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THE OCCURRENCE OF METHOXYLATED/HYDROXYLATED AND PARENT PBDES IN MARINE ENVIRONMENT OF SOUTH KOREA

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Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used in consumer products, including electronic appliance, textiles, and vehicles. The major concerns are their bioaccumulation and toxicities evidences and also they could be transformed and metabolized to dioxin-like analogs¹. Recently, methoxylated (MeO-) and hydroxylated (OH-) BDEs are received attention because it is reported that they have higher toxicities than parent PBDEs, and are known to disrupt thyroid hormone for homeostasis, cause neurotoxic potential². Several studies on MeO- and OH-BDEs in marine biota, especially focusing on algae, have been done to identify their concentration to find out the formation mechanism², and to verify the biological metabolism and bioaccumulation in the food web³. However, more research focusing on the relative distribution in biotic and abiotic media and comparison on various environments are required to gain broader understanding on the fate and contribution of PBDEs and their structural analogs in marine environment. Therefore, in this study, the concentration and specific distribution characteristics of PBDEs (mono- to deca-) MeO-, and OH-BDEs (tri- to penta-) were investigated in sediment, sea water, and bivalves collected from 23 sites in the southern coastal area of South Korea. This study makes an attempt to better understand the fate, possible origins, and formation mechanisms of the structural analogs, and also makes a comparison of mechanism with the inland environment from the previous study^{4,5} done in South Korea. To the best of our knowledge, this is the first study investigating the relative distributions of PBDEs and structural analogs in marine environment and comparison with various environment.

Materials and methods

Sampling area and conditions

The samples comprising of three matrixes (sediment, water and bivalve) in each study sites were collected from February 25th, 2015 to May 22th, 2015. Twenty sites nearby sea in Jinhae and Gosung-Jaran bay were surveyed (Jinhae bay: JH1-9, Gosung bay: GS1-6, Jaran bay: JR1-5), and three off shore sites located almost 40 km far away from inland with no point source were surveyed (Gal island: GI1-3) (Fig. 1).

Sample treatment and Analytical procedure

The samples were separated into two sets, one for analyzing parents PBDEs and MeO-PBDEs, and the other for analyzing OH-PBDEs. SPE-DEX 4790 using 50 mm Atlantic C18 disks (Horizon, Salem, NH, USA) was used for the surface sea water extraction. For sediment and water filter samples, accelerated solvent extractor (ASE300; Dionex, Sunnyvale, CA, USA) was used, and bivalve samples were extracted with 1N KOH and LLE was conducted to extract target compounds from the aqueous layer (1N KOH). All samples were cleaned up with multi-layer silica gel columns. Finally, PBDEs and MeO-BDEs were analyzed by GC/HRMS (JMS-800D; JEOL, Tokyo, Japan), and OH-BDEs were analyzed by LC/MS/MS (Agilent 1200/6460QQMSD, Agilent Technologies, USA).

Results and discussion

Concentration and relative distribution in marine environment

The concentration and relative distribution of PBDEs and their structural analogs was shown in Figure 2. The average concentration of PBDEs were 1.87 ng/g dw in sediment, 1.07 ng/g lw in bivalve, and 124 pg/L in sea water, and those of MeO- and OH-BDEs were 0.71, 0.401 ng/g dw in sediment, 239, 14.2 ng/

g lw in bivalve, 0.008, 4.69 pg/L in sea water, respectively. The concentration of PBDEs in sediment and bivalve in this study was lower than previous study in Hongkong (18.2 ng/g dw in sediment, 58.2 ng/g lw in mussel)⁶, and similar concentration of sea water was observed compared with previous reporting in Canada (125 pg/L)⁷. In case of MeO- and OH-BDEs, the concentration of sediment in this study was higher than was detected previously in China⁸ (24 pg/g dw of OH-BDEs) while the concentration of the bivalve and sea water were lower compared to other studies in mussel from Baltic sea (1043ng/g lw of OH-BDEs, 255 ng/g lw of MeO-BDEs)⁹ and in sea water from Canada (29.8 pg/L of OH-BDEs)⁷. All the sites had similar distribution of total PBDEs and structural analogs in the order of PBDEs>>MeO-BDEs=OH-BDEs for sediment and sea water. However, MeO-BDEs was dominant in bivalves followed by OH-BDEs and PBDEs (Figure 2), and it indicated predominance of methylation mechanism from brominated compounds in biotic media.

