

Contamination of Polybromodiphenylethers (PBDEs) in Sewer system of Hochiminh City and Estuary of Saigon-Dongnai River

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Introduction

Brominated flame retardants (BFRs) are chemicals commonly used in flammable consumer and industrial products, such as plastics, textiles, electrical and electronic equipment. Global demand for BFRs has increased from an estimated 145 kilotons in 1990 to 310 kilotons in 2001 (Alaee et al. 2001). Polybromodiphenylethers (PBDEs) and Hexachlorododecanes (HBCD) are of the most used BFRs with production of 67.5 kilotons for PBDEs and 16.7 kilotons for HBCD in 2001 (Alaee et al. 2001). Release of PBDEs and HBCD from relevant products have led to their ubiquity in the environment and bio-accumulation in animals and human body. Scientific evidences suggest relationship between bio-accumulation of some PBDEs congeners and adverse outcomes in animals such as reproductive/developmental effects, neurotoxicity and endocrine disruption. In vitro toxicological studies also demonstrate that hydroxylated metabolites of lower brominated PBDEs can compete with the thyroid hormone, thyroxine, for binding to the transport protein and transthyretin (Darnerud et al. 2001; Birnbaum & Staskal, 2004). Considering toxicity of PBDEs, the Stockholm Convention recently put Tetra-, Penta-, Hexa- and Hepta-BDEs in the new list of POPs. This movement has led to increasing demand of publish for more understanding on current contamination of PBDEs in environment, foods and humans.

With regard to contamination trend of BFRs in environment, Tanabe et al. (2007) showed increasing environmental contamination of PBDEs in several areas of Asia-Pacific, suggesting existence of high PBDEs levels in some particular hotspots such as ewaste-recycling places, industrialized and urbanized areas. However, there are still gaps on PBDEs contamination for most of cities and industrialized areas in Vietnam.

Minh et al. (2007) assessed POPs levels in sediment collected from sewer system of Hochiminh city (HCMC) and estuary of Saigon-Dongnai River (GS-DN River) which has very important role in social and economic development in South Vietnam. An interesting finding of the study is that POPs were found with relatively high levels in sewer system of HCMC, suggesting sediment as secondary sources of POPs to food chains. Considering this result and the connection between PBDEs contamination and industrialization/urbanization, it is very important to continue further assessment for PBDEs contamination in such important areas. The outcomes will help to understand their current contamination and potential risk to environmental quality and human health.

Materials and Methods

In this study, fourteen surface sediment samples (0–5cm of depth) from sewer system of HCMC and the estuary of SG-DN River were collected in 2004 using stainless-steel grabs (Fig. 1). For convenient discussion, we classified samples in three categories: sediments from sewer system of HCMC (SW1-SW5; also named as the urban sediments), sediments from sub-urban areas of HCMC (SUB1-SUB6; hereafter named as the sub-urban sediments) and sediments from estuary of the SG-DN River (EST1-EST3; hereafter named as the estuary samples).

Sediment samples were stored in clean polyethylene bags and transported to our laboratory in boxes packed with dry ice. In the laboratory, the sediment samples were kept ES-Bank (Ehime University) until analysis. Moisture content of sediment was determined by gravimetric method by heating about 2g of wet sediment at 1300C for 12 hours. For TOC analysis, about 2–3g of dry sediment was treated with hydrochloric acid 6N to remove carbon in the inorganic carbonate form. The sample was then washed 3 times by water and dried again in oven at 1100C for 12 hours. The dry sample was grounded and subjected for TOC analysis using CHN coder (MT-5; Yanaco, Kyoto, Japan).

Chemical analysis of PBDEs and HBCD followed the method described previously (Minh et al. 2007b). In general, approximately 20 g of wet sediment sample was extracted with acetone by shaking a flask vigorously for 60 min. The soil solution was filtered and separated entirely by water-hexane re-distribution method. The aqueous layer was discarded and hexane layer was collected. The extract was concentrated subjected to gel permeation chromatography (GPC) for cleanup. The GPC fraction containing organohalogens was concentrated and passed through a column packed with 1.5 g of activated silica gel for further cleanup and fractionation. The fraction containing PBDEs was eluted by 80 ml of 5% dichloromethane in hexane (v/v) and the fraction containing HBCD was eluted by 100 ml of 20% dichloromethane in hexane (v/v). PBDEs were analyzed using GC-MS and concentrations of congeners from di- to nona-BDEs were summed to obtain the total concentration of PBDEs. Concentration of deca-BDE was remained individually. The HBCD fraction was evaporated

