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Residue and Ecological Risk Assessment of Polybrominated Diphenyl Ethers (PBDEs) in Sediment from CauBay River, Vietnam

Toan Vu Duc, Son Ha Viet

***Abstract*—**This research presents the first comprehensive survey of congener profiles (7 indicator congeners) of polybrominated diphenyl ethers (PBDEs) in sediment samples covering ten sites in CauBay River, Vietnam. 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 25.64ng g^{-1}, reflecting moderate to low contamination closely in conformity to other Asian aquatic environments. The general order of decreasing congener contribution to the total load was: BDE 47 > 99 > 100 > 154, similar to the distribution pattern worldwide. PBDEs had rare risks in the sediment of studied area. However, due to the propensity of PBDEs to accumulate in various compartments of wildlife and human food webs, evaluation of biological tissues should be undertaken as a high priority.

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

I. Introduction

POLYBROMINATED diphenyl ethers (PBDEs) are used commercially as additives in plastics and textiles, building materials, carpets, and in vehicles and aircraft. They are highly resistant to 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 [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.

II. 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 CauBay River were collected. Fig. 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 63µm sieve and kept at −20°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 10g) were spiked with 2ng of internal standard BB-155 and extracted for 12h using 100mL acetone/n-hexane (1:1 v/v) mixture in a cold soxhlet apparatus. One milliliter of isooctane was added to samples that were dried using a rotary evaporator and under nitrogen flow to about 1mL of final volume. Cleanup was performed using a multilayer column, composed of 10g of silica gel (activated overnight at 130°C, then deactivated with water, 5% w/w), followed by 10g of Florisil (activated for 16h at 650°C), 1g of anhydrous sodium sulphate, and lastly, 0.5cm of activated powdered copper at the top.

The column was washed with n-hexane/ acetone/ dichloromethane (8:1:1 v/v). Elution was carried out first by collecting 50mL of n-hexane and then 50mL of 1:1 n-hexane/dichloromethane (v/v). The two portions of eluent were concentrated by rotavapor to 10mL, and then to 1mL 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 0.25µm film thickness) and PolarisQ Ion Trap mass spectrometer. Limits of quantification (LOQs) were quantified for each

Toan Vu Duc is with the Department of Environment, Vietnam Water Resources University (e-mail: vuductoan@wru.edu.vn).

Son Ha Viet is with the Centre for High Technology Development - Vietnam Academy Science and Technology (e-mail: havietson@htd.vast.vn)

brominated class. LODs were 0.12 ng g^{-1} for tri-BDEs and tetra-BDEs, 0.18ng g^{-1} for penta-BDEs and hexa-BDEs, 0.25ng g^{-1} for hepta-BDEs and 0.20ng g^{-1} for BDE-209. Total organic carbon contents were determined using Apollo 9000 TOC analyzer (Tekmar-Dohrmann Co., USA).

Fig. 1 Map of the study area

III. Results and Discussion

The PBDEs concentrations in the collected sediment samples from CauBay River are shown in Table I. PBDEs were detected in all sediment samples. In industrial and urban sampling sites, ∑7 PBDEs concentrations ranged from 15.39 to 25.64ng g^{-1} dry weight (from M6 to M10), while those in agricultural sampling sites ranged from 8.93 to 12.47ng g^{-1} 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, 25.64ng g^{-1}). This area is polluted by wastewater of SaiDong industrial park. The other significant level of ∑7 PBDEs was found at sampling site close to DaiTu industrial parks (site M7) with PBDEs concentration are 22.17ng g^{-1} (Table I). 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 I 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 II. 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 I
PBDEs Concentrations (ng G^{-1}) and TOC (%) in the Sediment Samples

Sampling sites	TOC (%)	$\sum_7$ PBDEs [a]
M1	3.7	12.42
M2	2.1	8.93
M3	2.3	9.52
M4	2.5	10.59
M5	2.7	12.47
M6	3.8	15.39
M7	3.9	22.17
M8	4.4	25.64
M9	3.2	18.55
M10	3.5	20.46

(a): ∑7 PBDEs concentrations were calculated as the sum of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-209.

