

POLYCHLORINATED BIPHENYLS (PCBs) AND BROMINATED FLAME RETARDANTS (BFRs) IN SURFACE SEDIMENTS OF SURABAYA CITY, INDONESIA: A COMPARISON BETWEEN RIVERS AND COASTAL WATERS

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Abstract

The present study reports the contamination status of polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs) in river and coastal sediments of Surabaya city, Indonesia. Surabaya is the second largest city in Indonesia which is characterized by rapid urban and industrial development during recent decades. Concentration of PCBs and BFRs in sediments varied according to the location, being higher in rivers, probably because of their proximity to the sources than in coastal areas due to the reduction in their levels caused by the high hydrodynamic factors in the narrow strait of Surabaya waters. For instance, among the fourteen PBDE congeners analyzed in this study, only higher BDE congeners were detected in the coastal sediments (BDE-196, -197, -206, -207 and BDE-209), while almost all congeners were identified in rivers. Among PCBs, tetra to hepta-CBs were the predominant, except in one location with abundant tri- to tetra-CBs, implying specific sources of different technical formulations. The PBDE profiles corresponded with various other studies in which BDE-209 was predominant and attributed to possibly high usage of deca-BDE mixture and its large molecular size. In case of HBCDs, all HBCD isomers were detected with γ -HBCDs as the abundant isomer in most of the samples, the profiles being similar to technical mixtures.

Keywords: BFRs, PCBs, Surface sediments, River, Coastal waters, Contamination status

1. Introduction

Persistent organic pollutants (POPs) and emerging contaminants such as polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs) have recently become a matter of concern due to their increasing levels in the environment. Moreover, because of the properties such as low volatility, relatively persistent, chemically stable and bioaccumulative nature, environmental contamination by these compounds have been suspected to several problems and health risks to wildlife and human such as carcinogenicity, neurotoxicity, teratogenicity and hormone disruption.

PCBs have been used as heat-exchange fluids in electric transformers and capacitors, as additives in carbonless copy-paper, sealants and plastics under various brand names^{2,3}. BFRs, a group of chemicals consisting of organic compounds containing bromine, have been used for decreasing the flammability of various consumer products, effectively in plastics and textile applications. These compounds are used in electronic products, and generally exist in the printed circuit boards, connectors, plastic covers and cables of computers. Furthermore, BFRs have also been applied in various household products such as plastic covers, carpets, paints, upholstery, kitchen appliances, etc⁴. Therefore, sources of these compounds are present in our ambient environment including homes, offices, work places, public spaces, etc.

Surabaya is the second largest city in Indonesia with a total population of approximately 3 million. As an international trading city with three industrial areas, Surabaya has potential contamination sources of PCBs and BFRs. Moreover, the rapid growth of this city might significantly relate to high human activities and result in stresses on various environments, both land and coastal waters. As a result, bulky waste disposals containing PCBs, BFRs and other toxic substances are continuously loaded into the coastal waters through the rivers. Therefore, estuarine or coastal sediments could serve as media for the transport of contaminants into the aquatic environments⁵. Consequently, assessment of the contamination status of PCBs and BFRs in sediments from such media is needed for understanding and mapping their sources and pathways. The present study is aimed to

provide preliminary information on the levels, profiles and distribution of PCBs and BFRs in the rivers and coastal waters of Surabaya city.

2. Materials and Methods

2.1. Study Area and Sample Collection

Surabaya is located between 7°12'–7°21' South Latitude and between 112°36'–112°54' East Longitude, and situated at 3-6 meters above sea level. The city is surrounded by Madura Strait on northern and eastern parts, Sidoarjo Regency on the southern and Gresik regency on the western part (Figure 1) with a total area of around 33,306.30 km². Surabaya city is influenced by two seasons (dry season during May to October, and rainy season during November to April) with an average total rainfall of 181 mm. Thirty five coastal sediments and nineteen river sediments were collected from Surabaya coastal waters and watersheds using Van Veen Grab sampler during September 2008. Of these samples, only 38 sediment samples were used in the present study (14 river sediments; 24 coastal sediments). Details of sampling locations and sampling sites are shown in Figure 1. Samples were kept in ice boxes, transported to Japan and stored at -20°C in the Environmental Specimen Bank (*es*-Bank) of Ehime University prior to chemicals analyses.

