses were performed using negative chemical ionization mode and selective-ion monitoring with an Agilent 5973 instrument (Agilent Industries, Palo Alto, CA, USA) equipped with a DB-5 column (30m length, 0.25mm inner diameter, film thickness of 0.25 mm; J&W Scientific, Folsom, CA, USA). All congeners in our calibration solution were investigated, including PBDE 3,15,17, 28, 75, 49, 71, 66, 85, 138,154, 166, 183,190, 196, 197, 201, 202, 203, 206, 207, 208, and 209. Many of these congeners were correlated, some were found at low levels, and some were not detected. In this paper, we focused on four PBDE congeners (47, 99, 100 and 153) as they yielded the best quality results and were detected in at least 50% of the samples. These four congeners were quantified and expressed as ng/g on a wet weight basis unless noted otherwise. Lipid-adjusted concentrations are reported in Electronic Supplementary Material (ESM) Tables S1 and S2. The sum of these four congeners is reported as $\Sigma_4\text{PBDE}$.

Quality assurance activities included use of authentic standards (certified surrogate and calibration standard solutions, Cambridge Isotope Labs, MA), blanks, matrix spikes, duplicates, and analyses of standard reference materials (NIST SRM 1947, Lake Michigan fish tissue). For every 10 samples, 1 blank, 1 duplicate sample and 1 SRM sample were included as well as a recovery test and a drift check. Individual PBDE congeners were not detectable in blanks, surrogate recoveries ranged from 84 to 101%, duplicates were within 10%, and concentrations were within 15% of the certified determination for the SRMs. Non-detections were set to 0.5 method detection limits for statistical analyses. The method detection limit was defined as the amount of analyte detected when the signal-to-noise ratio of the peak was equal to three.

Statistical analyses

Initially all data were explored using descriptive and univariate approaches. Hepatic PBDE concentrations were reported as mean $\pm$ standard deviation, as well as using median and interquartile ranges (25th to 75th percentile). The tissue residue data were log-transformed to achieve a normal distribution prior to statistical analysis. ANOVA (Tukey's post hoc) tests were used to compare mean PBDE-congener levels across available variables of interest (e.g., geographic region, sex). Pearson correlations were used in assessing associations among differing congeners. SPSS Statistics 19.0 software and R version 3.0.2 were used for statistical analyses, and a p -value <0.05 was considered statistically significant.

Results

Liver tissues from river otters collected throughout Wisconsin all contained detectable levels of PBDE-47, PBDE-99, PBDE-100, and PBDE-153 (Table 1). The non-lipid-adjusted Σ_4 PBDE concentration averaged 16.3 ± 16.4 ng/g, and ranged from 0.5 to 72.9 ng/g. The Σ_4 PBDE median was 11.3 ng/g and interquartile range was 5.6–18.9 ng/g. The mean lipid content in livers was $1.2 \pm 0.5\%$. When adjusted for hepatic lipid content, the arithmetic mean of the sum of the Σ_4 PBDE was 1377 ± 1485 ng/g lipid (see ESM Table S1 for lipid-adjusted results).

The most abundant congener in river otter livers was PBDE-47 (9.8 ± 12.0 ng/g), which accounted for 57% of the Σ_4 PBDE. PBDE-47 levels significantly exceeded those of the three other congeners ($p < 0.05$; Table 1; Fig. 1). PBDE-100 was the second most abundant congener, accounting for 18% of the total (2.9 ± 2.6 ng/g), followed by PBDE-99 (17% of total; 2.7 ± 3.4 ng/g), and then PBDE-153 (9% of total; 1.4 ± 2.3 ng/g). Levels of PBDE-100 and PBDE-99 were both significantly higher than PBDE-153 ($p < 0.001$ and $p < 0.01$, respectively). Concentrations of individual congeners were significantly correlated (correlation coefficient ranged from 0.463 to 0.895; $p = 0.005$) (Table 3). There were no significant differences among congener levels when sex or geographic region of sampling was considered (Table 1).

For bald eagles from Michigan, all ($n = 33$) but two individuals contained detectable levels of the four PBDEs in liver tissue (Table 2). The arithmetic mean Σ_4 PBDE concentration was 74 ± 267 ng/g, and ranged from 0 to 1539 ng/g. The Σ_4 PBDE median was 21.2 ng/g and

interquartile range was 5.7–28.9 ng/g. The mean lipid content in eagle livers was $2.6 \pm 1.2\%$. When adjusted for hepatic lipid content, the arithmetic mean of the sum of the PBDE congeners was $5274.5 \pm 19,896.1$ ng/g lipid (ESM Table S2).

