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Investigation of bioaccumulation and biotransformation of polybrominated diphenyl ethers, hydroxylated and methoxylated derivatives in varying trophic level freshwater fishes

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HIGHLIGHTS

- Bioaccumulation in seven fresh water fishes was higher for MeO-BDEs than OH-BDEs.
- Different internal distribution was found between PBDE and structural analogues.
- Potential biotransformation was suggested for OH- and MeO-BDEs in fish.

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ABSTRACT

The concentrations and distributions of polybrominated diphenyl ethers (PBDEs) and their hydroxylated and methoxylated derivatives (OH- and MeO-BDEs) were determined in seven representative fish species from a river in the Republic of Korea. The PBDEs and their derivatives were found to be accumulated in the internal organs of the fish to different extents. PBDEs were preferentially accumulated in the internal organs rather than muscle tissue, and especially, showed increasing accumulation tendencies with increasing bromination level in liver. The OH-BDEs and MeO-BDEs were preferentially accumulated in the liver and gastrointestinal tract, respectively. MeO-BDE concentrations were found to increase according to relative trophic level, suggesting that the PBDE derivatives can be biomagnified to a greater extent than the parent PBDEs in freshwater food webs. In a comparison with the dissolved analyte concentrations in the water that were measured by using semi-permeable membrane devices, the greater uptake of non-ortho substituted MeO-BDEs by fish was observed.

1. Introduction

Polybrominated diphenyl ethers (PBDEs), brominated flame retardants and chemical pollutants, have been regulated under the Stockholm Convention since 2009 because of their toxicities, persistence, and bioaccumulation tendencies. As such, there has been a lot of research into the behavior of these chemicals in the environment. Thanks to pioneering studies (Hites, 2004; Yogui and Sericano, 2009), the risks associated with PBDEs in most environmental compartments are quite well understood, but they are still relatively rarely monitored in aquatic environments, especially freshwater systems. It is not easy to detect dissolved PBDEs in aquatic media because of their strong hydrophobicity. Trace concentrations of PBDEs in water bodies, however, can accumulate in aquatic organisms through the food web, and PBDEs have been found in various species of fish and other aquatic organisms (Law et al., 2006; Stapleton et al., 2004a, 2006).

The structural analogues of PBDEs have also become of interest recently because they can have relatively similar, or even stronger toxicity than PBDEs in the environment. The hydroxylated- and methoxylated-brominated diphenyl ether (OH- and MeO-BDE, respectively) structural analogues of PBDEs were not synthesized for industrial use but they have been widely detected in marine environment around the world (Haraguchi et al., 2011; Löfstrand, 2011; Routti et al., 2009; Stapleton et al., 2006). It has been suggested that ortho-substituted PBDE structural analogues (e.g., 6-OH- and 6-MeO-BDE47) are natural compounds in the marine

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environment (Wiseman et al., 2011), like other marine halogenated natural compounds. The OH-BDEs and MeO-BDEs are easily absorbed by biota, and they are sometimes more toxic and bioaccumulative than PBDEs (Athanasiadou et al., 2008; Hamers et al., 2008; Harju et al., 2007). PBDEs, OH-BDEs and bromophenols can be transformed through multiple pathways to form other persistent toxic compounds, such as polybrominated dibenzo-*p*-dioxins and dibenzofurans (Arnoldsson et al., 2012a,b), so the fates of both PBDEs and their derivatives in aquatic ecosystems, including their potential to be bioaccumulated, biomagnified and biotransformed, should be investigated in detail.

There is much less information available on the behavior of the structural analogues of PBDEs. The major and relatively well-known congeners, such as 6-OH-BDE47 and 6-MeO-BDE47, have previously been studied in marine biota but the distributions and behaviors of other PBDE analogues have not yet been investigated in any detail (Kelly et al., 2008; Wen et al., 2015). It is suggested, from previous *in vivo*/*vitro* studies, that the biotransformation of PBDEs to form OH-BDEs and MeO-BDEs is possible in some fish species (e.g., rainbow trout and common carp), but was not observed from the field monitoring due to lack of current investigation, and controversies over the magnitude of transformation (Liu et al., 2012; Shen et al., 2012; Zeng et al., 2012). There are no clear results showing biotransformation of MeO-BDEs from PBDEs yet but possibility of bacterial methylation of PBDEs to MeO-BDEs by intestinal microflora and microorganisms in sediments were suggested (Haglund et al., 1997). The results of controlled laboratory studies cannot easily be applied to the field, and it is difficult to extrapolate biotransformation mechanisms observed in one species to other organisms in the food web. It is recommended, therefore, that field monitoring studies are needed to determine the actual occurrence and distributions of OH-BDEs and MeO-BDEs in various organisms.