2.2. Chemical Analysis

2.2.1. Extraction and Clean-up

BFRs and PCBs were analyzed using the method described by Minh et al.⁶ with slight modification. Briefly, 10-15 g of freeze dried sediment sample was spiked with ¹³C₁₂-BDEs (¹³C₁₂-BDE-3, -15, -28, -47, -99, -153, -154, -183, -197, -207 and -209), ¹³C-HBCD (α -, β - and γ -¹³C₁₂-HBCD) and ¹³C₁₂-PCBs as labeled recovery internal standards (LRIS) for measuring the extraction efficiency and losses during extraction and clean-up. The sample was liquid-liquid extracted using a mixture of 50% of acetone/hexane (v/v), shaken vigorously for 60 minutes using an electric shaker (SR-2W model, TAITEC, Japan) and ultra-sonified for 15 minutes. The extract was then centrifuged and the supernatant was collected. The extract was concentrated to about 1~2 ml in a rotary evaporator. As the first step of clean-up procedure, the concentrated extract was passed through a multi layer silica gel column using 25% of DCM/Hexane (v/v) as the solvent for elution. For further clean-up, the extract was treated with concentrated H₂SO₄ prior to gel permeation chromatography (GPC). The GPC fraction containing organohalogens was concentrated and passed through a column packed with 4 g of activated silica gel for final purification and fractionation. The fraction containing PBDEs was eluted by 80 ml of 5% dichloromethane in hexane (v/v) and the fraction containing HBCDs with 100 ml of 25% dichloromethane in hexane (v/v). The fraction containing PBDEs was concentrated to 5 ml and treated with activated copper strings. ¹³C₁₂-labeled BDE-139 was added as a labeled instrument performance and matrix internal standard (LIPMIS) prior to gas chromatography analysis. For the HBCDs fraction, the solution was evaporated, transferred to a glass vial and spiked with 10 ng of HBCD-*d*₁₈ (α -, β - and γ -HBCD-*d*₁₈) as an internal standard prior to LC-MS-MS analysis.

2.2.1. Instrumental Analysis

Quantification of PBDEs was carried out by a gas chromatograph coupled with a mass spectrometry detector (GC-MS) in the negative chemical ionization mode. A liquid chromatography with a tandem mass spectrometry detector (LC-MS-MS) using electrospray ionization was used for assessing the isomeric composition of HBCDs.

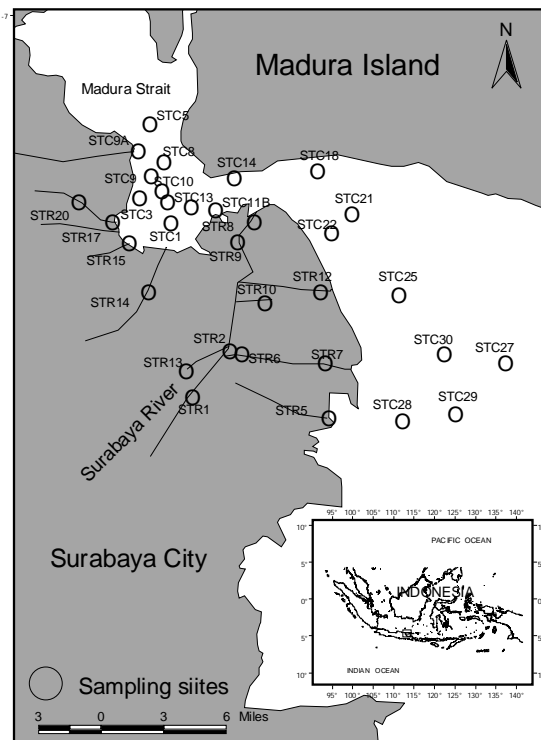


Figure 1. Study area and sampling sites; STR:river sites, STC:coastal sites.

