

# RESIDUE AND RISK ASSESSMENT OF POLYBROMINATED DIPHENYL ETHERS (PBDES) IN SEDIMENT FROM CAUBAY RIVER, VIETNAM

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**Abstract:** *This research presents the assessment of congener profiles (7 indicator congeners) of Polybrominated diphenyl ethers (PBDEs) in sediment samples covering ten sites in CauBay River, Hanoi. Chemical analyses were carried out in gas chromatography–mass spectrometry (GC–MS) for tri- to hepta- brominated congeners. Results pointed out a non-homogenous contamination of the sediment with  $\sum_7$  PBDE values ranging from 8.93 to 25.64 ng g<sup>-1</sup>, reflecting moderate contamination closely in conformity to other Asian environmental sediment. The general order of decreasing congener contribution to the total load was: BDE 47 > 99 > 100 > 154, similar to the PBDEs distribution pattern worldwide. PBDEs had low environmental risks in the sediment of studied area. However, due to the propensity of PBDEs to highly accumulate in various compartments of wildlife and human food webs, further evaluation of ecological risk assessment in CauBay River should be undertaken as a high priority.*

**Keywords:** Residue, Risk assessment, PBDEs, Sediment.

## 1. INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are used commercially as additives in plastics and textiles, building materials, carpets, and in vehicles and aircraft with half-lives on the order of 2–10 years. In computers, these compounds are commonly used in printed circuit boards, components such as connectors, cables, plastic covers and parts of keyboards and monitors. They are highly resistant to acids, bases, heat, light, oxidizing and reducing compounds and, as a result, are extremely persistent when released into the environment. The use of PBDEs has increased over the last 30 years with production estimated to be about 3000–5000 tons in Europe. Deca-BDE is the largest mix on the market and makes up over 80% of the total PBDE production, whereas penta-BDE and octa-BDE products constitute about 12% and 6%, respectively, of the total PBDE production [1]. The presence of high levels of these compounds in samples from remote areas suggests that they may now have been

distributed worldwide as a result of long range atmospheric transport. PBDEs have been associated with endocrine disruption, reproductive/developmental toxicity including neurotoxicity and cancer. Sediments are major sinks for these contaminants in aquatic environments and their study is an important step in mapping possible pollution sources and exposure pathways which facilitate PBDE bioavailability to sediment dwelling organisms.

Hanoi city, the capital of Vietnam, is the centre of culture, politics, economy and trade for the whole country. The CauBay River, a very important channel to discharge various wastewaters from domestic and industries in Hanoi, has upstream from LongBien district and downstream at KieuKy commune, GiaLam district. CauBay River also is the only sources to supply irrigated water to communes which have agricultural activities at the downstream. PBDEs pollution will seriously affect irrigated water quality of these communes. However, to our knowledge, few data are available for the contamination of PBDEs in this river. These objectives of this research are to assess the residue and ecological risk assessment of PBDEs in sediment from CauBay River to fill this gap.

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## 2. MATERIALS AND METHODS

The sampling was carried out in April 2013, during the dry season. A total of 10 sediment samples in 10 sites along Cau Bay River were collected. Figure 1 shows the study area and the sampling locations. The surficial sediment was collected with a stainless steel grab. All the samplers were freeze-dried, homogenized, passed through a 63  $\mu\text{m}$  sieve and kept at  $-20^\circ\text{C}$  until extraction. All the equipments used for sample collection, transportation, and preparation, were free from PBDEs contamination. A mixed standard solution of 7 PBDE congeners, including BDE-28, -47, -99, -100, -153, -154, -209 as well as the internal standard 2,2',4,4',6,6'-hexabromo biphenyl (BB-

155) were purchased from AccuStandard (New Haven, USA).

