

DISTRIBUTION OF POLYBROMINATED DIPHENYL ETHERS IN FISH TISSUES FROM THE PEARL RIVER DELTA, CHINA: LEVELS, COMPOSITIONS, AND POTENTIAL SOURCES

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Abstract—Fish tissues from three different farming types (freshwater farmed, seawater farmed, and seawater wild fish collected from the Pearl River Delta of South China), including skin, gills, gastrointestinal tract (GIT), liver, and muscle, were analyzed for polybrominated diphenyl ethers (PBDEs). In general, the dry weight based concentrations of Σ_{10} PBDE (sum of BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, and -183) in fish tissues followed the sequence of liver > gill > skin > GIT and muscle. The BDE congener profiles varied with fish species. Decabrominated diphenyl ether was detected in 37.4% of the total 187 samples, and this ratio may actually have been underestimated because the reporting limit for BDE-209 was considerably higher than those for other congeners. Decabrominated diphenyl ether was the dominant BDE congener in skin and GIT, and less abundant in gills, muscle, and liver. Except for skin, no significant difference in BDE-209 lipid-normalized concentrations was observed among fish tissues. These results from most previous studies that reported low bioaccumulative potential of BDE-209. Combined with the likelihood that BDE-209 can be debrominated into lower brominated congeners that tend to be more toxic than BDE-209, the abundant occurrence of BDE-209 could continue to pose prolonged health risk to the ecological environment.

Keywords-Polybrominated diphenyl ethers Tissue distribution Fish Bioaccumulation China

INTRODUCTION

Since the 1970s, brominated fire retardants (BFRs) have been widely used as additives in a variety of manufacturing processes. Of the 75 different types of BFRs, polybrominated diphenyl ethers (PBDEs) have received the most attention. As a result of the widespread use of BFRs, PBDEs have been found in almost all natural media including air [1], sediments [2], biota [3], polar bear liver [4,5], and even in human adipose tissue, blood, and milk [6–9]. Polybrominated diphenyl ethers are structurally similar to classic persistent organic pollutants, but they are more hydrophobic as the K_{ow} values of PBDEs are approximately one to several orders of magnitude greater than those of typical persistent organic pollutants.

Polybrominated diphenyl ethers are known to bioaccumulate in aquatic organisms. Different PBDEs profiles have been found in organisms of high trophic levels, while similar profiles have been obtained in organisms of low trophic levels and in sediments [10,11]. These results can be attributed to different metabolic and bioaccumulative abilities among species, in addition to different exposure processes. Highly brominated BDE congeners, e.g., BDE-209, were expected to have low availability for biological uptake due to their strong affiliation to the solid phase and large molecular sizes. However, BDE-209 was found in some biota in recent years [11], especially in organisms in lower trophic levels such as mussels in marine environments heavily polluted with BDE-209 [12]. Whether and how highly brominated PBDEs are bioaccumulated by aquatic biota has become a hotly debated topic in recent years. Low dietary uptake efficiency of BDE-209 was achieved in laboratory experiments using fish species, and several lower debrominated metabolic congeners were detected [13,14]. Other experiments suggest that BDE congeners (including BDE-99, -183, and -209) were debrominated into less brominated congeners in fish species upon dietary exposure [15–17]. Despite these previous efforts, bioaccumulation and debromination of PBDEs in biota have remained largely unclear. Because most previous studies have focused on fish muscle and liver, the available data are limited in addressing these issues.

The present study, through a detailed analysis of PBDE concentrations and compositional profiles in various tissues of freshwater fish and seawater wild and farmed fish, aimed to further our understanding of bioaccumulation and biotransformation of PBDEs in fish species, particularly the highly brominated congeners. Specifically, fish samples collected from the Pearl River Delta (PRD) within Guangdong Province, South China, were analyzed for BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, -183, and -209. The PRD houses a vast number of manufacturing plants that are heavy users of BFRs and has been importing large quantities of electronic wastes. It is hypothesized that abundant PBDEs, especially deca-BDE, are widespread in the environment of the PRD [18,19].

