BROMINATED FLAME RETARDANTS IN SURFACE SEDIMENT: WITH TEMPORAL VARIATION OF SEDIMENTARY PBDEs CONCENTRATION

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Introduction

Polybrominateddiphenyl ethers (PBDEs), especially commercial pentabromodiphenyl- and octabromodiphenyl ether, have been regulated as persistent organic pollutants (POPs) since 2009 and POP RC adopted a recommendation on the listing of hexabromocyclododecanes (HBCDs) in Annex A (i.e., prohibition of production, use, export, and import of the chemicals) in Stockholm Convention in 2012[1]. Even though EU and World Health Organization presented no risk to human health, the potential risk of tetrabromobisphenol A (TBBPA) is still scarce[1]. In Korea, the national inventory of the conventional POPs such as PCDD/Fs, PCBs, and OCPs in freshwater sediments were already completed in 2009. Our previous study reported nationwide distribution of sedimentary PBDEs in four major river basins[2]. However, there is little known about TBBPA and HBCDs in freshwater sediment in Korea.

Nakdong River is the longest river in Korea and supplies over 90% of drinking water to the surrounding region[2]. The water quality of Nakdong River was poor and several big environmental accidents such phenol spill and 1,4-dioxane and perchlorate issue had been occurred due to many industrial complexes located along the river. So, the dredging operations had been performed in highly polluted sites to restore the water quality and ecosystem vitality. However, the sedimentary residual levels of various POPs including PBDEs and physicochemical properties such as grain size and content of total organic carbon (TOC) of sediment might be changed via sediment reflux, transport, and re-sedimentation[3-5]. Our previous research had reported a hotspot for PBDEs contamination in Nakdong River basin[2]. So, re-evaluation of the temporal variation of PBDEs concentration according to change of physicochemical properties of sediment after dredging activity are needed.

Our aims in this study were 1) to investigate the levels of TBBPA and HBCDs and spatial distribution of BFRs 2) to re-evaluate the temporal variation of PBDEs concentration 3) to investigate the spatial distribution profiles of BFRs in mainstream of Nakdong River and several important streams in this basin. To our knowledge, this study is the first report on the concentration and spatial distribution of TBBPA and HBCDs in freshwater sediment in Korea.

Materials and methods

Twenty-four sampling sites comprising main stream of Nakdong River (NR01~NR10, 10 sites), lakes as water sources of tributaries joining the river (NL01~NL08, 8 sites), and important streams passing through big industrialized cities (NS01~NS06, 6 sites) in Nakdong River basin were selected (Fig. 1).Surfaces sediments (below 10 cm) were collected using a Petite Ponar® grab sampler or a spade. All the collected samples were stored in amber bottles to prevent photo-degradation of target compounds. Sediment samples dried at room temperature were sieved with 230 meshes and homogenized. After spiking $^{13}C_{12}$ labeled PBDEs (MBDE-MXE, Wellington laboratories, Guelph, ON, Canada), $^{13}C_{12}$ labeled TBBPA and HBCD from Cambridge Isotope Laboratories (USA), 10 g of samples were extracted using accelerated solvent extractor (ASE350, Dionex, Sunnyvale, CA, USA) with a mixture of dichloromethane and hexane (3:1) (J.T.Baker, Phillipsburg, NJ, USA). To remove sulfur disturbance in sediment samples, the extracted samples were treated with activated copper granules and then a half of the sample was used for analysis of PBDEs and another was used for analysis of TBBPA and HBCDs. The pretreatment procedures for PBDEs, TBBPA, and HBCDs followed our previous researches[2,6].The recoveries of the labeled PBDEs, TBBPA and HBCDs for recovery standard (BDE138L for PBDEs and Fenoprop for TBBPA and HBCDs) were 80~100%, 70~110%, and 60~120%, respectively. Limit of detection (LOD) was defined as three times standard deviation of background peaks in the procedural blanks.

The LOD for PBDEs (except for DeBDE209), DeBDE209, TBBPA and HBCDs ranged from 1.0 to 20 pg/g, 40 pg/g, 50 pg/g and from 6.0 ~ 25 pg/g, respectively.

