SPATIAL AND VERTICAL DISTRIBUTION OF BROMINATED FLAME RETARDANTS IN SEDIMENTS FROM MANILA BAY, THE PHILIPPINES

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Abstract

Brominated flame retardants, including polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), as well as PCBs were determined in surface and core sediments from Manila Bay, the Philippines. Organohalogen compounds analyzed in the present study were detected in most of the surface sediment samples, indicating ubiquitous pollution by these contaminants. Concentrations of BDE-209 were slightly higher than those of PCBs, probably because of the extensive usage of PBDEs in the Philippines. HBCD levels were two orders of magnitude lower than those of PCBs and PBDEs, suggesting that HBCDs are not extensively used in the Philippines. Concentrations of analytes were higher in the eastern part of the bay, implying municipal and industrial areas could be pollution sources of these chemicals. Results of sediment core analysis indicated highest concentrations of PCBs and PBDEs in the sediment layer deposited in the late 1990s. Although no obvious trend was observed for HBCDs due to low levels, it may increase in the future if usage is extended to developing countries.

Introduction

The use of brominated flame retardants (BFRs) has been increasing, especially in the last two decades, and as a result environmental contamination by BFRs is of growing concern[1-3]. Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are primarily used as additive BFRs, and are easily released into the environment during use and disposal of the products. Bioaccumulation of PBDEs and HBCDs as well as other persistent organic pollutants such as polychlorinated biphenyls (PCBs) have been reported in quantifiable levels in wildlife[4, 5]. Although contamination by BFRs has been a serious problem in Asian developing countries, information on the present status and temporal trend of BFRs pollution is limited. The coastal area is considered to play a major role as a sink for environmental contaminants. Manila Bay, located in the northern Philippine island of Luzon, is one of the largest protected bays of Southeast Asia, with a surface area of 1980 km^2 and an average water depth of 18 m. About 17 million people live in Metro-Manila and large-scale municipal and industrial activities take place

in the watershed of the bay; this condition has caused significant eutrophication to the system. In addition, the bay also receives a wide range of chemicals from agricultural fields, mining areas and an active volcanoe. Therefore, a survey of anthropogenic contaminants in Manila Bay is necessary to evaluate and monitor the fate and toxicological effects in the tropical aquatic environment. In this study, the spatial distribution and vertical profile of PBDEs and HBCDs as well as PCBs were investigated in 33 surface sediments and a sediment core from Manila Bay, the Philippines.

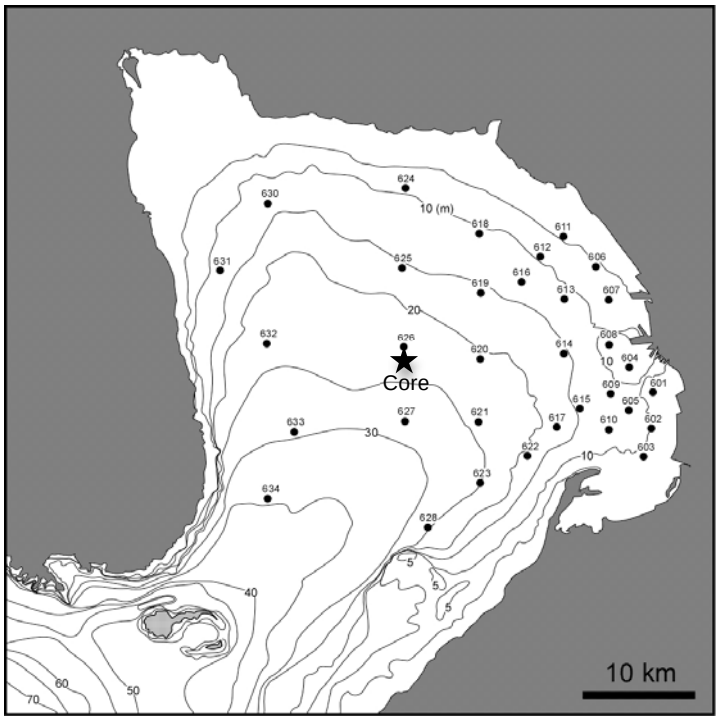

Fig. 1. Sampling locations

Materials and Methods

Samples

A total of 33 surface sediments and one sediment core were collected from Manila Bay, the Philippines, in June and November 2008 (Fig. 1). Surface sediment was taken using an Ekman grab and the top 3 cm was sampled. The sediment core was collected using a gravity core sampler and sliced at 2 cm intervals after transporting to the lab. All sediment samples were stored at -25 ˚C until chemical analysis.