MATERIALS AND METHODS

Sample preparation and extraction

The sampling method was detailed by Meng et al. [20]. Forty individual fish were chosen from the previous samples, based on the occurrence of PBDEs, fish farming type, and living and feeding habits of fish species (Table S1, "S" des-

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ignates tables and figures in the Supplemental Data thereafter; all found at http://dx.doi.org/10.1897/07-366.S1). The species under consideration include three freshwater farmed fish, bighead carp (Aristichthys nobilis), mandarin fish (Siniperca chuatsi), and northern snakehead (Nemipterus virgatus), one seawater farmed fish, crimson snapper (Lutjanus erythropterus), and one wild marine fish, golden thread (Nemipterus virgatus), with eight individuals from each species. Fish individuals were thawed and dissected carefully to obtain samples of gastrointestinal tract (GIT), muscle, gills, liver, and skin. Approximately 20 g (wet wt) of fish muscle was taken from the fish back. Skin (without muscle layer and squama) was taken from both sides of the fish back. All GITs were cut open, and food, digest fluid, and fat around GIT were cleared. Gills and livers were washed to clear sediment and blood. Overall, 187 samples were acquired and they were processed according to the method of Meng et al. [20]. Lipid contents were determined gravimetrically using 20% of the extraction before processing on a gel permeation chromatography column in all the samples. Because the lipid contents in fish skin were extremely low (muscle on skin was razed off), the muscle lipid content was taken as the skin lipid content if the measured skin lipid content was lower than that in muscle.

Instrumental analysis

Procedures were performed in accordance with Mai et al. [18]. Polybrominated diphenyl ethers were measured with a Shimadzu Model 2010 gas chromatograph coupled with a model QP2010 mass spectrometer (Shimadzu, Kyoto, Japan) using negative chemical ionization in the selected ion monitoring mode. A DB-XLB (30 m \times 0.25 mm inner diameter, 0.25 µm film thickness) capillary column (J&W Scientific, Folsom, CA, USA) was used for the determination of BDE congeners except for BDE-209. For BDE-209, a CP-Sil 13 CB $(12.5 \text{ m} \times 0.25 \text{ mm} \text{ inner diameter, } 0.2 \text{ }\mu\text{m} \text{ film thickness})$ capillary column (Varian, Palo Alto, CA, USA) was used as the same detected method as other PBDEs. The reporting limits for all tri- to hepta-BDEs congeners and BDE-209 were 0.2 and 10 ng/g, respectively, for 1 g of dry sample. All reported data were normalized to dry sample weight except where indicated.

Quality assurance/quality control

For each batch of 20 fish samples, a procedural blank, a spiked blank, a matrix spiking sample, and a matrix spiking duplicate were processed. The spiked samples contained 10 PBDE congeners (BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, and -183). The recoveries of surrogate standards ¹³C-polychlorinated biphenyls-141 and polychlorinated biphenyls-209 in the procedural blank, spiked blank, matrix spiking duplicated, and fish samples were $67.6 \pm 32.9/57.0 \pm 24.2$ (mean \pm standard deviation), 78.4 \pm 23.4/61.2 \pm 15.0, 109.2 \pm 27.5/82.9 \pm 22.5, and 92.8 \pm 25.3/72.2 \pm 19.5%, respectively. The average recoveries of spiked BDE congeners in spiked blank and matrix spiking duplicate samples were 84.0 \pm 22.8 and 76.3 \pm 38.6% respectively. Low concentrations of BDE-47 were found in procedural blanks, which were either lower or slightly higher than the reporting limit, but were much lower than those in samples. For BDE-209, no significant signal was found in procedural blanks. Hence, blank values were not subtracted from the sample measurements. Reported concentrations were not surrogate recovery corrected.



Fig. 1. Concentrations (ng/g dry wt) of the sum of brominated diphenyl ether-28, -47, -66, -85, -99, -100, -138, -153, -154, and -183 in different fish tissues. The error bars represent the standard deviation of the means. GIT = gastrointestinal tract.

Data analysis

The sum of BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, and -183 was designated as Σ_{10} PBDE, and the sum of Σ_{10} PBDE and BDE-209 was designated as Σ_{11} PBDE. For samples with PBDE concentrations below the reporting limits, zero was used for calculation. Mann–Whitney *U* and Kruskal–Wallis nonparametric tests were used to compare the difference between two independent samples and among more than two samples, respectively. Statistical significance was defined at *p* < 0.05. All these analyses were conducted using SPSS[®] Version 13.0 (SPSS, Chicago, IL, USA).