Samples (about 10 g) were spiked with 2 ng of internal standard BB-155 and extracted for 12 h using 100 mL acetone/*n*-hexane (1:1 v/v) mixture in a cold soxhlet apparatus. One milliliter of isoctane was added to samples that were dried using a rotary evaporator and under nitrogen flow to about 1 mL of final volume. Cleanup was performed using a multilayer column, composed of 10 g of silica gel (activated overnight at  $130^\circ\text{C}$ , then deactivated with water, 5% w/w), followed by 10 g of Florisil (activated for 16 h at  $650^\circ\text{C}$ ), 1 g of anhydrous sodium sulphate, and lastly, 0.5 cm of activated powdered copper at the top.

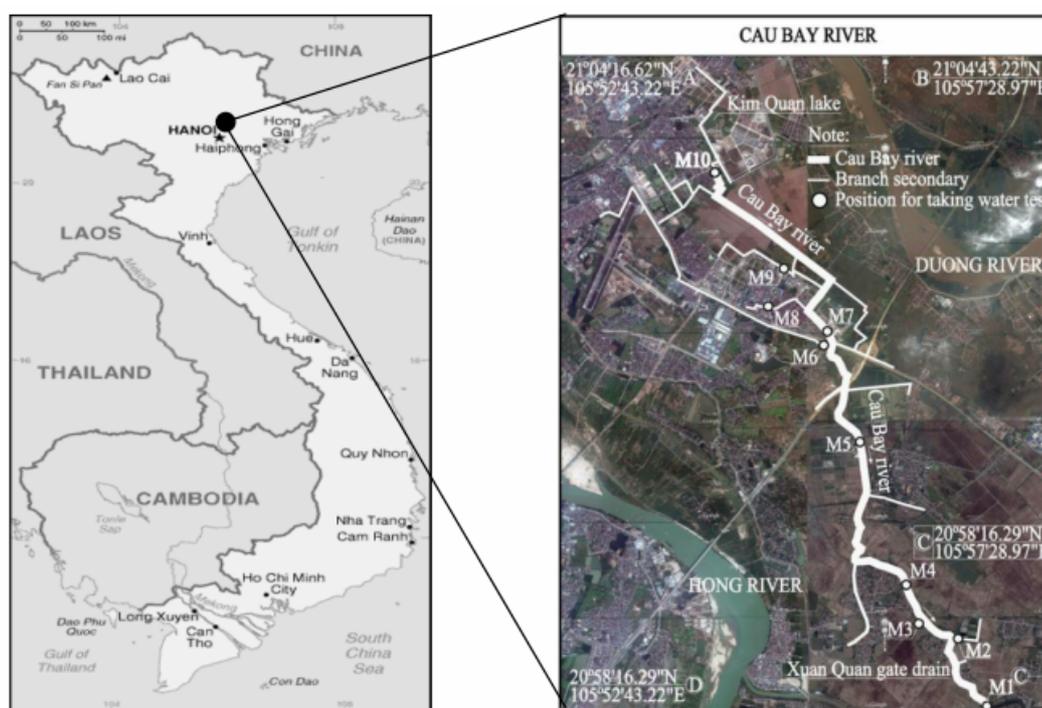


Figure 1. Study area and sampling locations

The column was washed with *n*-hexane/acetone/dichloromethane (8:1:1 v/v). Elution was carried out first by collecting 50 mL of *n*-hexane and then 50 mL of 1:1 *n*-hexane/dichloromethane (v/v). The two portions of eluent were concentrated by rotavapor to 10 mL, and then to 1 mL under nitrogen flow. The samples were analyzed with the gas chromatograph (Trace GC 2000, USA) equipped with Rtx-5MS capillary column (30m

length x 0.25 i.d. mm x 0.25  $\mu\text{m}$  film thickness) and PolarisQ Ion Trap mass spectrometer. Limits of quantification (LOQs) were quantified for each brominated class. LODs were  $0.12 \text{ ng g}^{-1}$  for tri-BDEs and tetra-BDEs,  $0.18 \text{ ng g}^{-1}$  for penta-BDEs and hexa-BDEs,  $0.25 \text{ ng g}^{-1}$  for hepta-BDEs and  $0.20 \text{ ng g}^{-1}$  for BDE-209. Total organic carbon contents were determined using Apollo 9000 TOC analyzer (Tekmar-Dohrmann Co., USA).