Field monitoring studies using semi-permeable membrane devices (SPMDs), which accumulate freely dissolved hydrophobic organic compounds from the aquatic environment as mimicking the organisms (Chęć et al., 2008; Rastall et al., 2006), can be useful in determining the possibility of biological metabolic transformation of OH-BDEs and MeO-BDEs from PBDEs. That is, SPMDs can reflect the bioavailable concentration of PBDEs in the aquatic environment while excluding any impact of the biological transformation of the PBDEs by enzymatic reactions as might occur in biota. Thus, comparing the chemical concentrations accumulated in SPMDs and in biota collected in the same sampling area can give quantitative comparable information between the potential for the biotransformation of PBDEs into their derivatives in fish and accumulation of those compounds from the water environment.

In this study, mono- to deca-BDEs and tribrominated to pentabrominated OH- and MeO-BDE derivatives were monitored in seven representative species of fish from the freshwater Nakdong River, Republic of Korea. The PBDEs and PBDE derivatives were analyzed in the internal organs of the fish to profile internal preferential distribution and compared with SPMD samples. The purpose of the study was to investigate the possibility of the PBDEs and their structural analogues being bioaccumulated and biomagnified in a freshwater food web.

2. Materials and methods

2.1. Target analytes

The target analytes were 27 mono- to deca-BDEs (BDEs 3, 7, 15, 17, 27, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, and 209), 18 tri- to penta-brominated MeO-BDEs (3′-MeO-BDE28, 5-MeO-BDE47, 6-MeO-BDE47, 4-MeO-BDE49, 2-MeO-BDE68, 5′-MeO-BDE99, 5-MeO-BDE100, 4′-MeO-BDE101, and 4-MeO-BDE103, eight MeO-BDEs that were identified from their relative retention time, and one unidentified tri-brominated MeO-BDE), and 10 tri- to penta-brominated OH-BDEs (3′-OH-BDE28, 6-OH-BDE47, 6-OH-BDE100, six OH-BDEs that were identified from their relative retention time, and one unidentified tri-brominated OH-BDE). A mixture of $^{13}C_{12}$-labeled PBDEs (MBDE-MXE, Wellington Laboratories) were used as internal standards, while $^{13}C_{12}$-labeled BDE 138 was used as a recovery standard. $^{13}C_{12}$-labeled 6-OH-BDE47, 6-OH-BDE100, 6-MeO-BDE47, and 6-MeO-BDE100 were used as internal standards in the OH-BDE and MeO-BDE analyses, as appropriate. Detailed information on the target compounds and on how the PBDE structural analogues were identified and substituent positions assigned was previously published (Kim et al., 2014a; Lacorte et al., 2010).

2.2. Sampling area and conditions

The fish samples were collected in the lower part Nakdong River basin (35°17′21.52″N, 128°59′40.03″E) six times between November 2011 and June 2012 (Table 1). A detailed biological description of the fish and sampling information of water and sedimentary organic matter and monitoring result is given in the supporting information (S1, Fig. S1, and Table S1). The relative trophic position (T_{pos}) was determined (Levels I–III, Table 1) to estimate the biomagnification potential in the freshwater food web. The analyzing condition of stable isotopic ratio and calculation method of relative trophic position was given in the supporting information (S3).

2.3. Analytical procedure

Each fish sample (20–80 g) was spiked with internal standards and extracted by hexane, hexane:dichloromethane (1:1) and dichloromethane and cleaned up by multi-layer silica column treatment (S2). The SPMD dialysis procedure has been published previously (Kim et al., 2014a,b). The OH-BDEs in the extracts were derivatized using an acetylation reaction in pyridine that has been described previously (Lacorte and Ikonomou, 2009). The PBDEs and structural analogues were quantified by GC-HRMS and satisfied all relevant QA/QC parameters (S3).

3. Results and discussion

3.1. Concentrations and distributions

The PBDE concentrations in the muscle samples ranged from 0.15 to 9.4 ng/g-ww, and the OH-BDE and MeO-BDE concentrations were 0.12–6.3 ng/g-ww and 3.2–35 ng/g-ww, respectively (Table S2). The PBDE concentrations in the fish samples were lower than the concentrations that have been found in brown trout from Norway (0.3–407 ng/g-ww; Marjussen et al., 2008) and in *Barbus graellsi* from Spain (1.3–297.9 ng/g-ww; Eljarrat et al., 2004). Only one field monitoring study in which MeO-BDE concentrations were measured in fish was available to compare with our results that were similar or lower than our samples as 0.7–50 ng/g-lw in cod, sculpin, and salmon from Canada (Kelly et al., 2008).

The relative contributions of the PBDEs, OH-BDEs, and MeO-BDEs to the total concentrations and the homologue distribution profiles in the muscle samples are shown for each fish species in Fig. 1. As shown, the concentrations of PBDE structural analogues were several times higher than the concentrations of PBDEs. The structural analogue patterns were mostly dominated by the MeO-BDEs, which contributed 60–75% of the total