

Brominated flame retardants in Korean river sediments, including changes in polybrominated diphenyl ether concentrations between 2006 and 2009

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Introduction

Brominated flame retardants (BFRs) accounted for more than fifty percent of the total FR market in Korea until 2004, but the BFR market in Korea has continuously decreased in size since 2004. This reflects worldwide trends in the FR market that have been caused by the risks of BFRs causing harmful effects in environmental ecosystems and humans becoming appreciated, which led to some BFRs being restricted in the European Union and elsewhere¹. The commercial polybrominated diphenyl ether (PBDE) mixtures ‘pentabromodiphenyl ether’ and ‘octabromodiphenyl ether’ have been classified and regulated as persistent organic pollutants (POPs) since 2009 and the hexabromocyclododecanes (HBCDs) were classified as POPs in 2013^{2,3}. The European Union and the World Health Organization have found that tetrabromobisphenol A (TBBPA) does not present an appreciable risk to human health, but it is still considered possible that it presents a small amount of risk⁴. A Korean national inventory of ‘conventional’ POPs in freshwater sediments was completed in 2009⁵. Like this purpose, there was nationwide BFRs investigation focusing the distribution of PBDEs in sediments in four major river basins in Korea⁵ but little is still known about the distributions and profiles of other BFRs, especially TBBPA and the HBCDs, in freshwater sediments in Korea, indicating the needs of expanded BFRs investigation including TBBPA and the HBCDs. Moreover, the residual concentrations of various POPs, including PBDEs, in the sediment, and the geochemical compositions of the sediment, such as the total organic carbon (TOC) contents and grain size values, might be affected by sediment reflux, transport, and re-sedimentation⁶⁻⁸. Therefore, it is necessary to evaluate the temporal changes in the PBDE concentrations in Nakdong River basin sediments, and their relationships with changes in the geochemical compositions of the sediment. The aims of the study presented here were (1) to determine the TBBPA and HBCD concentrations and spatial distributions, (2) to evaluate the temporal changes of PBDEs concentrations according to the temporal variations of TOC and grain size between two years, and (3) to investigate the BFR profiles in sediments from the main channel of the Nakdong River and from several other nearby rivers.

Materials and methods

Nakdong River is the longest river in Korea, and it is used to supply over 90% of the drinking water of the people living in its basin⁵. Twenty-four sampling sites comprising main channel of Nakdong River (NR01~NR10, 10 sites), lakes as water sources of tributaries joining the river (NL01~NL08, 8 sites), and important other streams passing through big industrialized cities (OS01~OS06, 6 sites) in Nakdong River basin were selected (Fig. 1). Surface sediments (2 cm deep) 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. The pretreatment procedures for PBDEs, TBBPA, and HBCDs followed our previous researches^{5,9}.

Results and discussion:

3.1. Concentrations of BFRs in sediment

PBDEs, TBBPA, and HBCDs were detected in all of the samples collected from the Nakdong River basin, indicating that the widespread use of these chemicals in household and industrial products, such as textiles, electronics, and furniture, in the area has led to them being released into the aquatic environment. The concentrations of the sum of the 27 PBDE congeners analyzed (Σ 27PBDEs) were 0.55–300 ng g⁻¹ dry weight (dw), the BDE 209 concentrations were 0.39–190 ng g⁻¹ dw, the TBBPA concentrations were 0.05–150 ng g⁻¹ dw, and the total HBCD concentrations (sum of α -, β -, and γ -HBCDs) were 0.11–19 ng g⁻¹ dw (Fig. 1). The

BDE 209 concentrations found in this study were generally comparable to BDE 209 concentrations found in sediment samples from Japan, Spain, and the USA, but were much lower than BDE 209 concentrations found in sediment samples from China and the Netherlands⁵. There have been a number of studies of PBDEs in sediment, including general monitoring studies and studies of the relationship between particle size and PBDE concentration^{6,7}, and studies of the debromination of commercial PBDE mixtures^{5,8}, but little is known about the occurrence and behavior of TBBPA and HBCDs in freshwater sediments around the world. TBBPA is released less easily into the environment from products than are PBDEs because most commercial TBBPA is used as a reactive BFR, chemically bound to polymers¹. PBDEs, however, are additive BFRs, which are not chemically incorporated into products, meaning that they can be released into the environment relatively easily when the products are produced, used, and disposed of¹. The different ways in which TBBPA and PBDEs are incorporated