### 3. RESULTS AND DISCUSSION

#### 3.1. PBDEs Contamination status

The PBDEs concentrations in the collected sediment samples from CauBay River are shown in Table 1. PBDEs were detected in all sediment samples. In industrial and urban sampling sites,  $\sum_7$  PBDEs concentrations ranged from 15.39 to 25.64 ng g<sup>-1</sup> dry weight

(from M6 to M10), while those in agricultural sampling sites ranged from 8.93 to 12.47 ng g<sup>-1</sup> dry weight (from M1 to M5). It is observed that the highest value corresponded with site near wastewater lake from resident area of SaiDong ward, LongBien District (site M8, 25.64 ng g<sup>-1</sup>). This area is polluted by wastewater of SaiDong industrial park.

**Table 1. PBDEs concentrations (ng g<sup>-1</sup>) and TOC (%) in the sediment samples**

Sampling sites	TOC (%)	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-209	$\sum_7$ PBDEs
M1	3.7	0.26	1.38	1.18	1.37	0.42	0.63	7.18	12.42
M2	2.1	0.32	1.28	1.47	1.19	0.39	0.74	3.54	8.93
M3	2.3	0.27	1.77	1.36	0.78	0.42	0.75	4.17	9.52
M4	2.5	0.21	1.47	1.17	0.69	0.34	0.54	6.17	10.59
M5	2.7	0.19	2.46	1.85	0.79	0.44	0.56	6.18	12.47
M6	3.8	0.24	2.17	1.57	0.88	0.34	0.43	9.76	15.39
M7	3.9	0.18	4.18	3.28	0.87	0.56	0.82	12.28	22.17
M8	4.4	0.31	5.28	4.16	1.72	0.37	0.94	12.86	25.64
M9	3.2	0.55	2.85	2.55	0.92	0.59	0.74	10.35	18.55
M10	3.5	0.36	3.16	2.65	1.23	0.48	0.73	11.85	20.46

$\sum_7$  PBDEs concentrations were calculated as the sum of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-209.

The other significant level of  $\sum_7$  PBDEs was found at sampling site close to DaiTu industrial parks (site M7) with PBDEs concentration are 22.17 ng g<sup>-1</sup> (Table 1). At present, there is no Vietnamese standard on the maximum allowable concentration of total PBDEs in sediment, nor is there official quantitative information on the cumulative use of PBDEs in Hanoi. The analytical results in Table 1 indicated the wide occurrence of PBDEs in the sediment of CauBay river.

A comprehensive comparison of PBDEs levels in recently collected sediments from

various locations in Vietnam and in the world is presented in Table 2. It can be recognized that among the reported locations in Vietnam, the residue of PBDEs in sediment of the Hochiminh City canals are highest followed by CauBay river, ThiNai Lagoon and Saigon – Dongnai estuary. The result indicates Hanoi City itself likely comprises sources of PBDEs pollution. Furthermore, the sediment levels of PBDEs in CauBay river are comparable to those found in the highly polluted areas of Lake Mjøsa (Norway) and lower than those in Hong Kong marine sediments.

**Table 2.  $\sum_7$  PBDEs concentrations (ng g<sup>-1</sup>) in the sediment samples of different countries**

Location	$\sum_7$ PBDEs concentrations (ng g <sup>-1</sup> )	Sources
Vietnam		
+ CauBay river	8.93 - 25.64	This study
+ ThiNai Lagoon	0.03 – 8.93	Stefania et al. (2013) [8]
+ Hochiminh City canals	< 0.12 – 119.0	Minh et al. (2009) [5]
+ Saigon-Dongnai estuary	< 0,02 - 0,065	Minh et al. (2009) [5]
Hong Kong marine sediments	1.7–53.6	Liu et al. (2005) [3]
Pearl river delta	0.15 – 13.03	Zheng et al. (2004) [10]