RESULTS AND DISCUSSION

PBDE levels in fish tissues

Polybrominated diphenyl ethers were detected in all tissue samples and the data are summarized in Table S2 (http://dx. doi.org/10.1897/07-366.S1). The Σ_{10} PBDE concentration range in liver, gills, skin, GIT, and muscle were 0.25 to 21.0, 0.02 to 6.99, 0.13 to 27.4, 0.07 to 5.95, and 0.01 to 3.65 ng/g, with median concentrations of 3.20, 0.78, 0.95, 1.77, and 0.46 ng/g, respectively, when all fish species were considered. Generally, liver samples contained the highest Σ_{10} PBDE levels among all fish species, followed by gills, skin, GIT, and muscle with a few exceptions (Fig. 1). For example, the levels of Σ_{10} PBDE in golden thread followed the sequence of skin > liver > gills > GIT and muscle, and the levels of Σ_{10} PBDE in GIT of bighead carp were higher than those in gills and skin. In addition, the residual levels of PBDEs (sum of the average Σ_{10} PBDE concentrations in liver, gills, skin, GIT, and muscle) in bighead carp, mandarin fish, northern snakehead, crimson snapper, and golden thread were 5.2, 9.7, 13.0, 18.8, and 11.8 ng/g, respectively. Seawater farmed fish tend to have higher PBDE concentrations than marine wild fish, consistent with the results from a global comparison of farmed and wild salmon [21]. The lowest concentration of PBDEs found in bighead carp may be attributed to its feeding habits, which differ substantially from those of the other four carnivorous fish species.



Fig. 2. Relative abundances of brominated diphenyl ether (BDE) congeners (compared to the sum of BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, and -183) in different fish tissues. GIT = gastrointestinal tract.

Congener profile in fish tissues

Only BDE-47 was detectable in all samples in terms of individual BDE congeners, and the detection frequency for BDE-28, -66, -85, -99, -100, -138, -153, -154, -183, and -209 was 90.3, 67.4, 18.7, 74.8, 82.4, 11.2, 62.6, 85.6, 54.0, and 37.4%, respectively. Figure 2 shows the relative abundances (to Σ_{10} PBDE) of eight BDE congeners (without BDE-85 and BDE-138 because of their low occurrence and concentration) in different tissues of five fish species. Clearly, BDE-47, -28, -100, and -154 were the dominant congeners in freshwater fish, while all but BDE-183 were considerably more abundant in seawater farmed fish. For seawater wild fish, BDE-47, -99, -100, and -154 were the main congeners in all tissues except for GIT. If fish of different farming types are compared, high relative abundances (to Σ_{10} PBDE) of BDE-99, -66, and -100 were found in seawater fish, while high abundances of BDE-47 and BDE-28 were found in freshwater farmed fish. Additionally, skins in mandarin fish, bighead carp, and golden thread had high abundances of BDE-85, -138, and -183. The difference of congener profiles among fish species may be attributed to different fish habitats, feeding habits, metabolizing ability, or bioaccumulative potentials. However, the abundance patterns were quite similar among tissues of each fish

species (Fig. 2), which may suggest that the PBDEs congener profiles in the natural environment are well reflected in any fish tissue.

Brominated diphenyl ether-47 was the most predominant congener besides BDE-209 in all tissue samples, with concentrations ranging from 0.03 ng/g in bighead carp gills to 14.7 ng/g in golden thread skins (Fig. 2 and Table S2; http://dx.doi.org/10.1897/07-366.S1). This result was in agreement with the results of previous studies [20,21]. Besides, BDE-28 was the second most abundant congener next to BDE-47 in all tissues of freshwater-farmed fish (Fig. 2 and Table S2; http://dx.doi.org/10.1897/07-366.S1). The relative abundance of BDE-28 (to Σ_{10} PBDE) varied with fish species; for example, it was greater than 12%, slightly higher than 7%, and below 5% in all tissues of northern snakehead, crimson snapper, and golden thread, respectively. Moreover, the relative abundances of BDE-28 were similar in individual tissues of each fish species (p > 0.05), especially in tissues of crimson snapper (7.2 \pm 0.2%), except for mandarin fish (p < 0.05). In addition, the relative abundances of BDE-99 were the same as or higher than those of BDE-100 in skins of all fish species, but lower than those of BDE-100 in other tissues, especially in freshwater farmed fish species (Fig. 2). It may have been attributed to the lower content of BDE-99 metabolizing enzymes in skin than in other tissues.