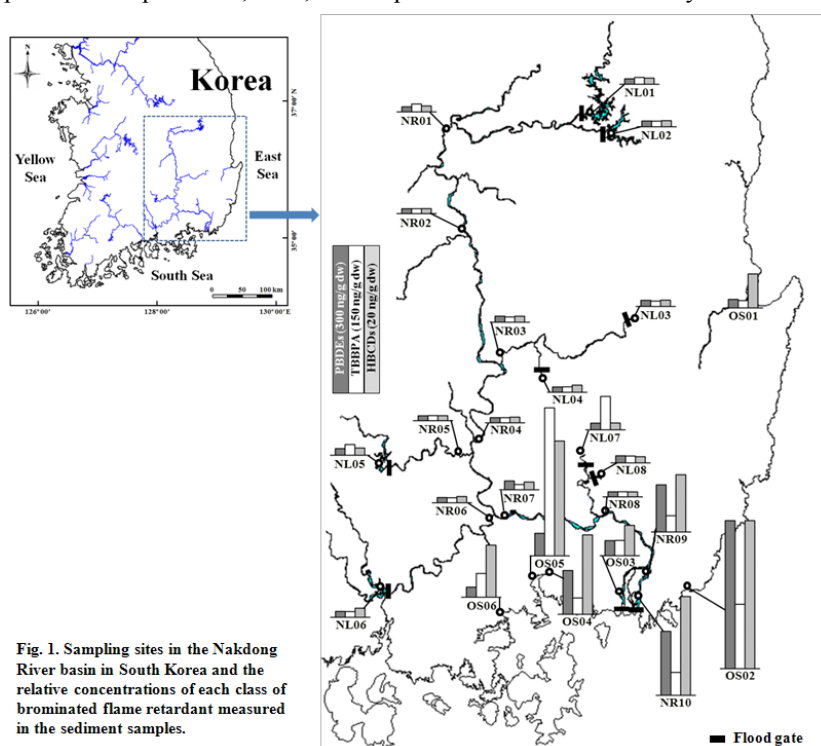


Fig. 1. Sampling sites in the Nakdong River basin in South Korea and the relative concentrations of each class of brominated flame retardant measured in the sediment samples.

into products will have caused more PBDEs than TBBPA to enter the environment, even though more TBBPA is used than PBDEs are used. However, TBBPA has been used as an additive BFR in electronic applications, in epoxy resins, and in polycarbonates. TBBPA has a much shorter anaerobic degradation half-life (TBBPA, 0.59 d; BDE 209, 700 d) in sediment and a weaker affinity for the sediment particle phase [i.e., octanol water partition coefficient, TBBPA, ~6; BDE 209, ~10] than the PBDEs^{5,10}. The HBCD concentrations found in this study were much lower than have been found in EU regions⁹, which reflects the fact that HBCD has been relatively little used (at less than 10% of TBBPA use and less than 20% of the commercial

decabromodiphenyl ether product use) in Korea.

3.2. Spatial distribution of BFRs and temporal variation of PBDEs

In general, the BFR concentrations in the downstream part of the Nakdong River, especially at sites NR09 and NR10, were much higher than the concentrations in the upstream and midstream parts of the river (Fig. 1). This result indicates that the BFRs in the sediment may have entered the river continuously from various point and non-point sources; the concentrations gradually increase in the downstream parts (NR09 and NR10), which are closed by flood gates at ordinary times, due to the repeated re-suspension and deposition of the BFR in the sediment. Moreover, the continuous discharge of effluent containing BFRs from STP and WWTP close to NR09 and NR10 also might affect the sedimentary BFRs. The BFR concentrations were higher in the sediment samples from the other rivers that pass through large industrialized cities (the OS samples) than in the samples from the Nakdong River and the lakes, and different BFR concentrations were found at each OS sampling site, showing that there were different BFR emission patterns in each of the cities. It was not possible to fully investigate which companies in the Nakdong River basin and the surrounding area manufacture, handle, and import BFRs. However, several sites (e.g., NR10, OS02, and OS04) with relatively higher BFRs concentration were located close to the STP outfall and industrial complex (within 1 km). Previous researches suggested that the leaching of BFRs in household products and manufacturing industries (e.g., electronics, upholstered furniture, textiles, etc.)

was a major input source into the water system⁹. The highest TBBPA concentration was observed at OS5 located close to an electronic industrial complex (within 0.5 km) which was also known as a major source of TBBPA due to the use of epoxy, phenol, and carbonate resins used in electronic industries¹.

