

Residue of Dioxin-Like Polychlorinated Biphenyls (DL-PCBs) in Sediment from CauBay River, Vietnam

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Abstract

An evaluation of dioxin-like polychlorinated biphenyls (DL-PCBs) contamination in sediment from CauBay River was carried out. Ten representative sediment samples were collected in April 2013. The analyzed results indicated the wide occurrence of contamination of DL-PCBs in the CauBay River. In industrial and urban sampling sites, Σ DL-PCB concentrations ranged from 14,254 to 17,369 ng·kg⁻¹ dw, while those in agricultural sampling sites ranged from 9,398 to 13,793 ng·kg⁻¹ dw. The value of (PCB126+PCB169)/(PCB77+PCB126+PCB169) in CauBay River ranged from 10.9% to 16.1%, suggesting that the DL-PCBs in CauBay river are attributable to both commercial PCBs and pyrogenic sources. The total TEQ value of DL-PCBs in the CauBay sediment samples ranged from 5.3 to 11.9 ng TEQ·kg⁻¹ dw. Due to the propensity of DL-PCBs to accumulate in various compartments of environment, further evaluation of ecotoxicology should be undertaken as a high priority.

Keywords: dioxin-like polychlorinated biphenyls, sediment, contamination, level

Introduction

Polychlorinated biphenyls (PCBs) are industrial products that constitute a global environmental health hazard of a solely anthropogenic origin. They are very resistant to decomposition and have an excellent insulating property as well as a high heat capacity. Their properties have led to many industrial applications but also make PCBs a major environmental pollutant. Studies in humans provide supporting evidence for potential carcinogenic and non-carcinogenic effects of PCBs (neurological, immune, endocrine, and reproductive effects).

PCBs have never been manufactured in Vietnam. PCBs were imported into Vietnam as industrial fluids such as hydraulic and heat transfer fluids, in gas turbines; as lubricating oils; and as plasticizers. They have been mainly used

as dielectric oil in transformers and in capacitors. Hanoi City, the capital of Vietnam, is the centre of economy and trade for the whole country. CauBay River, a very important channel to discharge various wastewaters from domestic and industries in Hanoi, is upstream from LongBien district and downstream from KieuKy commune, GiaLam district. It is noted that Gia Lam district belongs to suburban Hanoi, the capital of Vietnam that is experiencing rapid growth of industrial and human activities. The CauBay also is the only source of irrigated water to communes with agricultural activities downstream. PCB pollution will seriously affect irrigating water quality of these communes. However, to our knowledge, few data are available for the contamination of dioxin-like polychlorinated biphenyls (DL-PCBs) in this river as well as the other places in Vietnam. The objective of this research is to assess the levels and distributions of DL-PCBs in the surficial sediments from the CauBay to fill this gap.

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Experimental Procedures

The sampling was carried out in April 2013 during the dry season. Ten sediment samples in 10 sites along the CauBay 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 immediately transferred to the laboratory. The samples were freeze-dried and homogenized. All the equipment used for sample collection, transportation, and preparation, were free from DL-PCB contamination.

The levels of DL-PCBs in the sediment samples were determined using the method provided by the Japan's Ministry of the Environment [1]. First, a sediment sample was extracted with toluene for 16 h using a Soxhlet apparatus. After extraction, the $^{13}\text{C}_{12}$ -labeled DL-PCB internal standards were added to the extract to check the recovery of the dioxin congeners throughout the clean-up procedure. Then the extract was concentrated to approximately 1 mL with solvent exchange to hexane, shocked with concentrated sulfuric acid, purified with silica by gel column chromatography and the addition of reduced copper, and then activated charcoal/silica by gel column chromatography. After the addition of injection internal standard ($^{13}\text{C}_{12}$ -2,3',4',5-TeCB), each fraction was concentrated to 50 μL under a gentle stream of pure nitrogen gas. The samples were analyzed by high-resolution gas chromatography (GC)/high-resolution mass spectrometry (MS). The average recoveries were $100.0 \pm 13.4\%$ for 12 $^{13}\text{C}_{12}$ -labeled DL-PCB congeners. The method detection limits (MDLs) were $0.4\text{--}0.8 \text{ ng}\cdot\text{kg}^{-1} \text{ dw}$ for DL-PCBs. Duplicates of sediment samples were also performed and relative standard deviations were less than 15%. All concentrations were calcu-

lated with respect to the dry weight of sediment samples. Total organic carbon (TOC) of sediment sampling was analyzed using a TOC analyzer (TOC-VCPH, Shimadzu Corp., Japan). All DL-PCBs standards were purchased from Cambridge Isotope Laboratories, USA.