Location	$\sum_7$ PBDEs concentrations (ng g <sup>-1</sup> )	Sources
Singapore coasts	3.4 – 13.8	Wurl et al. (2005) [9]
River sediments of Portugal	20 <sup>(a)</sup>	Lacorte et al. (2003) [2]
Lake Mjøsa (Norway)	0.6 – 27	Schlabach et al. (2004) [7]
San Francisco estuary (USA)	< 0.12 – 211.8	Oros et al. (2005) [6]

a: mean value

Because of their high hydrophobicity, PBDEs were expected to be associated with organic-rich particles. Medium positive correlation ( $r^2 = 0.72$ ,  $n = 10$ ) between  $\sum_7$  PBDEs and total organic carbon (TOC) percentages in analyzed sediment sample were found. By evaluating the correlation between TOC and the concentration of PBDEs in sediments of CauBay river, ThiNai Lagoon and Saigon – Dongnai estuary, this study demonstrated that higher amounts of these pollutants mainly occurred in sediments with high TOC. In general, the TOC values in CauBay river (2.1 – 4.4 %, Table 1) are higher than those in the ThiNai Lagoon (0.33 – 1.95%) and Saigon – Dongnai estuary (0.49 – 1.5%). This could explain the higher concentrations of PBDEs in CauBay river in comparison with those in reported locations in Vietnam (Table 2).

### 3.2. Composition analyses

Concerning the composition analyses, PBDEs congeners could be detected from tri-BDE to deca-BDE in the collected sediment samples. BDE-209 was predominant congener

in sediment samples. The percentages of BDE-209 vary from 40.4% to 63.6%. In the past, BDE-209 is the largest mix on the market and makes up over 8% of the total PBDE production, whereas penta-BDE and octa-BDE products constitute about 12% and 6%, respectively, of the total PBDE production [1]. This is one of important factor to explain the predominance of BDE-209.

The mean percentages of 6 other selected PBDEs congeners compared with  $\sum_6$  PBDEs in the analyzed sediment samples from CauBay river followed the order: BDE-47 > BDE-99 > BDE-100 > BDE-154 > BDE-153 > BDE-27 (Figure 2).  $\sum_6$  PBDEs concentrations were calculated as the sum of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154. Individual congeners from the same homologue group are not formed in equal proportions. BDE-99 is preferentially synthesized over BDE-100. As a result, BDE-99 is present in commercial mixtures at concentration that are six-fold greater than BDE-100.

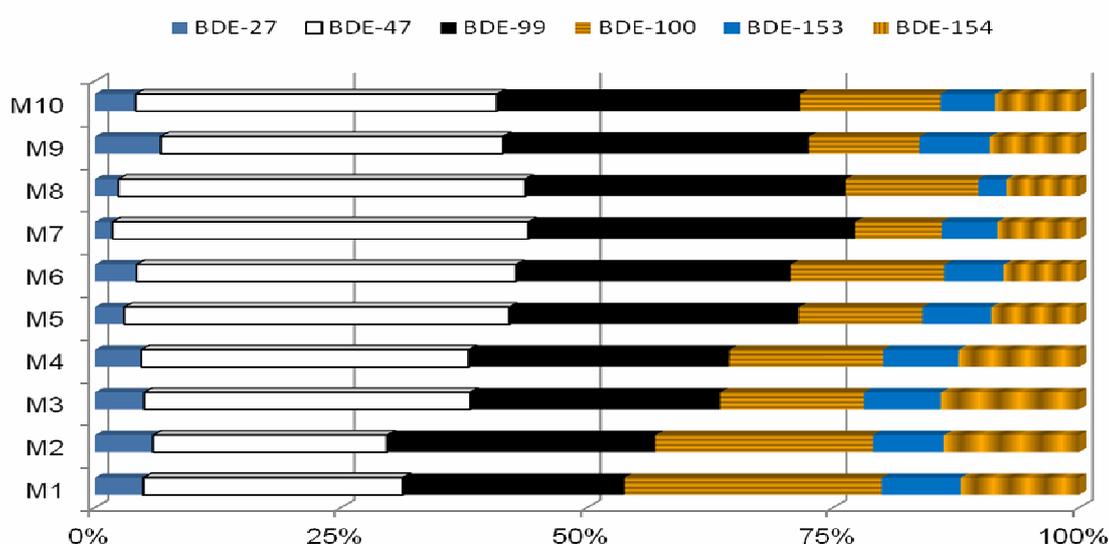


Figure 2. Mean percentages of 6 PBDE congeners compared with  $\sum_6$  PBDEs in sediment samples