Stapleton et al. [16] observed substantial debromination of BDE-99 to BDE-47 in caged carp following dietary exposure. Previous studies also used the BDE-47/BDE-99 ratio to describe the biotransformation of BDE-99 in different organisms collected from the same surroundings [12,22], and marked different values of the ratio among logical species of the St. Lawrence Estuary (downstream of the Great Lakes, USA) food web were obtained. The depletion of the BDE-99 concentration in some fish samples suggested that certain marine organisms possess the capacity to eliminate this specific congener. In the present study, the ratio of BDE-47/BDE-99 in different tissues was quite similar in seawater fish but different in freshwater fish. For example, the lowest value was found in skin, and higher values occurred in GIT and muscle of bighead carp and mandarin fish, or in liver and gills of northern snakehead. On the other hand, the levels of BDE-99 were substantially higher than those of BDE-47 in sediments [18], but were only slightly higher in the atmosphere [19] and riverine runoff of the PRD [23]. In addition, experiments demonstrated that the assimilation efficiency and biomagnification factor of BDE-99 are quite similar or slightly lower than those of BDE-47, despite their different effective cross sections and molecular weights [13,24]. Therefore, significantly lower BDE-99 concentrations compared to BDE-47 and different ratios of BDE-47/BDE-99 in fish species or tissues may be partly due to different metabolizing capabilities of fish species or tissues for BDE-99. Moreover, the ratio of BDE-47/BDE-100 did not vary much with different tissues of each fish species, e.g., it was slightly higher in freshwater fish (9.8 \pm 2.6) than in seawater fish (6.0 \pm 1.3). Similar results were also obtained by other studies [12,22].

Potential input sources of PBDEs to freshwater fish ponds

Fish skin is directly in contact with the living environment, and the above discussion of relative abundances of BDE congeners to Σ_{10} PBDE in different fish tissues demonstrates that the state of the natural environment is well reflected in any fish tissue. In light of this, skin is a sensitive indicator of environmental conditions. Because three different freshwater fish species, including filter-feeding and carnivorous species, were analyzed, the relationships among BDE congeners in skins of freshwater fish, species could be further examined using Pearson correlation analysis (Table S3; http://dx.doi. org/10.1897/07-366.S1) to determine possible sources of PBDEs to freshwater fish ponds in the PRD. Significant linear correlations were present among BDE-28, -47, -66, -85, -100, -153, and -154, and between BDE-153 and BDE-183 (p < 0.05), while no significant relationship was found between BDE-209 and other congeners (p > 0.05) except for BDE-183. This indicates that the penta-, octa-, and deca-BDE commercial formulas are all possible original sources of PBDEs to freshwater fish ponds in the PRD. A recent study also found that all the three commercial formulas were the potential sources for PBDEs in the atmosphere of Guangzhou, a metropolitan center in the PRD [19].

Occurrence of BDE-209

Decabrominated diphenyl ether is the major component (>96%) in the deca-BDE technical formula [25]. Unlike the penta- or octa-BDE technical mixtures that have been banned in Europe and the United States, deca-BDE is still in use worldwide, except for some U.S. states and Sweden. Although BDE-209 is thought to be less toxic than other lower brominated congeners, it can be debrominated by ultraviolet light [26] or by microorganisms [27] to lower brominated congeners. Therefore the fate and transformation of BDE-209 in environmental compartments have become a serious concern and merit more investigations. On the other hand, because BDE-209 is extremely hydrophobic (log $K_{\rm OW} \sim 10$) and bulky [28], it has been suggested that BDE-209 is low in bioavailability. However, previous studies concluded that high laboratory background [11] and inappropriate gas chromatographic techniques could result in erratic results, e.g., BDE-209 would degrade in the chromatographic column if the run time was too long [29] or column temperature was too high [11]. In addition, the reporting limit or detection limit for BDE-209 was usually much higher than those for other lower brominated BDE congeners in previous studies (Table 1). Therefore, the low detection rates for BDE-209 observed in previous studies [11,30] could have been due to experimental artifacts rather than the low bioavailability of BDE-209 as widely perceived.

In the present study, BDE-209 was detected in 70 of the total 187 samples with a range of 0.39 to 59.9 ng/g normalized by dry weight (Table S2; http://dx.doi.org/10.1897/07-366. S1), which were attributed to 22 skin, 18 gills, 11 GIT, 8 liver, and 11 muscle samples, respectively. However, this detection frequency was likely underestimated due to the much higher reporting limit for BDE-209 (10 ng/g) than that for other lower brominated BDE congeners (0.2 ng/g). As a result, the discussion herein should be applied to most samples analyzed in the present study. As shown in Figure 3a, BDE-209 was the dominant congener (to Σ_{11} PBDE) in the skin of mandarin fish and bighead carp, and the ratios (to Σ_{11} PBDE) in most fish species followed the sequence of skin, gills > GIT, muscle >liver. As the sequence of BDE-209 ratios (to Σ_{11} PBDE) in five tissue types did not change much with fish species, all data for individual tissue types were pooled together for further assessment (Fig. 3b). The highest and lowest BDE-209 ratios (to Σ_{11} PBDE) were found in skin and liver, respectively (mean/ maximum of 48.0/99.2% in skin and 8.2/83.3% in liver), and no significant differences of this ratio were found among fish

