OCCURRENCE OF BROMINATED FLAME RETARDANTS IN THE SEDIMENTS FROM INDUSTRIALIZED COASTAL REGIONS OF SOUTH KOREA

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Introduction

Flame retardant chemicals are added to many consumer products in order to prevent the fire. They are used worldwide inplastics, textiles, electronic circuitry and other common materials. TetrabromobisphenolA(TBBPA), polybrominateddiphenyl ethers(PBDEs), and hexabromocyclododecanes(HBCDs) are the most widely used brominated flame retardants(BFRs).With the ban on PBDE commercial mixtures in the developed countries, the demand for alternative non-PBDE BFRs has been increased. HBCD has been identified by Stockholm Convention asa substance of persistent organic pollutants(POPs)[1].Previous studies have shown that HBCDs have become ubiquitous and their levels have been increased in environmental matrices over the last two decades[2]. Bis(2,4,6 tribromophenoxy) ethane (BTBPE), one of alternative BFRs, has similar molecular structure tohexabrominatedPBDEsand, therefore, their physio-chemical properties and consequent environmental fate and toxicity could also be similar[3]. However, information on non-PBDE BFRs is still limited.

TBBPA and HBCD are widely used BFRs in Korea. The annual production volumes are estimated to be 30,136 and 2,173 ton for TBBPA and HBCD, respectively[4]. No information is available for the usage of BTBPE in Korea. Among BFRs, polybrominateddiphenyls(PBBs) andtris(2,3-di-bromopropyl phosphate) have been banned for production and use in Korea since 1999, while there are no restrictions on the production or use of TBBPA, HBCD and BTBPE. Recently, the Korean government has been encouragingcompany to voluntary phase-out BFRs such as Penta-BDE, Octa-BDE, Deca-BDE, and TBBPA[4]. There are few studies on the contamination of HBCD and TBBPA in the Korean environment[5,6]and none of data on BTBPE is reported.

In the present study, the contamination status of HBCD, BTBPE and TBBPA were examined in the marine sediments from two highly industrialized coastal regions, Busan and Ulsan,which have been designated as ‘special management coastal areas’ by the Korean governmentsince 1983. Busan is the second largest city and the foremost port area in Korea.BusanPort has been the marine gateway to Korea. In Ulsan, numerous industrial facilities includingpetrochemical, automotive, shipbuilding industries are sited all around the coastal areas.

Materials and methods

Chemicals and reagents

Reference standards of BTBPE (>96% purity), TBBPA were purchased from Cambridge Isotope Laboratories, Inc. (MA, USA). α-HBCD (>98%), β-HBCD (>98%), and γ-HBCD(>98%)were obtained from Wellington Laboratories, Inc. (Ontario, Canada).Theisotope-labeled internal standards such as ^{13}C-BTBPE (≥99%) and^{13}C-BDE139(≥99%)were obtained from Wellington Laboratories.The isotope-labeled standards of$^{13}C_{12}$-TBBPA (99%) and $^{13}C_{12}$-HBCDs (mixture of 3 isomers, 99%) were obtained from Cambridge Isotope Laboratories, Inc. All of the solvents used in these experiments were of capillary GC/GC–MS grade and were purchased from Burdick and Jackson (MI, USA). The ultrapure water was produced by a MILLI-Q Advantage A10 (France).

Liquid chromatography-tandem mass spectrometry

An Agilent 1200 HPLC system from Agilent Technologies (Waldbronn,Germany) connected to a triple quadrupole mass spectrometer API 3200 Applied Biosystems from MDS SCIEX (Toronto, Canada) was employed for identification and quantification of analytes. HPLC and tandem MS wereconnected via Turbo VTJ ionization source from AB SCIEX (Singapore). The injection volume was set to 10 µL and the chromatographic separation was accomplished using a Zorbax Eclipse C18 analytical column (4.6×150 mm, particle size 3 µm) proceeded by a low dispersion in-line filter (0.25 µm) from Agilent Technologies (USA). Oven temperature was set at 40^{0}C and flow rate was observed as 1 mL/min. The mobile phase was a binary mobile phase solvent system consisting of a mixture of ACN/MeOH (7:3) as mobile phase B and 5% of MeOH in ultrapure water as mobile phase A. Details of HPLC-APCI/MS/MS analysis can be found elsewhere[7].

Sample preparation and clean-up

Thirteen and twenty five marine sediment samples were collected using a Van Veen grab sampler in Ulsan and Busan, respectively, in February 2013 (Fig. 1).Approximately,2cm of surface sediment was taken by a stainless steel spatula and stored in a pre-combusted amber glass jar. The collected samples were stored at −20°C until analysis.The analytical methods for BFRs have been described in detail elsewhere[7]. Briefly, 10 g of freeze-dried sediment was fortified with 80 µL of (1 ng/µL) labeled internal standard mixtures and extracted by soxhlet with hexane and dichloromethane (DCM) (1:4, v/v) for 16h. The extract was cleaned up using a 6 g of 5% deactivated silica gel column with 7 mL of hexane: DCM (1:1, v/v), 15 mL of hexane, 20 mL of hexane:diethyl ether (3:1, v/v) and finally 20 mL of hexane:diethyl ether (1:1, v/v). The sample was evaporated to dryness by a gentle stream of nitrogen and subsequently solvent-exchanged with IPA: toluene (9:1, vv).13C-BDE 139 was spiked as a recovery standard before instrumental analysisusing HPLC-APCI-MS/MS.