As seen in the otters, PBDE-47 was the most abundant congener in the eagle livers, accounting for 51% of Σ_4 PBDE (37.6 ± 132.1 ng/g) (Table 1; Fig. 2). Levels of PBDE-47 were significantly greater than PBDE-153 ($p < 0.001$). In eagles, PBDE-99 was the second most abundant congener, comprising 18.9% of the total (14.1 ± 51.2 ng/g), followed by PBDE-100 (18.8% of total; 14.0 ± 48.4 ng/g) and PBDE-153 (8.6% of total; 8.6 ± 35.4 ng/g). PBDE-99 and PBDE-100 levels were both significantly ($p < 0.001$) higher than PBDE-153. As with otters, the individual congeners measured in eagle livers were all strongly correlated (r_p ranged from 0.857 to 0.957; $p = 0.001$) (Table 4). Sex or geographic sampling region did not influence PBDE levels.

Discussion

The four PBDE congeners studied here (PBDE-47, 99, 100, and 153) were detected in the liver tissues of all the Wisconsin river otters and most of the Michigan bald eagles. These congeners are major components of the common commercial penta-PBDE product mixture (Darnert, 2003). While penta-PBDE production has largely been regulated and phased out of the Great Lakes region, these congeners remain prevalent in the area's fish and wildlife (Gauthier et al., 2008; Gewurtz et al., 2011). Importantly and as elaborated upon below, PBDE concentrations reported here in the eagles are among the highest found in liver tissues of any wildlife. These findings indicate that mammalian and avian wildlife occupying high trophic levels within the Great Lakes region remain exposed to appreciable levels of PBDEs.

There currently is limited information on PBDE levels in mammalian wildlife (excluding marine mammals). Here we focused on the liver as it is a critical organ responsible for a majority of xenobiotic biotransformation activities. A study of otters ($n = 42$) from New Jersey, USA found seven detectable PBDEs (PBDE-47, 199, 99, 153, 154, 155, and 28); mean hepatic Σ_7 PBDE concentrations averaged 10.6 ng/g wet weight (236 ng/g lipid) (range: 0.82–436 ng/g wet weight) (Stansley et al., 2010). In mink (*Neovison vison*) trapped in the Great Lakes region, PBDE-47, 100, 99, 153 and 154 (primary components of a commercial mixture DE-71) were found in livers at concentrations that averaged 323 ng/g lipid (range: 29.4 to 2890 ng/g lipid) (Zhang et al., 2009). Both studies show somewhat similar results to the present study focused on otters from Wisconsin. These values in mink were much higher than mean hepatic Σ_7 PBDEs (2.4 ng/g lipid) in red fox (*Vulpes vulpes*) sampled in Belgium (Voorspoels et al., 2006).

Documented PBDE exposure studies in birds have largely focused on eggs and not liver (Chen et al., 2012). For eagles, we are unaware of another study reporting hepatic levels. Another study on bald eagles from the Great Lakes measured several PBDEs (PBDE-17, 28, 47, 99, 100, 153, 154, 183, 197, 207, 208, and 209) in plasma. The sum of these PBDEs averaged 5.7 ± 1.9 ng/g (range: 0.35 to 29.3 ng/g wet weight) (Venier et al., 2010). Hepatic PBDE levels in eagles from the current study can be compared to hepatic PBDE levels in other predatory birds, which reveals rather high exposures in Michigan. As examples,

sparrowhawks (*Accipiter nisus*) in Britain had liver Σ PBDE concentrations from 43.4 to 68,040 ng/g lipid (equivalent to 7.93 ng/g wet wt) (Crosse et al., 2013); cormorants (*Phalacrocorax capillatus*) in Japan had Σ PBDE levels from 330 to 2600 ng/g lipid (Watanabe et al., 2004); guillemots (*Cepphus grylle*) in Greenland had Σ PBDE levels from 0.8 to 9.5 ng/g lipid (Vorkamp et al., 2004). A study in northern China reported that livers from the common kestrel (*Falco tinnunculus*) had the highest mean PBDE value among eight predatory birds examined: 12,200 ng/g lipid with a maximum value of 40,900 (Chen et al., 2007). The current study found both mean (5274 ng/g lipid) and maximum (100,082 ng/g lipid) Σ PBDE concentrations among the highest reported for avian wildlife.