tissue, except for skin (p > 0.1). In addition, the highest and lowest BDE-209 concentrations occurred in skin and liver, with the median levels of 95.5 and 2.54 ng/g lipid weight, respectively (Fig. 3c). This may be attributed to the fact that liver is a primary tissue for biotransformation of organic compounds and BDE-209 has a low half-life time [14]. Our results were different from those obtained by some other previous studies, most likely due to different exposure processes [11,13,17] in which the highest BDE-209 level was usually detected in liver among fish tissues.

Decabrominated diphenyl ether is of special interest because it has been expected to have low bioavailability due to its large molecular size, and numerous previous studies reported nondetection of BDE-209 in aquatic biota (Table 1). However, some dietary experiments with fish species suggested that BDE-209 was bioaccumulative (Table 1). For example, 3.2% of total BDE-209 was accumulated by juvenile rainbow trout, which were fed at a rate of 1% of body weight per day with spiked food of 940 \pm 14 ng/g wet weight [17]. After 56 d of feeding with spiked food containing BDE-209 at 27.5 ng/g dry weight, juvenile lake trout were found to contain BDE-209 at 200 ng/g dry weight [14]. Decabrominated diphenyl ether was also found in organisms collected both from aquatic and terrestrial environments (Table 1). For example, BDE-209 was detected in 45.6% of the total 83 biota samples, and was the dominant BDE congeners in some fish species collected from the Pearl River estuary [31]. Extremely high levels of BDE-209 (2,150 \pm 1,040 and 2,870 \pm 1,930 ng/g lipid wt in muscle and liver of common kestrels, respectively) were detected in birds from northern China [32]. These results and the results from the present study suggest that BDE-209 may in fact be considerably bioaccumulative in both terrestrial and aquatic species, especially in biota from deca-BDE heavily polluted areas such as the PRD. The perception on the bioavailability of BDE-209 may need to be re-examined thoroughly.

It is worthwhile to note that, except for skin, no significant differences in the ratios of BDE-209 to Σ_{11} PBDE or BDE-209 concentrations were observed among gills, GIT, liver and muscle when BDE-209 concentrations were lipid normalized (p > 0.05). The extremely high concentration of BDE-209 in skin may be attributed to its low lipid content (Fig. S1; http://dx. doi.org/10.1897/07-366.S1). Clearly, as discussed in other previous studies [17,33], there was no correlation between BDE-209 concentration and the lipid content. Experiments of dietary uptake of BDE-209 by fish [13,17] or by rats [33,34] showed that the highest concentrations of BDE-209 occurred in plasma and blood-enriched tissues such as the liver. However, the BDE-209 concentrations in muscle, gills, and GIT were as high as those in liver in the present study, which may be indicative of the complexity in natural environments and food matrices as compared to controlled laboratory conditions. The distribution of BDE-209 in fish was likely dependent on the transport with lipid and/or proteins [24], and BDE-209 was distributed quickly to plasma and blood-enriched tissue, but slowly to adipose tissue in rats [33,34]. The reason for the high abundances of BDE-209 in low lipid tissues such as skin and muscle from the present study has yet to be clarified. Moreover, studies showed that hydrophobic organic compounds with effective cross sections >9.5 Å were considered unavailable for uptake through fish gills or GIT because the permeation through the membranes of the tissues was prevented [35,36]. However, the present study suggests that BDE-