This order also can be explained by the fact that lightly brominated BDEs are less persistent, have lower log  $K_{ow}$  and are more volatile than heavily brominated BDEs congeners. Therefore, heavily brominated BDE are more accumulative in the soil, whereas lightly brominated BDE are degraded and volatilised faster. PBDEs can undergo process of debromination. Thus, low percentages of lightly brominated BDE and a high percentage of brominated BDE in the analysed soil samples reflect their short-time release. The process of PBDE debromination was not take place significantly.

### 3.3. Risk assessment

It has been suggested that PBDEs biomagnify as they move along a food web. In addition, PBDEs can inhibit growth in colonies of algae as well as depress the reproduction of zooplankton. Based on the toxicity data of benthic organisms [4], the Multiple Species No Observed Effect Concentrations (MS-NOEC) of  $\Sigma$ PBDEs is 3.1 mg/kg dry weight of sediment. The hazardous quotient (HQ) calculated as the ratio of the measured level to the MS-NOEC was used to assess the environmental risk of  $\Sigma$ PBDEs in the sediment. When HQ values were less than 1, low adverse ecological effects were expected. When HQ values were greater than 1, frequent adverse ecological effects were expected. As for PBDEs, all the HQ values range from 0.003 to 0.008 indicating low risk (Fig.3).

## REFERENCES

1. De Wit. C.Y., (2002), An overview of brominated flame retardants in the environment, *Chemosphere*, 46 pp. 583–624.
2. Lacorte. S., M. Guillamon, E. Martinez, P. Viana, D. Barcelo (2003), Occurrence and specific congener profile of 40 polybrominated diphenyl ethers in river and coastal sediments from Portugal, *Environmental Science and Technology*, 37, pp. 892–898.
3. Liu. Y., J.G. Zheng, H. Yu, M. Martin, J.B. Richardson, M.H.W. Lam, P.K.S. Lam (2005), Poly- brominated diphenyl ethers (PBDEs) in sediments and mussel tissues from Hong Kong marine waters, *Marine pollution Bulletin*, 50, pp. 1173–1184.
4. Monia Renzi (2013), *Organic Pollutants - Monitoring, Risk and Treatment - Chapter 5 - Perfluorinated Organic Compounds and Polybrominated Diphenyl Ethers Compounds – Levels and Toxicity in Aquatic Environments: A Review*, Intech Publisher.

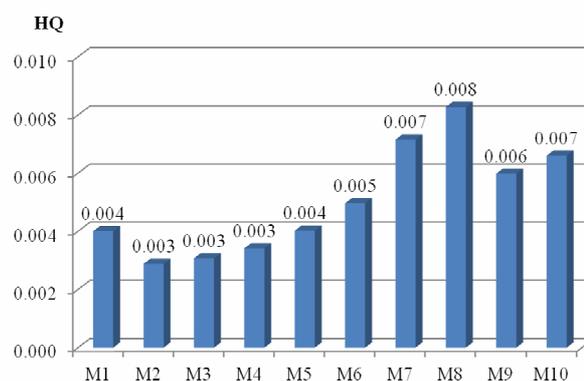


Figure 3. HQ values of PBDEs in the sediment sample

## 4. CONCLUSION

It is evident from the present study that PBDEs occur in relatively low to medium values in sediment samples of CauBay River, Vietnam. Medium positive correlation ( $r^2 = 0.72$ ,  $n = 10$ ) between  $\Sigma_7$  PBDEs and TOC percentages in analyzed sediment sample were also found. The mean percentages of 7 other selected PBDEs congeners in the analyzed sediment samples from CauBay river followed the order: BDE-209 > BDE-47 > BDE-99 > BDE-100 > BDE-154 > BDE-153 > BDE-27. Further research on PBDE distributions is needed to collect congener-specific data, especially for decabrominated ether (BDE-209), in biotic and abiotic compartments to determine their potential environmental fate in CauBay River.