All the congeners and isomers were quantified using the isotope dilution method to the corresponding $^{13}\text{C}_{12}$ -labeled congeners. The instrumental condition was kept as described previously by Minh et al.⁶. Fourteen PBDE congeners from mono- to deca-BDE (BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-206, BDE-207, and BDE-209), three HBCD isomers (α -, β -, γ -HBCD) and 61 PCB congeners were analyzed in this study. Concentrations of all the targeted BDEs congeners, HBCD isomers as well as PCBs were summed to obtain the values of Σ PBDEs, Σ HBCDs, and Σ PCBs respectively. Concentrations of all target contaminants are expressed as ng/g dry weight unless otherwise specified.

3. Results and Discussion

3.1 Occurrence of PCBs

Levels and profiles of Σ PCBs in sediments from coastal waters and rivers of Surabaya are shown in Fig. 2 and Fig. 4. Concentrations of PCBs were higher in river sites than coastal waters. In rivers, levels of PCBs ranged between 0.58-420 ng/g dw., while in coastal waters the levels were 0.15-3.0 ng/g dw. Higher levels of PCBs in sediments from rivers than coastal waters indicated that land based activities such urban, industrial, commercial, and harbor were the main sources of PCBs, whereas, the lower levels of PCBs in coastal waters might have been due to the influence of high hydrodynamic factors in very narrow channel of Surabaya coastal waters.

Among PCBs (Fig. 4), hexa- to hepta-CB homologues were predominant in sediments from rivers and coastal areas. However, PCBs profile at ST-R9, predominated by tri- to tetra-CBs, was absolutely different from others. The different profile at this site may be due to specific technical PCBs input different from other sites. For instance, cluster analysis on the similarity of PCB homologues (Fig. 3) shows that the composition of PCB homologues in sediments at STR9 was similar (85%) to some technical PCBs including Ar1242, Ar1016, and KC-300, while in the profiles in other sites were similar (65%) to other technical PCBs such as KC-600, Ar1260 and Ar1262. These results indicate the possible use of various PCBs formulations in the study area. However, the predominance of hexa-CB and hepta-CB in almost all sediments samples of the present study could be due to the larger application of higher congeners-containing PCBs formulations and the persistence of these larger congeners (number of chlorine atoms >5)⁷.

3.1 Occurrence of BFRs

As shown in Fig. 5, like PCBs, concentrations of BFRs were also higher in rivers (0.54-35 ng/g dw. for PBDEs and 0.03-5.4 ng/g dw. for HBCDs) than coastal waters (0.17-3.1 ng/g dw. for PBDEs and 0.002-0.82 ng/g dw. for HBCDs). Furthermore, PBDE congener profiles also showed different patterns between rivers and coastal areas in which river sediments contained both low and high PBDE congeners, while the coastal sediments had high PBDE congeners only.

Among the PBDE congeners detected, BDE-209 was most prominent in sediments. This result is in accordance with various studies worldwide⁸. The predominance of BDE-209 in sediments of the present study suggests that deca-PBDE mixture could be a major contributor of PBDEs into the Surabaya aquatic environment. Deca-BDE mixture is a commercial product of PBDEs containing >97% of BDE-209 and minor contributions by other congeners (0.3 to 3.0%) such as octa- and nona-BDE congeners⁹. The profile of PBDEs in the present study is similar to the largest selling commercial formulation used in Asia. For instance, total consumption of deca-BDE commercial mixture in Asia at 2001 was 7,600 ton, much higher than the consumption of penta- (150 tons) and octa-BDE mixtures (610 tons)⁸.

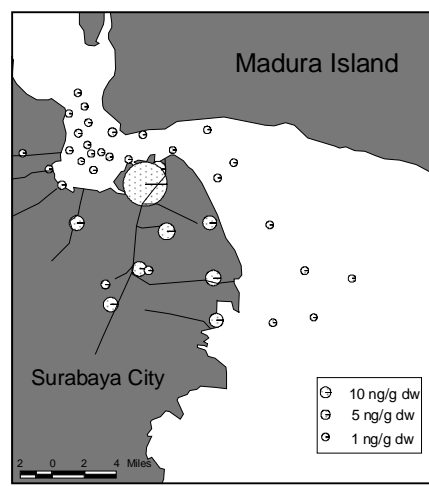


Figure 2. Levels and distribution of PCBs in surface sediments of Surabaya coastal waters and its watersheds.