The most dominant congener measured in both otter and eagle livers was PBDE-47. These results are in accordance with levels found in salmonids, lake trout and walleye (*Sander vitreus*) in the Great Lakes (Manchester-Neesvig, et al. 2001; Gewurtz et al., 2011; Batterman et al., 2007), and plasma samples in Michigan bald eagles (Venier et al., 2010). As discussed by Chen et al. (2012), PBDE-47 is among the most common PBDE congeners due to commercial abundance and biomagnification potential. However, it is not always the most dominant PBDE congener documented in the Great Lakes region. For example, herring gulls sampled from seven Great Lakes colonies indicated that PBDE-47 accounted for 24% of the Σ_{39} PBDE measured in egg pools while PBDE-99 accounted for 36% (Gauthier et al., 2008). Differences in congener distribution may be due to interspecies differences (feeding ecology of gulls vs. eagles), sampling location, sampling year, and tissue type. Nonetheless, the most abundant PBDE congeners in Great Lakes wildlife are penta-derived. While many pentabrominated mixtures are being phased out of commercial production, other PBDE congeners and non-PBDE flame retardant levels may increase.

Following PBDE-47, the next two most abundant congeners found in both the otters and eagles studied in the current study were PBDE-99 and PBDE-100 (Tables 1 and 2). Levels of these two congeners were quite similar in the otters and eagles. This similarity has been reported by others studying Great Lakes wildlife, including salmonids (Manchester-Neesvig, et al. 2001), bald eagles (Venier et al., 2010), and herons (*Ardea herodias*) (Champoux et al., 2009). Several studies have found PBDE-99 levels at least twice as high as PBDE-100 levels, such as in brains of river otters (Basu et al., 2007), and in eggs of herring gulls (Gauthier et al., 2008), American kestrels, and European starlings (Chen et al., 2012).

The least prominent congener measured in the current study was PBDE-153. Similar findings were reported in Lake Michigan salmonids (Manchester-Neesvig, et al. 2001), Michigan bald eagles (Venier et al., 2010), Great Lakes herring gulls (Gauthier et al., 2008), and European starlings (Chen et al., 2012). It is noted, however, that this is not always the case. For example, in sparrowhawks from Great Britain, hepatic PBDE-153 levels were nearly 2-fold greater than PBDE-100 and similar in value to PBDE-47 (Crosse et al., 2013). In brains of river otters, PBDE-153 comprised 30.5% of the total (Basu et al., 2007).

A number of factors may explain why levels and ratios of PBDE congeners differ across and within a species, including variances across species and their feeding ecologies, as well as geographic study regions. As discussed by Chen et al. (2012), differences between terrestrial and aquatic ecosystems in terms of PBDE exposure may be related to, for example, varying

trophic levels and systems, food sources, as well as bioaccumulation and biomagnification potential of specific congeners. In addition, the congeners focused upon here (PBDE-47, 99, 100, and 153) are generally found in a commercially available penta-product at a ratio of 9:12:2:1, respectively (Hites, 2004). Upon entry into the ecosystem and also entry into organisms and distributions across tissues, the ratio of these congeners may change. For example, while PBDE-99 is the most prominent component of this commercial mixture, a study of common carp (*Cyprinus carpio*) documented selective elimination of PBDE-99 following exposure (Stapleton et al., 2002).

Are the PBDE exposures documented in the current study of health concern to otters and eagles from across the Great Lakes? While there is limited toxicological evidence from wildlife in general, lab-based studies on species closely related to otters and eagles demonstrate potentially harmful effects associated with exposures. Exposure of captive mink to environmentally relevant levels of DE-71 (i.e., the lowest level tested, 1 ppm in the diet, yielded similar tissues residues as we report here in otter) resulted in adverse effects on offspring development and thyroid function (Zhang et al., 2009), and immune function (Martin et al., 2007), though changes in brain cholinergic function were not found (Bull et al., 2007). In ovo exposure of American kestrels to DE-71 resulted in physiological changes, including impacts to the thyroid, metabolic, and immune systems (Ferne et al., 2005; Fernie et al., 2009). While sharing similar physiological features to otters and eagles, toxic response to such PBDE mixtures could differ within our species of interest.

There are some limitations of our work that warrant mention. As samples were collected through state programs and somewhat opportunistically, specific age and time of death for otters and eagles, both important demographic variables, were unknown. While the feeding ecology of each species is well understood, the current study would have benefited from stable isotope analyses to establish trophic status. Nonetheless, the current study helps increase our understanding of PBDE contamination and bioavailability in the Great Lakes region by focusing on two wildlife sentinels. Future research is needed to better understand the extent of contamination posed by PBDEs (and other flame retardant chemicals) within the Great Lakes ecosystem on both temporal and spatial scales. This information is especially needed given new regulations, PBDE phase-out activities, and the emergence of alternative and new flame retardant chemicals. Further, many PBDEs are bioaccumulative and toxic, and when coupled with our findings showing that Michigan eagles have among the greatest exposures, more work is needed to increase understanding of whether PBDE exposures are related with adverse effects in wildlife.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jglr.2014.12.023>.