Results and discussion

3.1. Concentrations of BFRs in sediment

BFRs comprising PBDEs, TBBPA, and HBCDs were detected in all of the samples in Nakdong River basin, indicating widespread applications of BFRs and their release from various household and industrial products such as textiles, electronics, furniture, and etc. The sedimentary BFRs levels in Nakdong River basin ranged from 0.55 to 300 ng/g dry weight (dw) for Σ27PBDEs (sum of 27 PBDE congeners), 0.39 to 190 ng/g dw for DeBDE209, 0.05 to 150 ng/g dw for TBBPA, and 0.11 to 19 ng/g dw, respectively (Fig. 1).

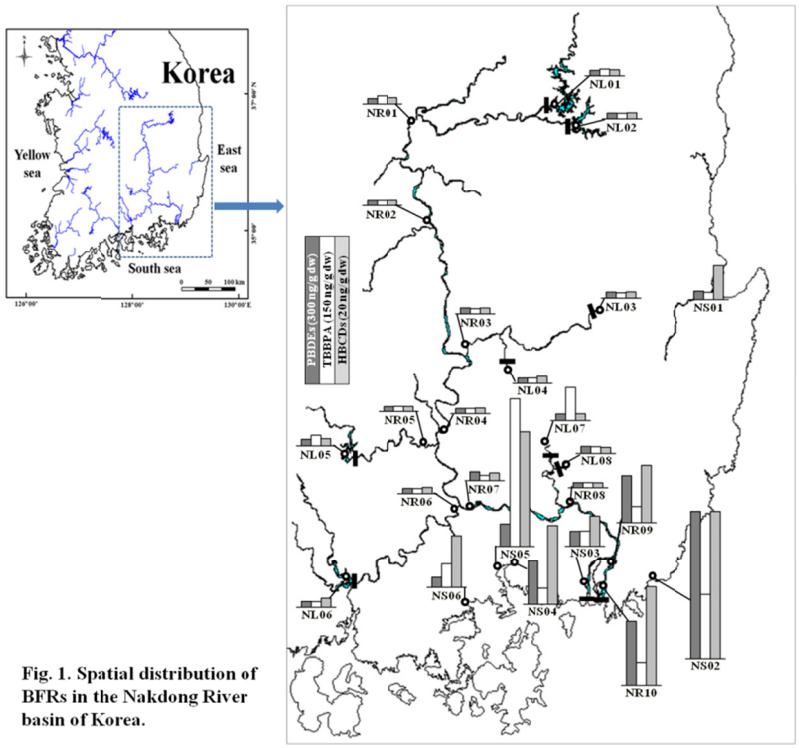

Fig. 1. Spatial distribution of BFRs in the Nakdong River basin of Korea.

DeBDE209 concentrations in this study were comparable to those in Spain, Japan, and USA but much lower than those in Netherland and China[2,7,8]. Notwithstanding various reports for PBDEs such as general monitoring study as above, particle size related PBDEs distribution[3,5], debromination of commercial PBDE mixtures[2,4] in sediment, there is little known worldwide about TBBPA and HBCDs in freshwater sediment. TBBPA concentrations in this study were higher than those in Scheldt basin, Netherland and comparable to those in Dongjiang river, China, whereas much lower than those in Skerene river, England close to BFRs manufacturing site[9,10]. Overall concentrations of TBBPA were similar with or lower than PBDEs in Nakdong River basin except some sampling sites, which was not well matched with more than two to seven times higher annual use amounts of TBBPA than PBDEs in Korea. It is known that the release of TBBPA from products to the environment is not easy compared to PBDEs because most commercial TBBPA used is reactive type, which is chemically bound to the polymer to be mainly used in plastic manufacturing. On the other hands, PBDEs are an additive type of BFR so they are not chemically incorporated with the products, indicating easily released to environment[11]. Therefore, this different usage type results in higher levels of PBDEs than TBBPA in environment regardless of their consumption amount. However, TBBPA has been also partially used as an additive type of BFR in electronic application as epoxy resin and polycarbonates (PC). This could be explained by the shorter half-life of TBBPA than PBDEs under anaerobic degradation in sediment[12,13]. HBCDs concentrations in this study were much lower than those in most of European regions except Sweden[7-9,14,15], reflecting small use amount in Korea (below 10% and 20% for TBBPA and deca-BDE, respectively).