Possible formation mechanism in marine environment

The concentration of PBDEs in nearby seas (JH, GS, JR) was much higher than the off shore site (GI), and the Mann whitney U test ($p < 0.05$) showed significant difference of concentration between them. However, MeO- and OH-BDEs were detected ubiquitously regardless of point source. Moreover, the concentration levels ortho-positioned MeO- and OH-BDEs, which are widely accepted as natural form, were 3-5 times higher than meta- and para forms. It supported the evidence that natural formation of structural analogs was predominant in marine environment. The possibilities of transformation from PBDEs also can be suggested by observation of significant correlations (Spearman correlation, $p < 0.05$) between PBDEs and their metabolites in bivalves and sediments. The detailed discussion on the fate, formation mechanism, and comparison between marine and inland environment will be presented during the conference.

Acknowledgements

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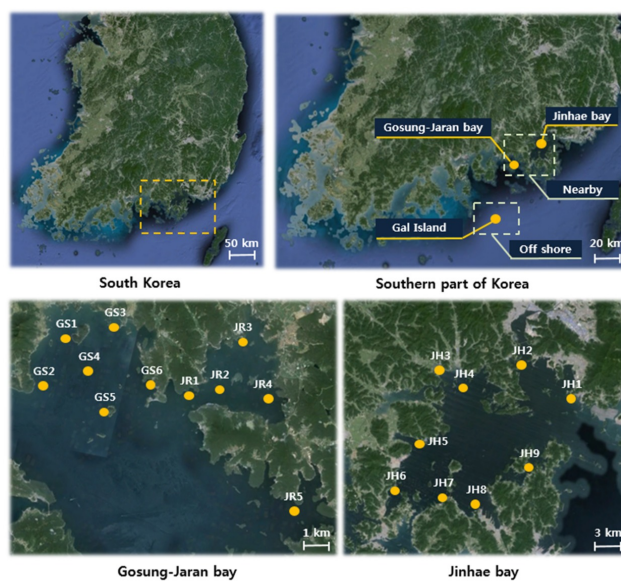


Figure 1. Sampling sites in the southern coastal area of Korea

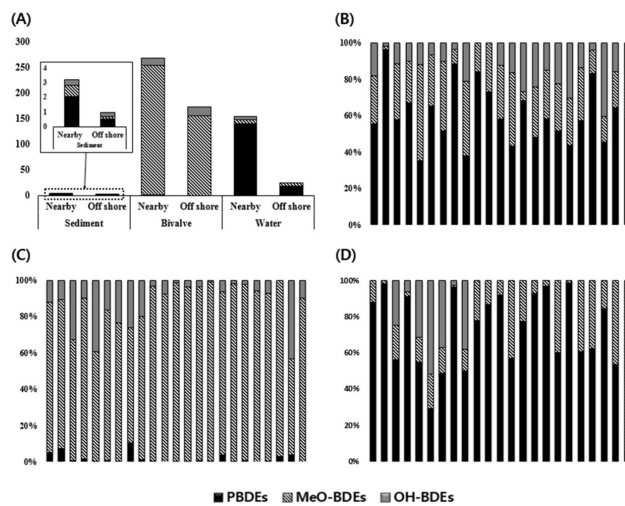


Figure 2. Concentrations of total PBDEs and structural analogs in sediment (ng/g dw), bivalves (ng/g lw), and sea water (pg/L) (A) and their relative distribution patterns in each media (Sediment (B), Bivalve (C), Sea water (D) from Korea bays