In addition, apart from its origin from commercial formulation, the predominance of BDE-209 in sediment could also be explained by the fact that this congener has large molecular size and hence highly hydrophobic; thus bind preferentially to the particle phases such as organic rich sediment particles. Though BDE-209 has been considered as a congener which does not bioaccumulate in aquatic food webs, loading of BDE-209 into the aquatic environment will significantly increase their existence in sediments and thus may present a long-term threat to biota as it may be broken down into more persistent, bioaccumulative, toxic, and mobile PBDE congeners in the environment¹⁰.

In case of HBCDs, three isomers were detected and γ -HBCD was predominant, followed by α - and β -HBCD (data are not shown). The profiles of HBCDs in sediments were relatively close to the composition in technical mixtures in which γ -HBCD constitutes larger proportion (α -10-13%, β -1-12%, and 75-89% γ -HBCDs)¹¹.

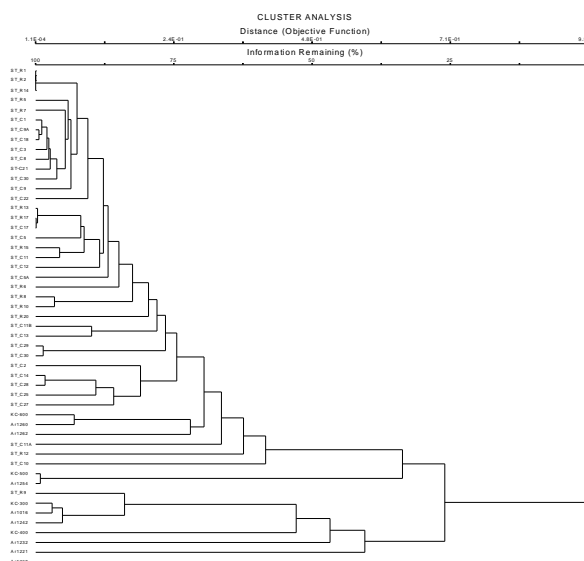


Figure 3. Similarity of sites based on profiles of PCB homologous.

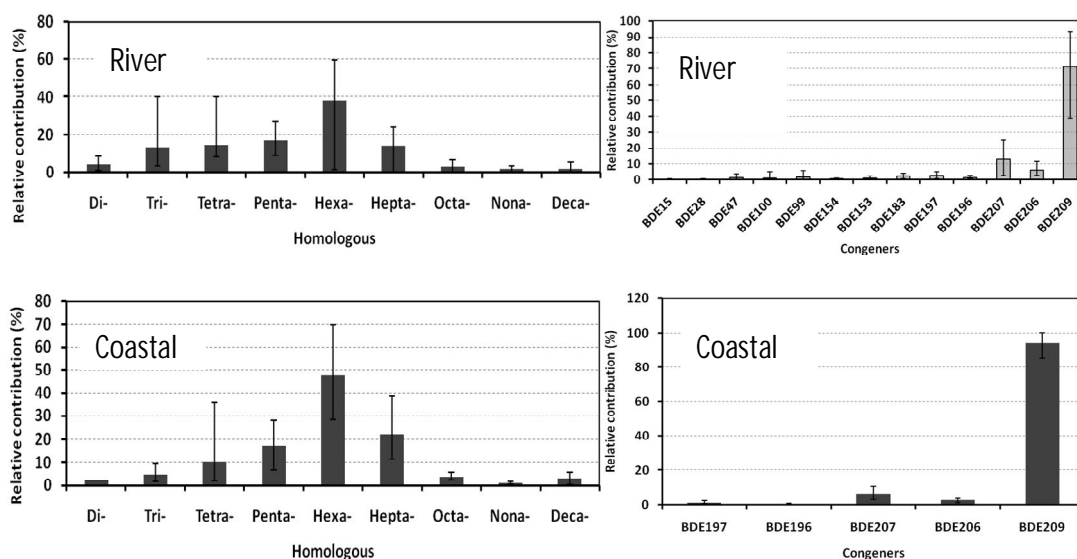


Figure 4. Profiles of PCBs and PBDEs in surface sediments of Surabaya coastal waters and its watersheds.