3.2. Spatial distribution of BFRs and temporal variation of PBDEs

Generally, the concentration levels of BFRs in downstream, especially NR09 and -10, were much higher than those in upstream and midstream of mainstream (Fig. 1), indicating the possibility of transfer and deposition of pollutants via river flow and point sources along downstream. The similar BFRs levels were observed among lacustrine samples (NL- labeled) and those levels were similar with the levels in upstream and midstream of mainstream, suggesting that 2.6 ng/g dw for PBDEs, 3.0 ng/g dw for TBBPA, and 0.3 ng/g dw were background concentrations (average concentration of lacustrine samples and NR01 to NR08 samples of mainstream) in

Nakdong River basin. However, the BFRs levels in some important streams passing thorough big industrialized cities (NS- labeled) higher than those in mainstream and lacustrine samples and showed different concentration variation according to each sampling site, revealing different use patterns of BFRs in each industrialized city. Actually, the exact investigation of the company manufacturing, handling, and importing BFRs in Nakdong River basin was limited, however the specific sites (e.g., NR10, NS02, 04, -05) showing relatively higher TBBPA and HBCDs concentration were closed to expandable polystyrene (EPS), Epoxy, and PC resins manufacturing and handling companies.

Table 1 showed the PBDEs concentrations, TOC, and grain size in comparative sites (12 sites) in 2009 (this study) and 2006[2]. The PBDEs concentrations in mainstream except downstream (i.e., NR09 and -10) showed decreasing trend compared to previous results of comparative samples including NL01 and -02 corrected in 2006, whereas there were over ten times higher concentration increase in downstream.

Table 1. PBDEs concentrations, TOC, and Grain size in comparative sites in 2009 (this study) and 2006*

Site		Σ_{27}PBDEs concentration (ng/g dry weight)			TOC (%)			Grain size	
		2009	2006*	2009/2006	2009	2006*	2009/2006	2009	2006*
Lake	NL01	1.7	1.9	0.85	0.27	0.28	0.96	silt	coarse silt
	NL02	2.3	1.3	1.8	0.45	0.31	1.5	silt	coarse silt
Mainstream	NR01	1.0	7.2	0.14	0.23	0.26	0.89	silty sand	very coarse silt
	NR02	0.59	12	0.05	0.18	0.21	0.86	sand	very coarse silt
	NR03	2.8	1700	0.002	0.20	1.08	0.19	sand	very coarse silt
	NR04	1.0	33	0.031	0.10	0.43	0.23	sand	medium silt
	NR05	0.55	5.5	0.10	0.15	0.18	0.83	sand	very coarse silt
	NR06	1.3	15	0.082	0.11	0.23	0.48	sand	coarse silt
	NR07	8.8	14	0.61	0.16	0.26	0.62	silty sand	coarse silt
	NR08	0.74	19	0.040	0.11	0.26	0.42	sand	coarse silt
	NR09	88	3.6	24	1.4	0.36	3.8	sandy silt	very coarse silt
	NR10	120	11	11	1.9	0.64	2.9	sandy silt	very coarse silt