Discussion of Results

The DL-PCB concentrations in the collected sediment samples are shown in Table 1. DL-PCBs were detected in all samples.

In industrial and urban sampling sites, $\Sigma\text{DL-PCBs}$ concentrations ranged from $14,254$ to $17,369 \text{ ng}\cdot\text{kg}^{-1} \text{ dw}$ (from M6 to M10, mean $15,777 \pm 1,261 \text{ ng}\cdot\text{kg}^{-1} \text{ dw}$), while those in agricultural sampling sites ranged from $9,398$ to $13,793 \text{ ng}\cdot\text{kg}^{-1} \text{ dw}$ (from M1 to M5, mean $11,921 \pm 1,687 \text{ ng}\cdot\text{kg}^{-1} \text{ dw}$). It is observed that the highest value corresponded with the site near a wastewater lake from resident area of SaiDong ward, LongBien District (site M8, $17,369 \text{ ng}\cdot\text{kg}^{-1} \text{ dw}$). Close to this site there are several small old transformers and the area is polluted by wastewater of SaiDong industrial park. The obtained results point out the wide occurrence of DL-PCBs in the CauBay. Due to the historical use of PCBs in Vietnam, the possible main sources of contamination in the sediment of CauBay river could originate from the dielectric oil which was widely used in Hanoi. DL-PCBs could be released by electrical accidents, and fire and mechanical damage of old transformers and capacitors. The surveys of possible PCB concentrations from this equipment is only allowed by an official Bay environmental agency. Until now, these results have not been published and thus it is impossible to calculate PCB quantities used in Hanoi.

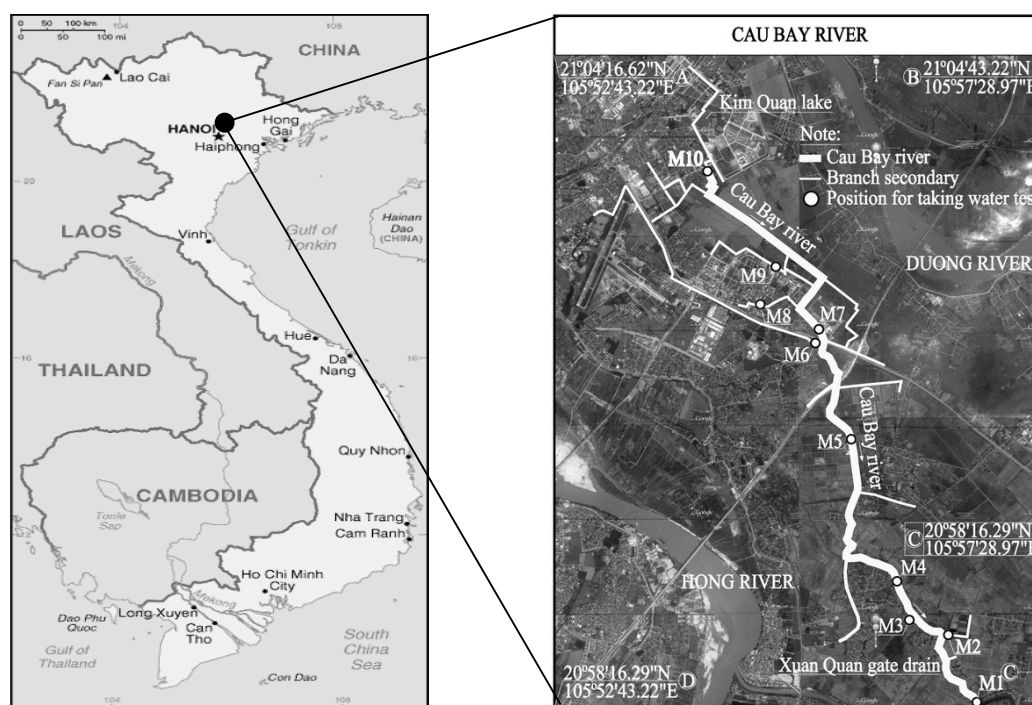


Fig. 1. Study area and sampling locations.

Table 1. TOC (%) and concentrations of DL-PCBs (ng·kg⁻¹ dw) in the sediment samples.