To compare the changes in the PBDEs concentrations with the temporal variation of the geochemical compositions with our samples collected in 2009, our study obtained data on PBDE concentrations and geochemical compositions such as the TOC contents and grain size values of the sediment samples collected in 2006, from our previous study and nationwide sediment monitoring data⁵. Finally, twelve sampling sites were matched, and there was a significant decrease in the temporal PBDE concentrations between 2006 and 2009. Moreover, there was no statistically significant difference ($p > 0.05$) of the distribution profiles of the PBDE congeners. These constant distribution profiles of the PBDE congeners with respect to the year indicated no new input source of the PBDEs in these sampling areas between the two sampling years. Table 1 shows the PBDE concentrations, the TOC concentrations, and the grain sizes at each of the 12 comparative sites in 2009 (this study) and in 2006⁵. The PBDE concentrations in the upstream and midstream parts of the river (i.e., excluding the downstream samples, NR09 and NR10) and in the lakes (samples NL01 and NL02) were lower in 2009 than in 2006. The PBDE concentrations were more than ten times higher in the downstream part of the river in 2009 than they were in 2006. Similarly, the TOC concentrations in the upstream and midstream parts of the main river channel, except for at site NL02, were lower in 2009 than in 2006, and the TOC concentrations in the downstream samples (NR09 and NR10) were higher in 2009 than in 2006. Previous study found that the TOC concentration was associated with the significant uptake of PBDEs by sediment⁷. The temporal change in the $\Sigma 27$ PBDEs concentration (defined as the 2009 concentration divided by the 2006 concentration) was highly significantly correlated with the temporal change in the TOC ($r = 0.942$, $p < 0.001$ including all of the Nakdong River samples and $r = 0.779$, $p < 0.01$ when samples NR09 and NR10 were excluded). Moreover, the TOC normalized PBDEs concentration between 2006 and 2009 also showed a significant decreasing trend ($p < 0.01$, Table S1). Particularly high PBDE concentrations were found when the TOC concentrations were higher than 1%, in both 2006 and 2009, and the concentrations and ratios are shown in bold in Table 1 when this was the case.

Table 1. Polybrominated diphenyl ether (PBDE) concentrations, total organic carbon (TOC) contents, and average grain size values found in sediment samples from the study sites in 2009 (this study) and in 2006⁵

Site	Total (Σ_{27}) PBDE concentration (ng/g dry weight)			TOC (%)			Grain size		
	2006*	2009	2009/2006	2006*	2009	2009/2006	2006*	2009	
Lake	NL01	1.9	1.6	0.84	0.28	0.27	0.96	coarse silt	silt
	NL02	1.3	2.3	1.8	0.31	0.45	1.5	coarse silt	silt
	NR01	7.2	1.0	0.14	0.26	0.23	0.89	very coarse silt	silty sand
	NR02	12	0.59	0.05	0.21	0.18	0.86	very coarse silt	sand
	NR03	1700 ^a	2.9	0.002^a	1.08^a	0.20	0.19^a	very coarse silt	sand
Main channel	NR04	33	1.0	0.031	0.43	0.10	0.23	medium silt	sand
	NR05	5.5	0.55	0.10	0.18	0.15	0.83	very coarse silt	sand
	NR06	15	1.3	0.082	0.23	0.11	0.48	coarse silt	sand
	NR07	14	8.8	0.61	0.26	0.16	0.62	coarse silt	silty sand
	NR08	19	0.74	0.040	0.26	0.11	0.42	coarse silt	sand
	NR09	3.6	88^a	24^a	0.36	1.4^a	3.8^a	very coarse silt	sandy silt
	NR10	11	130^a	12^a	0.64	1.9^a	2.9^a	very coarse silt	sandy silt

* Data taken from Lee et al., 2012⁵; ^a values in bold are for samples that had a total organic carbon concentration of more than 1%