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Location	Biota	BDE-209	LOD or RL	Reference
The PRD, China ⁴ Lab, (deca-BDE) Lab, (BDE-209) Lab, (BDE-209) Lab, (BDE-209) Western Scheldt Estuary, Europe The Ebro River, Spain United Kingdom United Kingdom United States Coastal water of Florida Demark North China South China South China Hong Kong	Fish tissue Rainbow trout Carp Lake trout Rainbow trout Invertebrate, fish Fish, shellfish Fish, shellfish Feral carp Fish Blue mussels Blue mussels Blue mussels Birds Eggs of waterbirds Fish Mussel	ND-59.9 ng/g dry wt Muscle 38 ng/g, liver 870 ng/g wet wt (0.02–0.13% was accumulated) ND (0.44% was accumulated and 7 products were detected) 200 ng/g dry wt 3.2% was accumulated Liver 3.4–37.2 ng/g wet wt ND ND ND ND ND ND ND ND ND Muscle 2.150 \pm 1,040, liver 2.870 \pm 1,930 lipid wt ND Muscle 2.150 \pm 1,040, liver 2.870 \pm 1,930 lipid wt ND–290 ng/g lipid wt ND–220 ng/g lipid wt ND–220 ng/g lipid wt	0.2 ng/g, ^b 10.0 ng/g, ^c dry wt 1.0 ng/g, ^d wet wt 	The present study [13] [14] [17] [17] [17] [17] [17] [17] [17] [17
^a PRD = Pearl River Delta, China	-			

^b RLs of BDE congeners except for BDE-209. ^c RLs of BDE-209. ^d LOD for all BDE congeners. ^e LODs for all BDE congeners except for BDE-209. ^f LODs for BDE-209.



Fig. 3. Relative abundances of brominated diphenyl ether-209 (BDE-209) (compared to the sum of BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, -183, and -209) in (**A**) tissues of mandarin fish, northern snakehead, bighead carp, golden thread and crimson snapper; (**B**) individual tissues pooled from mandarin fish, northern snakehead, bighead carp, golden thread and crimson snapper; and (**C**) concentrations of BDE-209 in individual tissues pooled from mandarin fish, northern snakehead, bighead carp, golden thread and crimson snapper; The error bars represent the standard deviation of the means. GIT = gastrointestinal tract.

209 could be accumulated in gills and GIT, as also demonstrated by Burreau et al. [24], since the BDE-209 concentrations based on lipid weight in gills and GIT from the present study were actually slightly higher than those in liver and muscle.

CONCLUSIONS

The Pearl River Delta, China, is located in a subtropical zone with heavy PBDE pollution stemming mainly from electronics and other manufacturing booms and electronic-waste dismantling activities. Although there have been considerable efforts to characterize the occurrence of PBDEs in the PRD, the present study was the first of its kind to examine the distribution of PBDEs in various tissues of fish collected locally. In particular, the occurrence of BDE-209, a major component in the deca-BDE technical mixture heavily used in the PRD, was thoroughly examined in fish tissues. The results suggested that BDE-209 is accumulative in fish tissues under natural environments, which is somewhat inconsistent with the prevailing notion that BDE-209 has low bioavailability, but consistent with increasing evidence that BDE-209 can be bioaccumulated in aquatic and terrestrial species. Amid the continuing use of BDE-209 worldwide, except for some U.S. states (e.g., California), and Sweden, the results from the present study point to the need to further assess the environmental fate of BDE-209, particularly its accumulation in biological species and humans.

SUPPORTING INFORMATION

Table S1. Fish samples selected from a previous study.

Table S2. Concentration of PBDEs in fish tissue for each fish species (mean + SD, ng/g dry wt).

Table S3. Pearson coefficients for PBDEs in skin of freshwater farmed fish specie.

Figure S1. Lipid percentages in different tissues of each fish species. The error bars were mean levels with standard deviation.

All found at DOI: 10.1897/07-366.S1 (117 KB PDF).

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REFERENCES

- Strandberg B, Dodder NG, Basu I, Hites RA. 2001. Concentrations and spatial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes air. *Environ Sci Technol* 35:1078–1083.
- Song WL, Ford JC, Li A, Mills WJ, Buckley DR, Rockne KJ. 2004. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 1. Lake Superior. *Environ Sci Technol* 38:3286– 3293.
- Sellström U, Kierkegaard A, de Wit C, Jansson B. 1998. Polybrominated diphenyl ethers and hexabromocycododecane in sediment and fish from a Swedish river. *Environ Toxicol Chem* 17: 1065–1072.
- Kannan K, Yun SH, Evans TJ. 2005. Chlorinated, brominated, and perfluorinated contaminants in livers of polar bears from Alaska. *Environ Sci Technol* 39:9057–9063.
- Muir DCG, Backus S, Derocher AE, Dietz R, Evans TJ, Gabrielsen GW, Nagy J, Norstrom RJ, Sonne C, Stirling I, Taylor MK, Letcher RJ. 2006. Brominated flame retardants in polar bears (*Ursus maritimus*) from Alaska, the Canadian Arctic, East Greenland, and Svalbard. *Environ Sci Technol* 40:449–455.
- Frkovic A, Zivkovic A, AlebicJuretic A. 1996. Organochlorine pesticide residues and polychlorinated biphenyls in human milk from northern Adriatic region (Croatia). *Fresenius Environ Bull* 5:474–481.
- Darnerud PO, Atuma S, Aune M, Cnattingius S, Wernroth ML, Wicklund-Glynn A. 1998. Polybrominated diphenyl ethers (PBDEs) in breast milk from primiparous women in Uppsala county, Sweden. Organohalogen Compounds 35:411–414.
- Atuma SS, Hansson L, Johnson H, Slorach S, deWit CA, Lindstrom G. 1998. Organochlorine pesticides, polychlorinated biphenyls and dioxins in human milk from Swedish mothers. *Food Additives and Contamination* 15:142–150.
- Kim BH, Ikonomou MG, Lee SJ, Kim HS, Chang YS. 2005. Concentrations of polybrominated diphenyl ethers, polychlorinated dibenzo-p-dioxins and dibenzofurans, and polychlorinated