TABLE II
$\sum_7$ PBDEs Concentrations (ng G^{-1}) in the Sediment Samples of Vietnam and the Other Countries

Location	$\sum_7$ PBDEs concentrations (ng g^{-1}) [a]
Vietnam	
+ CauBay river	8.93 - 25.64
+ ThiNai Lagoon	0.03 – 8.93
+ Hochiminh City canals	< 0.12 – 119.0
+ Saigon-Dongnai estuary	< 0,02 - 0,065
Hong Kong marine sediments	1.7–53.6
Pearl river delta	0.15 – 13.03
Singapore coasts	3.4 – 13.8
Portugal River sediments	20 [a]
Lake Mjøsa (Norway)	0.6 – 27
San Francisco estuary (USA)	< 0.12 – 211.8

(a): Sources [2], [3], [5]-[10]

Because of their high hydrophobicity, PBDEs were expected to be associated with organic-rich particles. Medium correlation ($r2 = 0.72$, $n = 10$) between ∑7PBDEs 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 I) 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.

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.

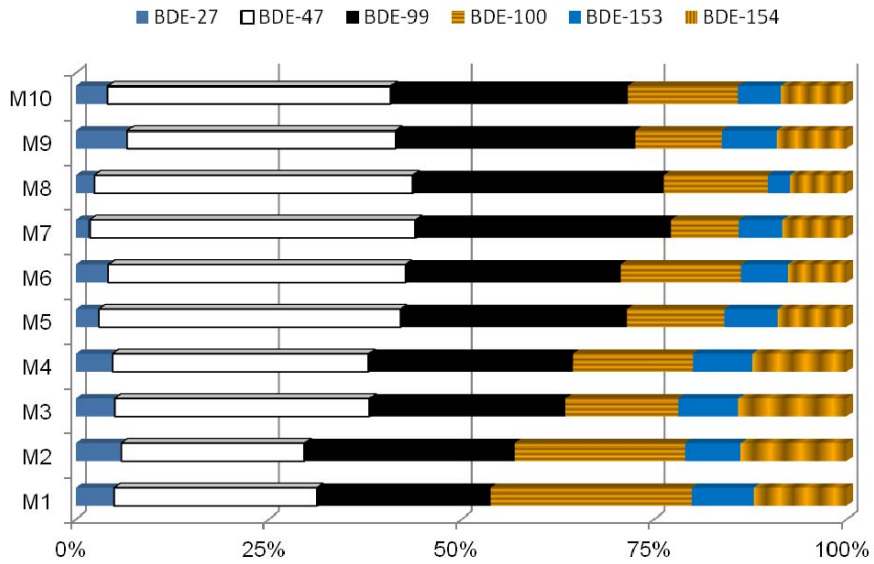

Fig. 2 Mean percentages of 6 PBDEs congeners in sediment samples

The mean percentages of 6 other selected PBDEs congeners compared with ∑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 (Fig. 2). ∑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.

This order also can be explained by the fact that lightly brominated BDEs are less persistent, have lower log Kow 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. 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 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 ecological risk of each PBDE in the sediment.

When HQ values were less than 1, rare 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).

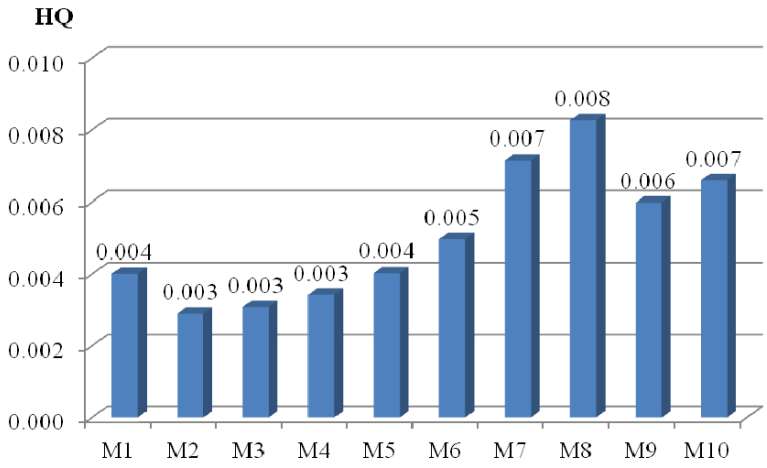

Fig. 3 HQ values of PBDEs in the sediment samples

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