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5. Minh. N. H., Minh. T. B., Isobe. T., Tanabe. S., (2010), “Contamination of “Polybrominated diphenylethers in the sewer system of Hochiminh city and estuary of Saigon – Dongnai river”, Fifth International Symposium on Brominated Flame Retardants, pp. 41-49, April, Kyoto.
6. Oros. D.R., D. Hoover, F. Rodigari, D. Crane, J. Seriano (2005), Levels and distribution of Polybrominated diphenyl ethers in water, surface sediments and bivalves from the San Francisco Estuary, Environmental Science Technology, 39, pp. 33–41.
7. Schlabach. M., E. Fjeld, H. Gundersen, E. Mariussen, G. Kjellberg, E. Breivik (2004), Pollution of Lake Mjøsa by brominated flame retardants, Organohalogen Compounds, 66, pp. 3779–3785.
8. Stefania Romano, Rossano Piazza, Cristian Mugnai, Silvia Giuliani, Luca Giorgio Bellucci, Cu Nguyen Huu, Marco Vecchiato, Stefano Zambon, Nhon Dang Hoai, Mauro Frignani (2013), PBDEs and PCBs in sediments of the Thi Nai Lagoon (Central Vietnam) and soils from its mainland, Chemosphere 90, pp. 2396 – 2402.
9. Wurl. O., J.P. Obbard (2005), Organochlorine pesticides, polychlorinated biphenyls and Polybrominated diphenyl ethers in Singapore’s coastal marine sediments, Chemosphere, 58, pp. 925–933.
10. Zheng. G.J., M. Martin, B.J. Richardson, H.X. Yu, Y. Liu, C.H. Zhou, J. Li, G.J. Hu, M.H.W. Lam, P.K.S. Lam (2004), Concentrations of Polybrominated diphenyl ethers (PBDEs) in Pearl River Delta sediments, Marine Pollution Bulletin, 49, pp. 520–524.

#### **Tóm tắt:**

### **ĐÁNH GIÁ MỨC ĐỘ TỒN LƯU VÀ RỦI RO SINH THÁI CỦA POLYBROM DIPHENYL ETE (PBDE) TRONG TRẦM TÍCH SÔNG CẦU BÂY, VIỆT NAM**

*Nghiên cứu trình bày các kết quả đánh giá về các đồng phân điển hình (7 đồng phân chỉ thị) của họ chất Polybrom Diphenyl Ete (PBDE) trong các mẫu trầm tích sông Cầu Bây, Hà Nội. Quá trình phân tích hóa học được thực hiện trên thiết bị sắc ký khí khối phổ (GC-MS) với các đồng phân từ nhóm ba đến nhóm bảy. Kết quả cho thấy có sự ô nhiễm  $\sum_7$  PBDE trong khoảng 8,93 đến 25,64 ng g<sup>-1</sup>, ứng với mức ô nhiễm trung bình trong môi trường trầm tích ở các nước châu Á. Phần trăm các đồng phân chủ yếu giảm dần theo trật tự: BDE 47 > 99 > 100 > 154, tương ứng với phân bố của PBDE trên thế giới. Rủi ro môi trường do PBDE ở mức độ thấp trong khu vực nghiên cứu. Tuy nhiên, do PBDE có khả năng tích tụ cao trong các thành phần môi trường và chuỗi thức ăn, cần tiếp tục có các nghiên cứu tiếp theo về rủi ro sinh thái trong sông Cầu Bây.*

**Từ khóa:** Tồn lưu, Đánh giá rủi ro, PBDE, trầm tích

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