biphenyls in human blood samples from Korea. *Sci Total Environ* 336:45–56.

- Liu Y, Zheng GJ, Yu H, Martin M, Richardson BJ, Lam MHW, Lam PKS. 2005. Polybrominated diphenyl ethers (PBDEs) in sediments and mussel tissues from Hong Kong marine waters. *Mar Pollut Bull* 50:1173–1184.
- Voorspoels S, Covaci A, Schepens P. 2003. Polybrominated diphenyl ethers in marine species from the Belgian North Sea and the western Scheldt estuary: Levels, profiles, and distribution. *Environ Sci Technol* 37:4348–4357.
- Labandeira A, Eljarrat E, Barceló D. 2007. Congener distribution of polybrominated diphenyl ethers in feral carp (*Cyprinus carpio*) from the Llobregat River, Spain. *Environ Pollut* 146:188–195.
- Kierkegaard A, Balk L, Tjärnlund U, De Wit CA, Jansson B. 1999. Dietary uptake and biological effects of decabromodiphenyl ether in rainbow trout (*Oncorhynchus mykiss*). *Environ Sci Technol* 33:1612–1617.
- Tomy GT, Palace VP, Halldorson T, Braekevelt E, Danell R, Wautier K, Evans B, Brinkworth L, Fisk AT. 2004. Bioaccumulation, biotransformation, and biochemical effects of brominated diphenyl ethers in juvenile lake trout (*Salvelinus namaycush*). *Environ Sci Technol* 38:1496–1504.
- Stapleton HM, Alaee M, Letcher RJ, Baker JE. 2004. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (*Cyprinus carpio*) following dietary exposure. *Environ Sci Technol* 38:112–119.
- 16. Stapleton HM, Letcher RJ, Baker JE. 2004. Debromination of polybrominated diphenyl ether congeners BDE 99 and BDE 183 in the intestinal tract of the common carp (*Cyprinus carpio*). *Environ Sci Technol* 38:1054–1061.
- Stapleton HM, Brazil B, Holbrook RD, Mitchelmore CL, Benedict R, Konstantinov A, Potter D. 2006. In vivo and in vitro debromination of decabromodiphenyl ether (BDE 209) by juvenile rainbow trout and common carp. *Environ Sci Technol* 40: 4653–4658.
- Mai BX, Chen SJ, Luo XJ, Chen LG, Yang QS, Sheng GY, Peng PA, Fu JM, Zeng EY. 2005. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environ Sci Technol* 39:3521–3527.
- Chen LG, Mai BX, Bi XH, Ran Y, Luo XJ, Chen SJ, Sheng GY, Fu JM, Zeng EY. 2006. Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China. *Environ Sci Technol* 40:709–714.
- Meng X-Z, Zeng EY, Yu L-P, Mai B-X, Luo X-J, Ran Y. 2007. Persistent halogenated hydrocarbons in consumer fish of China: Regional and global implications for human exposure. *Environ Sci Technol* 41:1821–1827.
- Hites RA, Foran JA, Schwager SJ, Knuth BA, Hamilton MC, Carpenter DO. 2004. Global assessment of polybrominated diphenyl ethers in farmed and wild salmon. *Environ Sci Technol* 38:4945–4949.
- Law RJ, Alaee M, Allchin CR, Boon JP, Lebeuf M, Lepom P, Stern GA. 2003. Levels and trends of polybrominated diphenylethers and other brominated flame retardants in wildlife. *Environ Int* 29:757–770.
- Guan Y-F, Wang J-Z, Ni H-G, Luo X-J, Mai B-X, Zeng EY. 2007. Riverine inputs of polybrominated diphenyl ethers from the Pearl River Delta (China) to the coastal ocean. *Environ Sci Technol* 41:6007–6013.
- 24. Burreau S, Axelman J, Broman D, Jakobsson E. 1997. Dietary uptake in pike (*Esox lucius*) of some polychlorinated biphenyls,