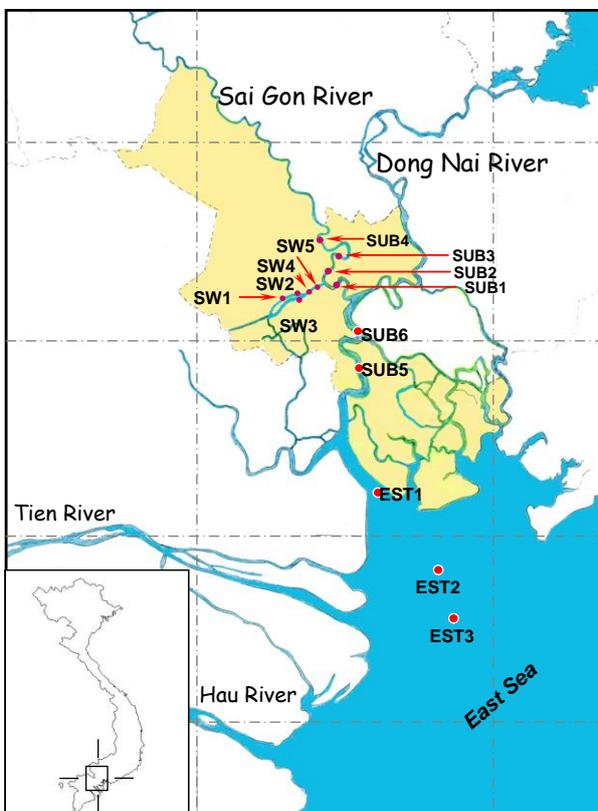


Fig. 1: Sampling location in HCMC and estuary of SG-DN River

and analyzed by Quattro Micro API triple-quadrupole mass spectrometer (Waters/Micromass, Tokyo, Japan) equipped with Alliance 2795 LC separation module (Waters, Tokyo, Japan).

Results and Discussion

Table 1 showed concentration of PBDEs, BDE-209 and HBCD with sampling locations. For purpose of comparison between Bromine compounds and Chlorine compounds, concentration of PCBs and DDTs were also given appropriately. Although concentration of PBDEs varied in wide range, they were detected in all sediments from sewer system of HCMC and in the estuary of SG-DN River, suggesting widespread contamination of these pollutants in the areas. Concentration of Σ PBDEs, varied from <0.01 to 15 ng/g dry wt, while those of BDE 209 ranged from <0.2 to 110 ng/g. Generally, in the same sediments, levels of BDE 209 were five to ten times higher than Σ PBDEs, implying high accumulation of BDE 209 in sediments. Levels of Σ PBDEs and BDE 209 were significantly higher in the sewer system of HCMC than those in the sub-urban areas and the estuary. In particular, Σ PBDEs ranged from 6.5 - 15 ng/g in HCMC sewer system but only from <0.01 - 1.4 ng/g in the sub-urban and the estuary. Similar result was also observed for BDE 209 (48 - 110 ng/g in HCMC's sewer system and <0.2 - 9.8 ng/g in the sub-urban areas and the estuary). This result implies clearly that the urban areas may serve as secondary pollution sources for PBDEs to the aquatic environment.

Table 1: PBDEs, BDE-209 and HBCDs (ng/g dry wt) in HCMC and GS-DN River's estuary

	Latitude	Longitude	TOC	PCBs	DDTs	Σ PBDEs	BDE-209	Σ HBCDs
Sewer system (HCMC, Urban sediment)								
SW1	N10°45'05.2"	E106°41'00.9"	3.8	65	39	6.5	48	1.4
SW2	N10°44'58.5"	E106°40'15.1"	4.2	100	41	15	104	1.7
SW3	N10°44'37.0"	E106°39'04.0"	4.9	150	72	8.1	63	1.3
SW4	N10°45'39.5"	E106°41'47.6"	3.2	46	21	6.5	77	0.94
SW5	N10°45'49.7"	E106°41'56.2"	4.6	76	37	11	72	1.9
Mean			4.1	88	42	9.4	73	1.4
Sub-urban sediments (HCMC)								
SUB1	N10°46'06.6"	E106°45'12.3"	1.9	8.5	4.7	1	5.3	0.64
SUB2	N10°45'55.5"	E106°42'42.6"	3.8	22	23	1.5	7.7	0.34
SUB3	N10°47'55.0"	E106°43'34.0"	2.8	3.8	1.1	0.12	2.7	< 0.1
SUB4	N10°48'38.0"	E106°43'17.0"	3.1	8.8	5.5	0.83	9.8	1.6
SUB5	N10°50'21.9"	E106°42'15.6"	2.1	0.33	0.21	< 0.01	< 0.2	< 0.1
SUB6	N10°36'91.8"	E106°46'51.0"	1.5	1.6	1.8	0.045	0.92	< 0.1
Mean			2.5	7.5	6.1	0.7	5.3	0.9
Estuary sediment (SG-DN River)								
EST1	N10°23'66.6"	E106°49'47.1"	1.3	1.2	0.82	0.065	< 0.2	< 0.1
EST2	N10°14'97.7"	E106°55'29.7"	1.5	0.49	0.43	< 0.01	< 0.2	< 0.1
EST3	N10°07'18.2"	E106°57'80.4"	0.49	0.73	0.39	< 0.01	< 0.2	< 0.1
Mean			1.1	0.81	0.55	0.028	< 0.2	< 0.1