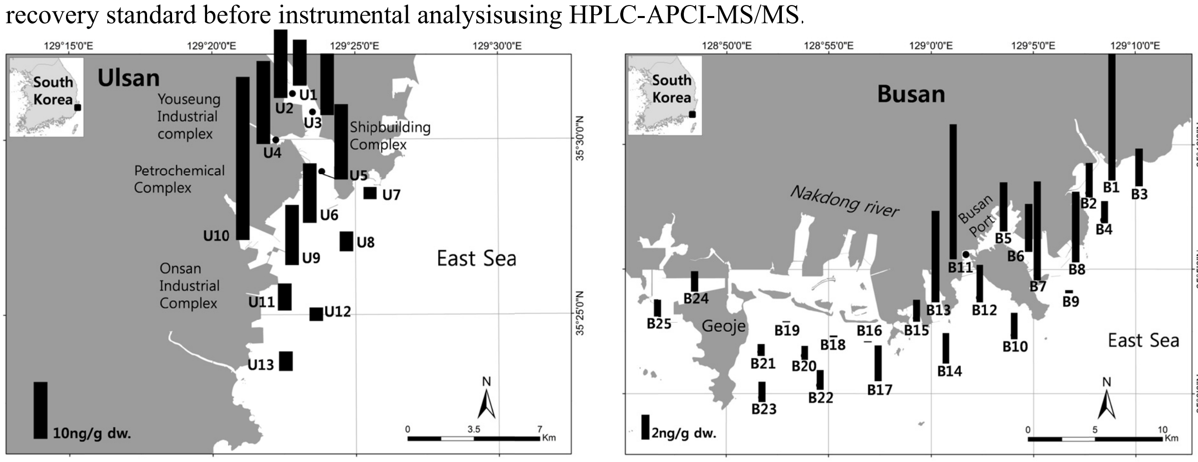
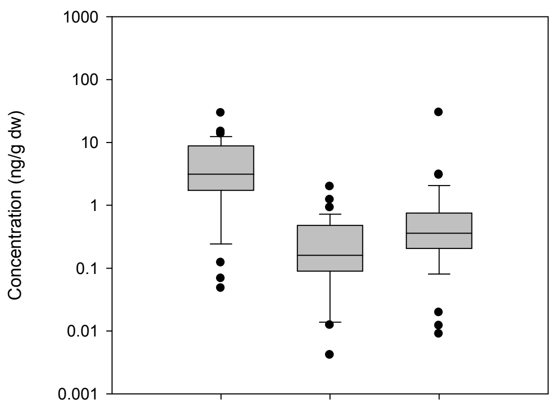


Figure1. Sampling locations and spatial distribution of HBCDs in the surface sediments from Ulsan (left) and Busan (right)

Results and discussion

Brominated flame retardents wereubiquitouslydistributed along the Korean coastal environment(Table 1).HBCD and BTBPE compounds were detected inall of sediment samples. TBBPA was detected in 97%of the samplesanalyzed.The overall concentrations of HBCDs(sum of 3 isomers), TBBPA and BTBPE in all the sediment samples werein the rang of 0.05-29.3 ng/g dw(mean:5.49±5.80), n.d.-1.97(0.31±0.39) and 0.01-29.7(1.39±4.78), respectively. Among the target analytes, HBCDs showed the highestconcentration followed by BTBPE and TBBPA(Fig. 2).Although TBBPA is the most abundantly usedBFRs in Korea, the median concentrations of TBBPA in the sediment was17 and 4times lower than those of HBCDs and BTBPE, respectively. This result could be due to their different application processes; HBCDs and BTBPE are additive type BFRs, while TBBPA is a reactive BFR.TBBPA is bound chemically to the polymer structure, and, thus, the release of TBBPA into the environment is limited. The environmental levels of these three BFRs are still much lower than that of PBDEs (6.4-110 ng/g dw)in the coastal sediments from



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both regions[5], however, we should pay attention to them because their consumption is steadily increasing.

Theconcentration of HBCDs in the Korean sediments is lower than the values noted in Europe but higher than China and USA. The TBBPAconcentration is lower than that of China but comparable to Europe and USA.The BTBPE concentration is similar to that of China except for that detected atstation U10 in Ulsan[9-11].This differencereflects well the regional market demand of BFRs.

Table 1. Concentration(ng/g dry weight) of HBCDs, TBBPA and BTBPE in the sediments form Busan and Ulsan.