polychlorinated naphthalenes and polybrominated diphenyl ethers administered in natural diet. *Environ Toxicol Chem* 16:2508–2513.

- La-Guardia MJ, Hale RC, Harvey E. 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ Sci Technol* 40:6247–6254.
- Söderström G, Sellström U, de Wit CA, Tysklind M. 2004. Photolytic debromination of decabromodiphenyl ether (BDE 209). *Environ Sci Technol* 38:127–132.
- Zennegg M, Kohler M, Gerecke AC, Schmid P. 2003. Polybrominated diphenyl ethers in whitefish from Swiss lakes and farmed rainbow trout. *Chemosphere* 51:545–553.
- Darnerud PO, Eriksen GS, Jóhannesson T, Larsen PB, Viluksela M. 2001. Polybrominated diphenyl ethers: Occurrence, dietary exposure, and toxicology. *Environ Health Perspect* 109:49–68.
- Watanabe I, Tatsukawa R. 1987. Formation of brominated dibenzofurans from the photolysis of flame retardant decabromobiphenyl ether in hexane solution by UV and sun light. *Bull Environ Contam Toxicol* 39:953–959.
- Dodder NG, Strandberg B, Hites RA. 2002. Concentrations and spatial variations of polybrominated diphenyl ethers and several organochlorine compounds in fishes from the northeastern United States. *Environ Sci Technol* 36:146–151.
- Xiang C-H, Luo X-J, Chen S-J, Yu M, Mai B-X, Zeng EY. 2007. Polybrominated diphenyl ethers in the biota and sediments of the Pearl River Estuary, South China. *Environ Toxicol Chem* 26:616– 623.
- 32. Chen D, Mai B, Song J, Sun Q, Luo Y, Luo X, Zeng EY, Hale RC. 2007. Polybrominated diphenyl ethers in birds of prey from northern China. *Environ Sci Technol* 41:1828–1833.
- Mörck A, Hakk H, rn U, Wehler EK. 2003. Decabromodiphenyl ether in the rat: Absorption, distribution, and excretion. *Drug Metab Dispos* 31:900–907.
- Sandholm A, Emanuelsson BM, Wehler EK. 2003. Bioavailability and half-life of decabromodiphenyl ether (BDE-209) in rats. *Xe-nobiotica* 33:1149–1158.
- Opperhulzen A, van der Volde EW, Gobas FAPC, Liem DAK, van der Steen JMD. 1985. Relationship between bioconcentration in fish and steric factors of hydrophobic chemicals. *Chemosphere* 14:1871–1896.
- Opperhuizen A, Sijm DTHM. 1990. Bioaccumulation and biotransformation of polychlorinated dibenzo-p-dioxins and dibenzofurans in fish. *Environ Toxicol Chem* 9:175–186.
- 37. Eljarrat E, De La Cal A, Raldua D, Duran C, Barcelo D. 2004. Occurrence and bioavailability of polybrominated diphenyl ethers and hexabromocyclododecane in sediment and fish from the Cinca River, a tributary of the Ebro River (Spain). *Environ Sci Technol* 38:2603–2608.
- Allchin CR, Law RJ, Morris S. 1999. Polybrominated diphenylethers in sediments and biota downstream of potential sources in the UK. *Environ Pollut* 105:197–207.
- Johnson-Restrepo B, Kannan K, Addink R, Adams DH. 2005. Polybrominated diphenyl ethers and polychlorinated biphenyls in a marine foodweb of coastal Florida. *Environ Sci Technol* 39: 8243–8250.
- Christensen JH, Platz J. 2001. Screening of polybrominated diphenyl ethers in blue mussels, marine and freshwater sediments in Denmark. *J Environ Monit* 3:543–547.
- Lam JCW, Kajiwara N, Ramu K, Tanabe S, Lam PKS. 2007. Assessment of polybrominated diphenyl ethers in eggs of waterbirds from south China. *Environ Pollut* 148:258–267.