Table 1. Comparison of BFRs concentrations (ng/g dw.) in sediments measured in this study with other locations worldwide.

Location	Sampling Year	<i>n</i>	∑PBDEs	∑HBCDs	References
Surabaya, Indonesia	2008	12	0.17-35	0.002-5.4	Present study
Jakarta Bay, Indonesia	1998	7	0.03-57	nd-0.96	[12]
Busan Bay, Korea	2003-2004	20	14.4-2253	1.8-2.6	[13, 14]
Ulsan Bay	2003-2005	20	3.42-286	4.2-5.4	[13, 14]
Jinhae Bay, Korea	2003-2004	20	2.0-14	na	[13]
Nekdon Estuary, Korea	2005	1	25	1.8	[14]
Tokyo Bay, Japan	2002-2003	6	0.94-19	0.06-2.3	[6]
Singapore	2003	3	3.4-13.8	na	[13]
Bo Sea, China	2006	16	0.37-2781	na	[15]
Yangtze River, China	2002-2004	32	0.16-94.6	na	[16]

n = number of samples, na= not available, ∑PBDE= sum of PBDEs, ∑HBCD= sum of HBCDs

The magnitudes of contamination of BFRs in sediments from Surabaya coastal waters and its watershed (Table 1) showed that levels of PBDE are higher than those measured in Jinhae Bay and Nakdon Estuary (Korea), Tokyo Bay (Japan) and Singapore coastal area; however the levels were lower than those in Jakarta Bay in Indonesia, Busan Bay and Ulsan Bay in Korea and Bo Sea and Yangtze River in China. In the case of HBCDs, levels of this compound in Surabaya coastal waters and its watersheds are relatively similar with those in sediments from Ulsan Bay in Korea, but higher than those observed in Busan Bay and Nakdon Estuary in Korea and Tokyo Bay in Japan. The levels, however, are lower when compared with those in Jakarta Bay.

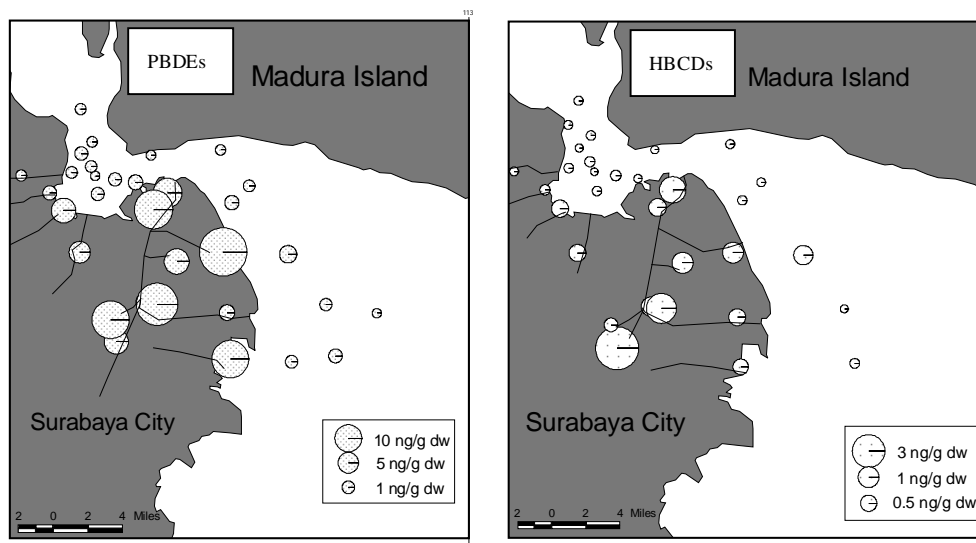


Figure 5. Levels and distribution of BFRs in sediments collected from Surabaya coastal waters and its watersheds.

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