Chemical analysis

Sediment samples were analyzed following the method described elsewhere[6, 7] with some modifications. Briefly, 5 g of freeze-dried sediment was spiked with surrogates ($^{13}C_{12}$-PBDEs and $^{13}C_{12}$-HBCDs) and extracted with hexane/acetone using an ultrasonic extractor. The extract was purified with multi-layer column chromatography and concentrated sulfuric acid. Sulfuric acid was removed by liquid-liquid extraction using hexane and hexane-washed water. The hexane layer was concentrated, cleaned with gel permeation chromatography (GPC), and fractionated with an activated silica gel column chromatography. The fraction containing PBDEs was treated with activated copper strings to remove sulfur. $^{13}C_{12}$-BDE-139 was spiked as an internal standard and subjected to GC-MS analysis. Concentrations of all the targeted BDE congeners (from mono- to nona-brominated), except BDE-209, were summed to obtain

Table 1. Concentrations of organohalogen compounds (ng/g dry) in surface sediments from Manila Bay

ID	Sediment Charactaristic	Depth (m)	Water content (%)	PCBs	BDE-209	∑PBDEs	HBCDs
601	mud	5	79	55	35	4.0	1.1
602	mud	5	62	13	1.7	0.08	0.07
603	mud	5	79	16	13	2.3	0.31
604	mud	5	66	61	74	8.2	1.5
605	silt	10	75	9.2	32	3.9	0.08
606	mud	5	68	17	14	1.8	0.21
607	mud	7	68	61	28	2.1	0.53
608	mud	10	70	110	110	18	2.8
609	mud	10	75	38	80	9.8	0.56
610	mud	12	69	12	14	1.1	1.0
611	silt	5	65	39	14	2.2	0.58
612	mud	8	75	17	22	2.9	0.11
613	sandy silt	10	50	1.6	13	1.6	0.02
614	silt	15	65	19	20	1.5	0.30
615	mud	12	72	21	40	2.9	0.31
616	mud	12	77	19	18	1.2	0.14
617	mud	17	69	16	18	2.1	0.06
618	silt	10	63	6.1	7.3	<0.10	0.05
619	mud	15	74	12	16	1.0	0.07
620	silt	20	75	4.9	15	1.0	0.03
621	silt	24	72	4.4	4.6	0.13	0.09
622	mud	20	65	3.1	15	0.80	0.13
623	sandy silt	25	60	1.2	1.7	0.00	0.04
624	silt	7	69	4.2	3.7	0.26	0.12
625	mud	14	70	3.2	4.1	0.59	0.06
626		22	71	2.9	6.5	0.55	0.06
627	sandy silt	27	73	2.8	3.2	0.33	<0.02
628	sandy silt	25	53	<0.50	0.90	0.12	<0.02
630		12	68	0.23	1.0	<0.10	<0.02
631	sandy silt	20	66	2.7	1.2	0.27	<0.02
632	sandy silt	22	69	2.1	3.3	0.44	0.86
633	silt	28	69	1.6	2.5	0.21	0.04
634	silt	34	70	1.6	1.1	0.16	0.02

concentration of ∑PBDEs. Concentrations of BDE-209 were shown separately. The HBCDs fraction was evaporated and spiked with HBCDs-d_{18} prior to LC-MS/MS analysis. Concentrations of PBDEs and HBCDs were expressed as ng/g dry weight unless stated otherwise.