PBDEs: Sum of BDE-28, 47, 99, 100, 153, 154, 183, 196, 197, 206, 207

HBCDs: Sum of α -HBCD, β -HBCD and γ -HBCD

HBCD were found in eight samples with level ranging from <0.1 to 1.7 ng/g (dry wt). This range is much lower compared to those of PBDEs, demonstrating low contamination of this group in the environment. Similar with PBDEs, among the three categories, sediments of the sewer system contains higher level of HBCD compared to sub-urban and estuary sediments. This fact may imply that emission and release of PBDEs in urban areas should be one of significant sources to the environment. Therefore, further studies to identify original sources and pathways of such chemicals may be needed to propose adequate management approaches.

Table 2 provides a short comparison of PBDEs and BDE-209 in sediments from different locations in the world. It can be seen in the table that levels of PBDEs and BDE-209 in sediments from HCMC and SG-DN River are much lower compared to those in Europe, Japan, Korea and China. This finding is consistent with results observed in study using green mussels as bioindicator for monitoring BFRs in Asia-Pacific (Tanabe et al., 2007). Tanabe et al. also found much higher levels of PBDEs in Korea, China, Hong Kong and Philippines compared to Cambodia, Vietnam, Malaysia and thus suggested countries such as Korea, China, Hong Kong and Philippines may act as emission sources of PBDEs to the region.

Table 2: Geographical comparison of PBDEs and BDE 209 in sediment

Location	Type of sediment	PBDEs	BDE-209	Reference
<i>North America</i>				
US	The Great Lakes	0.49-6.3	6.6-242	Song et al., 2004, 2005a, 2005b
<i>Europe</i>				
Belgium	Western Scheldt river	85-272	2842-8413	Covaci et al., 2005
Netherlands	rivers & estuaries	0.6-17.6	4-510	De Boer et al., 2003
Spain	Cinca River	0.4-34.1	2.1-39.9	Eljarrat et al., 2004
UK	river	0.5-16.8	0.6-119	Allchin et al., 2001
<i>Asia</i>				
China (1)	Qingdao near-shore	0.1-5.5		Yang et al., 2003
China (2)	Pearl River Estuary & South China Sea	0.04-94.7	0.4-7340	Mai et al., 2005
China (3)	Hong Kong coastal	4.39-52.07	nd-2.7	Liu et al., 2005
Korea (1)	Coastal areas	0.25-1.0	0.22-493	Moon et al., 2007a
Korea (2)	Industrial areas	0.03-5.0	2.0-2248	Moon et al., 2007b
Japan (1)	Tokyo Bay	0.05-3.6	0.89-85	Minh et al., 2007b
Japan (2)	rivers & estuary	0.013-2.4		Choi et al. 2003
Vietnam (1)	urban areas	6.5-15	48-104	present study
Vietnam (2)	river & estuary	<0.01-1.4	<0.2-9.8	present study

- All concentration in ng/g dry wt

Examination of congener profiles of PBDEs may give insights into usage pattern of commercial mixtures of PBDEs (Minh et al. 2007b). In this study, we recognize that when being included, BDE-209 accounts for more than 90% total concentration. On the other hand, if BDE-209 is excluded, three congeners of tetra-mixture (BDE-47, -99 and -100) contribute more less similar percentage compared to those of octa-mixture (BDE-153, -154, -183; Data

not shown). These facts may suggest existence of all three BDE commercial mixtures in the environment of Vietnam. While the deca-mixture dominates environmental releases, the tetra-mixture and the octa-mixture perhaps contributes similar inputs to the environment.

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