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Fig. 1. Concentrations (ng/g wet weight) of four individual polybrominated diphenyl ether congeners (PBDE-47, -100, -99, and -153) in livers of wild river otters ($n = 35$) captured during the 2009–2010 trapping season in Wisconsin.

Fig. 2. Concentrations (ng/g wet weight) of four individual polybrominated diphenyl ether congeners (PBDE-47, -100, -99, and -153) in livers of wild bald eagles ($n = 33$) from Michigan sampled between 2009 and 2011.

Median, interquartile range (IQR), mean $\pm$ standard deviation, and range of polybrominated diphenyl ether (PBDE) congener levels (ng/g wet weight) in livers of wild river otters captured from three geographical regions of Wisconsin during the 2009–2010 trapping season.

Table 1

Sex	Regions									
	All otters (n = 35)	Male (n = 23)	Female (n = 10)	Unknown (n = 2)	North (n = 25)	Central (n = 3)	South (n = 7)			
PBDE-47	Median	5.3	4.9	5.3	4.2	9.5	12.2			
	IQR	2.7–10.4	2.7–11.9	N/A	2.1–9.3	5.6–10.4	3.9–19.4			
	Mean $\pm$ SD	9.3 $\pm$ 12.0	9.5 $\pm$ 13.1	9.7 $\pm$ 10.9	8.9 $\pm$ 13.3	8.5 $\pm$ 2.6	12.5 $\pm$ 10.1			
	Range	0.1–61.8	0.1–61.8	0.1–30.0	0.1–61.8	5.6–10.4	0.1–29.5			
PBDE-100	Median	2.2	2.3	1.1	2.1	1.0	5.4			
	IQR	0.9–4.7	1.3–5.4	0.4–3.8	N/A	0.4–4.1	2.1–7.0			
	Mean $\pm$ SD	2.9 $\pm$ 2.6	3.2 $\pm$ 2.8	2.2 $\pm$ 2.2	2.1 $\pm$ 2.8	1.8 $\pm$ 2.0	4.7 $\pm$ 2.8			
	Range	0.1–11.2	0.1–11.2	0.2–6.3	0.1–4.1	0.4–4.1	0.1–7.6			
PBDE-99	Median	2.1	2.2	2.0	2.1	0.6	2.6			
	IQR	0.5–3.2	0.6–3.2	0.4–3.3	N/A	0.4–4.0	1.4–8.9			
	Mean $\pm$ SD	2.7 $\pm$ 3.4	3.0 $\pm$ 4.0	2.1 $\pm$ 1.6	2.1 $\pm$ 2.8	1.7 $\pm$ 2.0	5.3 $\pm$ 6.9			
	Range	0.1–18.9	0.1–18.9	0.2–5.1	0.1–4.0	0.4–4.0	0.1–18.9			
PBDE-153	Median	0.3	0.3	0.9	0.2	0.3	2.0			
	IQR	0.2–1.7	0.2–2.5	0.3–1.8	N/A	0.1–0.4	0.3–3.4			
	Mean $\pm$ SD	1.4 $\pm$ 2.3	1.6 $\pm$ 2.7	1.2 $\pm$ 1.2	0.2 $\pm$ 0.1	0.3 $\pm$ 0.2	2.0 $\pm$ 1.7			
	Range	0.1–12.2	0.1–12.2	0.2–3.8	0.1–0.3	0.1–3.4	0.1–4.4			
Σ_4 PBDE	Median	11.3	11.3	11.0	9.7	11.3	26.1			
	IQR	5.6–18.9	5.6–23.5	3.7–20.1	N/A	6.7–18.9	8.5–41.0			
	Mean $\pm$ SD	16.3 $\pm$ 16.4	17.3 $\pm$ 18.0	15.2 $\pm$ 14.4	9.7 $\pm$ 13.0	12.3 $\pm$ 6.2	24.4 $\pm$ 16.4			
	Range	0.5–72.9	0.5–72.9	1.2–42.4	0.5–18.9	6.7–18.9	0.5–42.0			

Table 2

Median, interquartile range (IQR), mean $\pm$ standard deviation, and range of polybrominated diphenyl ether (PBDE) congener levels (ng/g wet weight) in livers of wild bald eagles captured from Michigan between 2009 and 2011.

