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

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HIGHLIGHTS

- BFRs were analyzed in sediment samples from the Nakdong River basin, South Korea.
- Sampling sites close to manufacturing facilities showed high BFR concentrations.
- Temporal change of PBDEs correlated with the geochemical compositions of sediment.
- It is estimated that the commercial PBDE and HBCD products were released locally.

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ABSTRACT

Brominated flame retardants were analyzed in sediment samples from the Nakdong River basin, Korea. The total concentrations of the 27 polybrominated diphenyl ethers (PBDEs), including decabrominated diphenyl ether (BDE 209), analyzed were 0.55–300 ng g^{-1} dry weight (dw), the BDE 209 concentrations were 0.39–190 ng g^{-1} dw, the tetrabromobisphenol A (TBBPA) concentrations were 0.05–150 ng g^{-1} dw, and the total hexabromocyclododecane (sum of α-, β-, γ-HBCDs) concentrations were 0.11–19 ng g^{-1} dw. The PBDE and HBCD concentrations were comparable to or lower than the concentrations found in sediments from other countries, whereas the TBBPA concentrations were comparable to or higher than the concentrations found in other countries. The TBBPA concentrations were similar to or lower than the PBDE concentrations, even though more than twice as much TBBPA as total PBDEs is consumed in Korea, and this phenomenon was probably caused by TBBPA and PBDEs being used differently during the manufacture of products, and their different half-lives in sediment and affinities for the particle phase in aquatic environments. Sediment samples from several sampling sites close to facilities where expandable polystyrene, epoxy, and polycarbonate resins are manufactured and handled had relatively high TBBPA and HBCD concentrations. Temporal changes in the PBDE concentration strongly correlated with temporal variations in the geochemical compositions such as total organic carbon content and grain size value of the sediment. The PBDE and HBCD distribution profiles in the sediment samples indicated that commercial PBDE and HBCD products were released locally.

1. Introduction

Flame retardants (FRs) are used to decrease the flammability of polymers and other combustible materials. Brominated flame retardants (BFRs) accounted for more than fifty percent of the total FR market in Korea until 2004 (Cischem, 2009), because BFRs were then both more cost-effective and more effective in resisting the thermal decomposition of flammable materials than were organophosphorus, inorganic, and nitrogen-containing FRs (Cischem, 2009). However, the BFR market in Korea has continuously decreased in size since 2004, whereas the inorganic FR market size has increased as shown in Table 1. This reflects worldwide trends in the FR market that have been caused by

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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 elsewhere. The commercial polybrominated diphenyl ether (PBDE) mixtures 'pentabromodiphenyl ether' and 'octabromodiphenyl ether' have been classified and regulated as persistent organic pollutants (POPs) since 2009 (COP 4, 2009) and the hexabromocyclododecanes (HBCDs) were classified as POPs in 2013 (COP 6, 2013). 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 risk (EFSA, 2011). A Korean national inventory of 'conventional' POPs (including polychlorinated dibenzo-*p*-dioxins and dibenzofurans, polychlorinated biphenyls, and nine organochlorine pesticides) in freshwater sediments was completed in 2009 (Lee et al., 2012a). Like this purpose, there was nationwide BFRs investigation focusing the distribution of PBDEs in sediments in four major river basins in Korea (Lee et al., 2012a) 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.

Lee et al. (2012a) reported the dominant contribution of commercial deca-BDE mixtures in 18 Korean freshwater sediments and contamination hotspot of PBDEs in Nakdong River basin. 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 basin (Lee et al., 2012a). But, the Nakdong River water quality is poor, and the many industrial complexes located along the river have caused several major environmental accidents, including the release of phenol, 1,4-dioxane, and perchlorate (Lee et al., 2011; 2012b). Highly polluted sites in the river have been dredged to attempt to improve the water quality and ecosystem vitality. However, 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-sedimentation (Zhao et al., 2010; Dinn et al., 2012; Salvadó et al., 2012). 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. To the best of our knowledge, this study is the first to describe the concentrations and spatial distributions of TBBPA and HBCDs in freshwater sediments in Korea.