*data taken from Lee et al., 2012

Similarly, the TOC contents in mainstream except NL02 were decreased and those in NR09 and -10 were increased. Dinn et al.[3] revealed the role of TOC content associated with significant uptake of PBDEs in sediment. In this study, the temporal variation of Σ27PBDEs concentration (i.e., ratio of the concentrations in 2009 and 2006) was highly correlated with the temporal variation of TOC ($r = 0.942$, $p < 0.001$; $r = 0.779$, $p < 0.01$, with exception of NR09 and -10). Moreover, significant high PBDEs concentrations were observed when the TOC contents were over 1% in 2006 and 2009. Canadian SQGs (Sediment quality guidelines) for PBDEs were corrected on the basis of 1% TOC when predicting the bioaccumulation of this chemical for benthic invertebrates[16]. So, our finding in onsite study similar with fundamental of Canadian SQG could be used as valuable data for Korean sediment quality guideline for PBDEs to protect freshwater ecosystem. In comparison of grain size of sediments in comparative sites in 2006 and 2009, the mean grain size in mainstream except NR09 and NR10 was changed from silt grade to sand grade, whereas the mean grain size of lacustrine samples and NR09 and NR10 maintained silt grade. This physical change was well matched with the variation of Σ27PBDEs in sediment, which the sampling sites where maintained grain size in 2009 showed similar PBDEs concentration (i.e., lacustrine samples) or higher concentration (i.e., downstream, NR09 and -10) compared to the result of 2006. Zhao et al.[5] reported that the sedimentary grain size of below 63 μm (i.e., silt grade) has higher PBDEs affinity than over 63 μm (i.e., sand grade). The grain sizes of all the sediment in 2006 were silt grade, where the grain sizes of most of the sampling sites showing decreased PBDEs concentrations in 2009 were changed into sand grade.

On the whole, the comparative study of PBDEs concentration in Nakdong River basin could re-evaluate temporal variation of PBDEs associated with physicochemical properties of sediment such as TOC and grain size. The sedimentary PBDEs concentration might be changed with the variations of physicochemical properties of sediment including TOC content and grain size after physical restoration for sediment such as dredging activity.

3.3. Distribution profiles of BFRs

The distribution profiles of BFRs in Nakdong River basin showed various compositions of sedimentary BFRs, indicating site-specific distribution according to use patterns of BFRs and existence of adjacent BFRs related company. TBBPA is normally used as epoxy resin for electronic application, whereas HBCDs is textile application as EPS and extrude polystyrene (XPS) foams. DecaBDE is most widely used in textiles and nylon application as various resin foam such as HIPS (high impact polystyrene), PE (polyethylene), PP (polypropylene), and etc[17]. DeBDE209 accounts for over 97% of commercial deca-BDE products such as Saytex-102E and DE-83R[18]. In this study, the most dominant congener in sediment from Nakdong River basin is DeBDE209, indicating ubiquitous contamination of DeBDE209 according to the widespread use of commercial deca-BDE products (> 99% of the total Korean commercial PBDE market). The commercial HBCDs mixture such as Saytex HBCD from USA consists of dominant γ-HBCD diastereomer (approximately 80%), β-HBCD (5-10%), and α-HBCD (5-10%)[19]. In this study, γ-HBCD (46.9 ± 14.0%) had relatively higher proportion than α-HBCD (36.4 ± 7.1%) and β-HBCD (16.6 ± 9.8%), indicating the usage effect of commercial HBCD mixture. However, the γ-HBCD contribution in sediment was lower than that in commercial HBCD mixture and had higher deviation than α-HBCD and β-HBCD. A possibility is anaerobic digestion of HBCD diastereomers in sediment, which are two times longer half-live of α-HBCD than those of γ-HBCD and β-HBCD[17]. Therefore, individual HBCD diastereomers might be transformed under anaerobic condition in sediment. In comparison of sampling sites (Fig. 2), γ-HBCD proportions of mainstream (NR) and lacustrine samples (NL) were lower than those of streams (NS) not joining the mainstream but passing through several industrial cities, suggesting different anaerobic condition such as water depth and flow. In addition, the higher deviations of HBCD diastereomers in NR samples than those in NL and NS samples could give a possibility that transition of individual HBCDs in mainstream could be more activated according to hydrodynamic properties such as water flow and indirect (i.e., treated wastewater and sewage) or direct input of HBCDs[6,17].

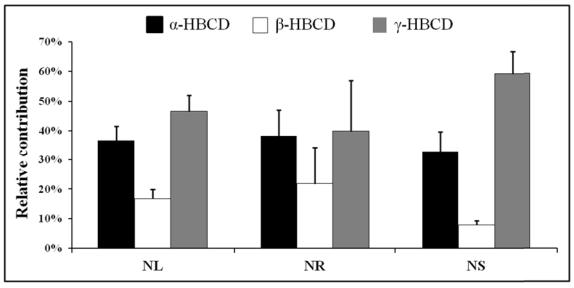

Fig. 2. Relative contributions of HBCD diastereomers in NL, NR, and NS samples

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