Study area		α-HBCD	β-HBCD	γ-HBCD	HBCDs	TBBPA	BTBPE	TOC(%)
Ulsan	min-max	0.28-4.33	0.12-2.48	1.69-23.15	2.18-29.26	0.07-0.70	0.15-29.74	0.79-2.67
	mean±SD	1.68±1.23	0.82±0.63	7.33±5.86	9.83±7.32	0.29±0.23	3.16±8.03	1.42±0.50
	median	1.35	0.78	6.69	10.77	0.18	0.69	1.33
Busan	min-max	0.03-2.13	n.d.-0.76	nd[a]-9.15	0.05-11.13	0.00-1.97	0.01-3.07	0.04-1.47
	mean±SD	0.52±0.59	0.20±0.24	1.44±2.37	2.26±3.09	0.16±0.45	0.32±0.61	0.88±0.39
	median	0.52	0.20	1.44	2.26	0.16	0.32	0.98

[a]n.d.; not detected.

The concentrations of BFRs in Ulsan are 2.18-29.26ng/g dw(mean: 9.83±7.32) for HBCDs, 0.07-0.70ng/g dw(0.29±0.23) for TBBPA and 0.15-29.74ng/g dw(3.16±8.03) for BTBPE (Fig. 1, Fig. 3and Table 1). In Busan, they are in the range of 0.05-11.13ng/g dw(2.26±3.09) for HBCDs, n.d.-1.97ng/g dw(0.16±0.45) for TBBPA and 0.01-3.07ng/g dw(0.32±0.61) for BTBPE(Fig. 1, Fig. 3 and Table 1). The levels of HBCDs and BTBPEare high in Ulsan compared to Busan, while the level of TBBPA is similar to each other.At both regions, theHBCD concentrationsshoweda negative gradient fromland toward offshore region(Fig. 1), indicating land based activitiesare the main source of BFRs to the marine environment. Especially,the highest concentration of HBCDs was detecedat U10 nearpetrochemial industrial complex, where BTBPE also showed the highest level. This results clearly reveal that petrochemical industry is the important source of BFRsin the marine environment. On the other hand, relatively high level of HBCDs were detected nearby densely populated areas in Busan.

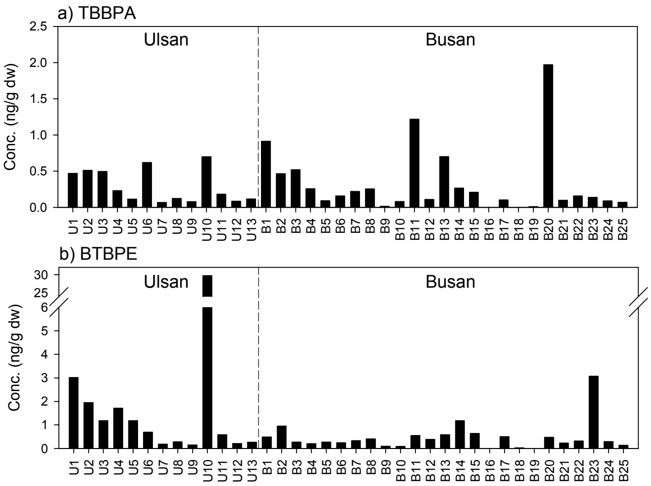

Figure 3. The distribution of (a) TBBPA and (b) BTBPE in the sediment from Ulsan and Busan

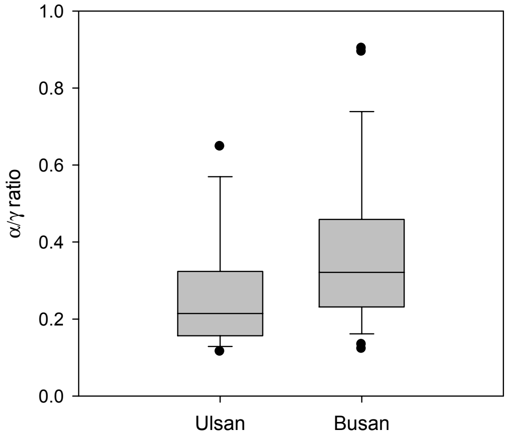

Figure 4. The α/γ ratio of HBCDs in the sediment from Ulsan and Busan

The mean concentrations of α-, β- and γ-HBCDs in both regions were 1.02±0.97 ng/g dw, 0.46±0.49 ng/g dw and 4.01±4.55 ng/g dw, respectively.Technical HBCD mixture consists mainly of the three diastereoisomers, α-, β- and γ-HBCDs, with a composition of 10–13%, 1–12%, and 75–89%, respectively. The mean α/γratiosin Ulsan and Busan were0.26±0.15 and 0.38±0.20, respectively(Fig. 4). The ratios in both regions are significantly different (*t*-test,p=0.058), indicating two regions are affected by the different type of HBCD sources. The ratio in Ulsan is more close to technical mixtures. It canbe expected that industrial effluents are dominantly responsible for the occurrence of HBCDs in Ulsan. On the other hand, urban activities (e.g. domestic sewage effluent)can be a major source of HBCDs in Busan, and, therefore, their chemical signatures are found to have more weathered and processed.

Acknowledgement
This work was supported by grants-in-aid Korea Institute of Ocean Science and Technology (Project No. PE99151).

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