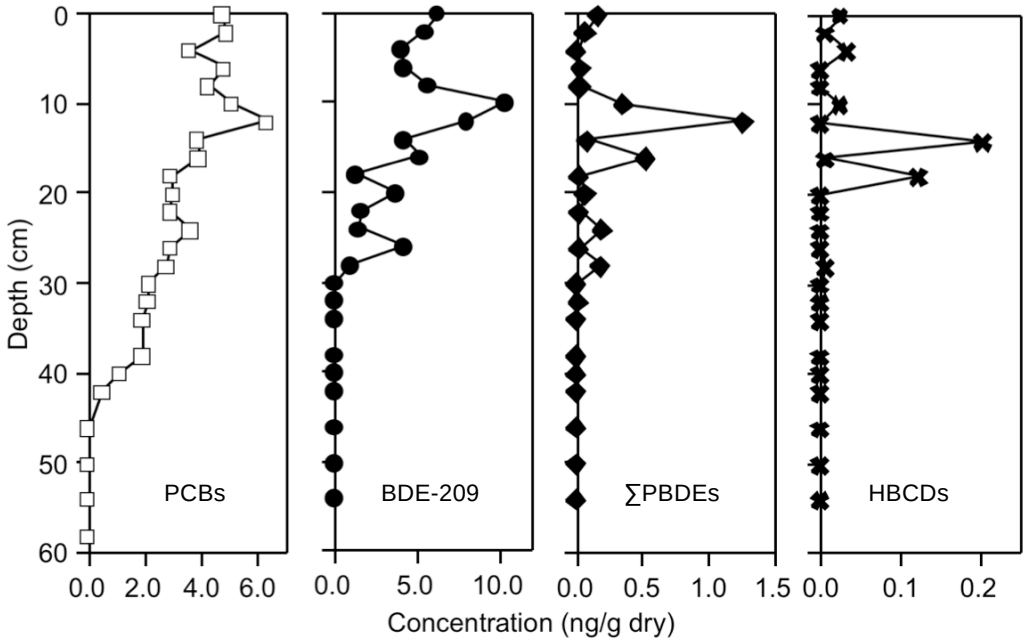

Fig. 2. Vertical profiles of PCBs, BDE-209, ∑PBDEs and HBCDs in the sediment core from Manila Bay

Results and Discussion

Spatial distribution

Organohalogen compounds analyzed in the present study were detected in most of the surface sediment samples, indicating ubiquitous pollution by these contaminants (Table 1). Concentrations of PCBs, BDE-209, ∑PBDEs and HBCDs in surface sediments ranged from <0.50 to 110, 0.90 to 110, <0.10 to 18 and <0.02 to 2.8 ng/g dry wt, respectively. Concentrations of BDE-209 were slightly higher than those of PCBs, probably because of the extensive usage of PBDEs in the Philippines. HBCD levels were two orders of magnitude lower than PCBs and PBDEs, suggesting that HBCDs are not extensively used in the Philippines or at least not available to the bay. These levels are baseline data for tracking future use since HBCDs were detected for the first time in this region. Levels of organohalogen compounds in the surface sediments were higher in the eastern part of the bay, in close proximity to the highly populated and industrial area of Metro-Manila, implicating industrial and municipal activities as sources of these compounds. Similar distribution patterns were observed in sediment samples from Tokyo Bay[7]. Concentrations of BDE-209 were one order of magnitude higher than ∑PBDEs, including mono- to nona-brominated congeners, which is consistent with the other reports dealing with sediment samples.

Vertical profile

Vertical profiles of PCBs, BDE-209, ∑PBDEs and HBCDs in the sediment core from Manila Bay are shown in Fig. 2. The result from core sediment analysis indicated increasing trends in the sediment layer

from 40 to 10 cm, and a steady state in the upper layers for PCBs and BDE-209. Concentrations of BDE-209 increased from the middle layer (28 cm) while PCBs were detected in the deeper (42 cm) layer. This phenomenon is consistent with the fact that commercial use of deca-BDE mixture started from the 1980s while PCBs had been used since the 1950s. The highest concentrations of PCBs, BDE-209 and ∑PBDEs were observed in the layer deposited in the late 1990s. In recent years ∑PBDEs showed a decreasing trend in the upper layers, which may be a result of the phasing-out of lower brominated PBDE products in the early 2000s. Although no obvious trend was observed for HBCDs due to the low levels, it may increase in the future if usage is extended to developing countries. To prevent future environmental pollution by these persistent contaminants and to evaluate ecological risks, further retrospective studies using sediment cores and archived samples from Asian developing countries are warranted.

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