Sex	Regions									
	All eagles (n = 33)	Male (n = 10)	Female (n = 19)	Unknown (n = 4)	Upper (n = 16)	Lower (n = 13)	Unknown (n = 1)			
PBDE-47	Median	8.8	10.4	7.8	9.5	7.2	10.2	12.8		
	IQR	3.3–15.6	5.5–18.1	1.7–14.5	1.7–28.4	0.9–16.3	3.2–15.6	7.6–113.3		
	Mean $\pm$ SD	37.6 $\pm$ 132.1	23.4 $\pm$ 43.7	49.6 $\pm$ 172.2	16.5 $\pm$ 21.1	9.2 $\pm$ 6.4	62.8 $\pm$ 187.3	44.6 $\pm$ 68.1		
	Range	0.0–758.1	0.4–146.6	0.0–758.1	0.0–47.2	0.0–18.2	0.2–758.1	6.1–146.6		
PBDE-100	Median	3.7	4.6	3.5	5.5	2.4	4.7	8.5		
	IQR	1.2–7.6	2.1–6.9	0.7–7.4	0.5–24.2	0.4–8.0	2.0–6.5	3.9–23.5		
	Mean $\pm$ SD	14.0 $\pm$ 48.4	6.6 $\pm$ 8.1	18.7 $\pm$ 63.6	10.1 $\pm$ 13.4	4.3 $\pm$ 2.8	23.9 $\pm$ 69.3	12.0 $\pm$ 11.3		
	Range	0.0–280.6	0.4–28.3	0.0–280.6	0.0–29.3	0.0–8.7	0.1–280.6	2.5–28.3		
PBDE-99	Median	3.4	3.5	3.4	4.8	2.8	4.1	5.8		
	IQR	1.1–7.0	2.0–7.3	0.6–5.1	0.7–20.4	0.5–4.8	1.9–7.3	3.1–26.6		
	Mean $\pm$ SD	14.1 $\pm$ 51.2	6.5 $\pm$ 9.7	19.2 $\pm$ 67.3	8.7 $\pm$ 11.3	4.1 $\pm$ 2.9	24.2 $\pm$ 73.4	11.8 $\pm$ 14.4		
	Range	0.0–296.8	0.4–33.2	0.0–296.8	0.0–25.0	0.0–8.8	0.1–296.8	2.5–33.2		
PBDE-153	Median	1.1	1.8	8-Jan	1.0	0.88	1.1	2.1		
	IQR	0.2–2.3	0.7–3.2	0.0–2.3	0.2–13.0	0.0–3.5	0.3–2.3	1.1–20.8		
	Mean $\pm$ SD	8.6 $\pm$ 35.4	4.3 $\pm$ 8.1	11.7 $\pm$ 46.4	4.8 $\pm$ 8.2	1.2 $\pm$ 1.0	15.8 $\pm$ 50.5	8.0 $\pm$ 12.6		
	Range	0.0–203.4	0.0–26.8	0.0–203.4	0.0–17.0	0.0–2.7	0.0–203.4	0.9–26.8		
Σ_4 PBDE	Median	21.2	22.9	16.5	20.8	13.7	23.4	28.9		
	IQR	5.7–28.9	10.8–29.9	4.3–27.4	3.1–96.1	1.9–28.0	9.2–26.6	16.6–183.5		
	Mean $\pm$ SD	74.3 $\pm$ 266.7	40.8 $\pm$ 69.0	99.2 $\pm$ 349.4	40.0 $\pm$ 53.6	18.8 $\pm$ 11.0	126.8 $\pm$ 380.3	76.4 $\pm$ 106.0		
	Range	0.0–1538.8	1.1–235.0	0.0–1538.8	0.0–118.5	0.0–32.2	0.3–1538.9	12.5–234.5		

Table 3

Pearson correlations of hepatic polybrominated diphenyl ether (PBDE) congeners of wild river otters ($n = 35$) captured during the 2009–2010 trapping season in Wisconsin. Values indicate Pearson coefficient (r_p) and all are statistically significant ($p < 0.005$).

	PBDE-47	PBDE-100	PBDE-99	PBDE-153
PBDE-47	1			
PBDE-100	0.694	1		
PBDE-99	0.634	0.895	1	
PBDE-153	0.463	0.540	0.574	1

Table 4

Pearson correlations of hepatic polybrominated diphenyl ether (PBDE) congeners of wild bald eagles ($n = 33$) from Michigan sampled between 2009 and 2011. Values indicate Pearson coefficient (r_p) and all are statistically significant ($p < 0.001$).

	PBDE-47	PBDE-100	PBDE-99	PBDE-153
PBDE-47	1			
PBDE-100	0.952	1		
PBDE-99	0.929	0.957	1	
PBDE-153	0.857	0.859	0.897	1