2. Materials and methods

2.1. Study sites

The Nakdong River, at 525 km long, is the longest river in Korea, and it has a basin of 23 384 km^2 (Lee et al., 2012a). The main river channel runs through a number of industrial regions, with chemical and textile facilities situated along the midstream section and plastic and rubber resin manufacturing facilities situated along the downstream section of the river. Some other rivers and streams in the river basin pass through industrial cities that contain textile, chemical, and electronics facilities and then flow directly into the sea. A total of 24 sampling sites, were selected along the main Nakdong River channel (samples NR01–NR10; 10 sites), in lakes that are sources of Nakdong River tributaries (samples NL01–NL08; 8 sites), and along other streams that pass through large industrialized cities (within 1 km) in the Nakdong River area but that are not tributaries of the Nakdong River (samples OS01–OS06; 6 sites) (Fig. 1).

2.2. Sample collection and experimental procedures

The collection of sediment samples was followed by sediment sampling protocol of Korea in 2009. Briefly, surface sediments (2 cm deep) were normally collected using boats with a Petite Ponar grab sampler in the middle of the rivers, lakes, and streams and the samples were stored in amber bottles to prevent the photodegradation of the target compounds. The collected sediment samples were dried at room temperature, and archived for the subsequent analysis of PBDEs after measuring the TOC contents and grain size values. The TOC contents in the sediment samples were analyzed using an elemental analyzer (vario MACRO cube, Elementar analysensysteme GmbH; Hanau, Germany), after removing the inorganic carbonate with H_2SO_4–$FeSO_4$. Grain size analysis of the sediment samples was performed using a particle size analyzer (Mastersizer 2000, Malvern Instruments; Malvern, United Kingdom).

The archived samples were passed through a 230 mesh sieve, and homogenized. A 10 g aliquot of each sediment was spiked with $^{13}C_{12}$-labeled PBDEs (mixture MBDE-MXE; Wellington Laboratories, Guelph, Canada), $^{13}C_{12}$-labeled TBBPA (Cambridge Isotope Laboratories, Andover, MA, USA), and $^{13}C_{12}$-labeled α-, β-, and γ-HBCD (Cambridge Isotope Laboratories) then extracted in an accelerated solvent extractor (ASE350; Dionex, Sunnyvale, CA, USA) using a 3:1 mixture of dichloromethane and hexane (J.T. Baker, Phillipsburg, NJ, USA). The extracted samples were treated with activated copper granules to remove sulfur, and each sample was split into two equal portions, half being analyzed for PBDEs and the other half for TBBPA and the HBCDs.

The extracts were prepared for PBDE, TBBPA, and HBCD analyses following procedures that we have previously published

Table 1
Total flame retardant market sizes, the amounts of brominated flame retardants imported into South Korea, and the proportions of all flame retardants used in different products in South Korea (2008).

		Market size (*t*)					Proportion of all FRs used in products (2008)	
		2004	2005	2006	2007	2008	Resin/foam	%
FR market		129 000	121 000	121 000	109 000	104 000	ABS	36
Chlorinated FRs		12 000	9 000	7 000	5 000	3 000	Epoxy	9
Phosphoric FRs		11 000	12 000	13 000	12 000	11 000	PU	7
Inorganic FRs		37 000	42 000	48 000	52 000	51 000	PC/ABS	7
Brominated FRs		69 000	58 000	53 000	40 000	39 000	PS	6
Amount imported (*t*)	TBBPA	41 000	36 000	39 000	31 000	31 000	PE	4
	Deca-BDE	17 000	13 500	7 000	4 300	4 000	Others	31

FR = flame retardant; TBBPA = tetrabromobisphenol A; Deca-BDE = commercial decabromodiphenyl ether product; ABS = acrylonitrile butadiene styrene; PU = polyurethane; PC = polycarbonate; PS = polystyrene; PE = Polyethylene.