We compared the sediment grain sizes in 2006 and 2009 and found that the mean grain size in the main river channel (except for at the downstream sites NR09 and NR10) changed from silt grade to sand grade, whereas the mean grain size in the lake samples and NR09 and NR10 remained silt grade. This physical change matched the change in the $\Sigma 27$ PBDEs concentrations in the sediment samples well, the sediment samples from the sites where the grain size remained the same between 2006 and 2009 containing similar PBDE concentrations (the

lake samples) in 2009 and 2006 or containing higher PBDE concentrations (the downstream samples NR09 and NR10) in 2009 than in 2006. Previous research found that sedimentary grains of below 63 μm diameter (i.e., silt grade) have stronger affinities (at least more than two times) for PBDEs than do grains of over 63 μm diameter (i.e., sand grade)⁶. All of the sediment samples in 2006 had silt grade grain sizes, and lower PBDE concentrations were found in 2009 at sites where the grain size had changed to sand grade.

3.3. Distribution profiles of BFRs

Different BFR concentration profiles were found in different sediment samples from the Nakdong River basin, and the site-specific patterns were probably caused by different BFR usage patterns and the presence of industrial facilities where BFRs are used. The dominant PBDE congener in the sediment samples from the Nakdong River basin was BDE 209, indicating that this PBDE congener was ubiquitous, and this would have been caused by the widespread use of commercial decabromodiphenyl ether products (which make up >99% of the total Korean commercial PBDE market). Commercial HBCD mixtures, such as Saytex HBCD, from the USA, are dominated by the γ -HBCD diastereomer (contributing approximately 80% of the total HBCD mixtures), and β -HBCD and α -HBCD each contribute 5–10% of the mixtures⁹. The γ -HBCD was found to contribute $46.9 \pm 14.0\%$ of the total HBCD concentration, higher than the α -HBCD contribution ($36.4 \pm 7.1\%$) and the β -HBCD contribution ($16.6 \pm 9.8\%$) in our samples. The γ -HBCD contribution to the total HBCD concentration was lower in the sediment than in commercial HBCD mixtures, whereas α -HBCD contribution to the total HBCD concentration was higher in the sediment than in commercial HBCD mixtures. Fig 2 shows the distribution profiles of HBCD diastereomers in three types of sampling sites. The γ -HBCD contributions to the

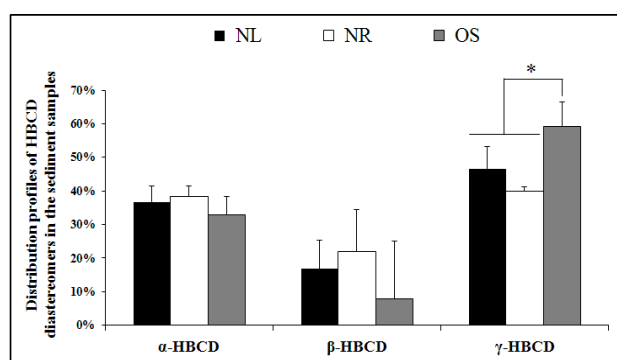


Fig. 2. Distribution profiles of the hexabromocyclododecane (HBCD) diastereomers in the sediment samples from the Nakdong River main channel (NR), the lakes (NL), and the other streams (OS).

total HBCD concentrations in the stream sediment (the OS samples) was significantly higher than in main river channel (the NR) and the lake sediments (the NL) and more similar to commercial HBCD mixtures. Moreover, the total HBCDs concentrations in the OS samples were higher than those in the NR and NL samples (Fig. 1). The OS sampling sites were located in industrial cities and very close to STP outfall within 1 km, which are regarded as HBCD sources^{9,10}. This result indicates that the HBCDs in the OS sediment samples might be more strongly affected by the local use of commercial HBCD mixtures than NR and NL sampling sites, which could lead relatively higher γ -HBCD composition in the OS samples. The relatively higher

α -HBCD contribution in the sediment samples than commercial HBCD products in this study could be explained by the different transformation rates of HBCD diastereomers in the anaerobic sediment conditions. It was reported that the anaerobic digestion half-life of α -HBCD is twice as long as those of γ -HBCD and β -HBCD¹⁰, which could lead the relatively higher α -HBCD composition in sediment than commercial HBCD products

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