Sampling sites	TOC	PCB 77	PCB 81	PCB 105	PCB 114	PCB 118	PCB 123	PCB 126	PCB 156	PCB 157	PCB 167	PCB 169	PCB 189	ΣDL-PCBs
M1	3.7	410	9	1900	140	5900	105	49	690	80	104	3	8	9,398
M2	2.1	440	12	3100	170	6500	120	49	710	90	120	5	10	11,326
M3	2.3	470	15	3500	190	6700	150	52	740	110	160	6	12	12,105
M4	2.5	510	19	3900	210	6900	190	56	790	160	220	9	19	12,983
M5	2.7	540	23	4200	230	7200	220	65	830	190	260	12	23	13,793
M6	3.8	560	25	4400	250	7300	235	69	890	210	274	15	26	14,254
M7	3.9	650	33	5100	310	8100	310	91	1200	360	360	25	35	16,574
M8	4.4	690	38	5300	360	8300	340	105	1400	390	380	27	39	17,369
M9	3.2	580	27	4600	260	7500	250	73	910	290	310	17	29	14,846
M10	3.5	610	31	4900	290	7900	290	82	1040	310	340	21	32	15,846

ΣDL-PCBs – sum of all DL-PCB congeners above.

In Vietnam, there are more than 11,800 old PCB-containing piece electrical equipment [2, 3]. This clearly indicates a huge contaminative source of PCBs in Vietnam.

When compared with other regions in Vietnam, the levels of DL-PCBs in CauBay sediment are highest, followed by the West Lake, which is located in the center of Hanoi [4]. The reported residues in these lakes are really remarkable and, together with our study, highlight the wide extent of contamination of DL-PCBs in Hanoi. The other areas in Vietnam such as Hue City and Can Gio District had lower DL-PCB contamination. Meanwhile, the levels of DL-PCBs in the CauBay are lower than those in sediment of urban areas in Osaka, Japan, and higher than residues found in Taiwan [4, 5].

The total organic carbon content (TOC) can have an influence on the sediment concentration of DL-PCBs as these compounds are highly sorptive with high KOC values. The Pearson correlation coefficient between TOC and the concentration of DL-PCBs in sediments of CauBay river is 0.56. This means that concentrations of DL-PCBs in sediments may have a medium positive relationship with high TOC. This is a preliminary result and could be assessed in further studies.

Concerning composition analyses, DL-PCB congeners could be detected from tetra-CB to hepta-CB in the collected sediment samples. The mean percentages of DL-PCB congeners in the sediment from CauBay river followed the order: PCB 118 > PCB 105 > PCB 156 > PCB 77 > PCB 167 > PCB 114 > PCB 123 > PCB 157 > PCB 126 > PCB 189 > PCB 81 > PCB 169. Among these congeners, PCB 126, PCB 169, PCB 81, and PCB 77 require the most attention. The toxic equivalency factors (TEF) of PCB 126, PCB 169, PCB 81, and PCB 77 are 0.1, 0.03, 0.0003, and 0.0001, respectively [6]. It is possible to assess the main source of DL-PCBs using the ratio of the sum of PCB 126 and PCB 169 to the sum of PCB 77, PCB 126, and PCB 169. The proportion of DL-PCBs in commercial PCBs was approximately 1%, whereas that from combustion sources was

approximately 50%. The value of (PCB126+PCB169)/(PCB77+PCB126+PCB169) in the CauBay range from 10.9% to 16.1%, with a mean of 12.9±1.8%, suggesting that the DL-PCBs in the CauBay are attributable to both commercial PCBs and pyrogenic sources.

At present, the value of toxic equivalence (TEQ) can be used to assess the toxic effect of DL-PCBs. In this study, the TEQ value for each sample was obtained from the concentrations of DL-PCBs using their toxic equivalency factors (TEFs) proposed by the World Health Organization in 2005 [6]. TEQ of non-ortho-substituted PCBs (PCB 77, 81, 126, and 169) and mono-ortho-substituted PCBs (PCB 105, 114, 118, 123, 156, 157, 167, 189) range from 5.0 to 11.4 ng TEQ·kg⁻¹ dw (mean 7.4±2.2 ng TEQ·kg⁻¹ dw) and from 0.3 to 0.5 ng TEQ·kg⁻¹ dw (mean 0.4±0.1 ng TEQ·kg⁻¹ dw), respectively. Non-ortho-substituted PCBs have higher toxic potential than mono-ortho-substituted PCBs. Regarding the calculated TEQ values above, the toxic effect of DL-PCBs in CauBay sediment is mainly contributed by non-ortho-substituted PCBs.

The total TEQ values of DL-PCBs in the river sediment samples range from 5.3 to 11.9 ng TEQ·kg⁻¹ dw with a mean 7.8±2.2 ng TEQ·kg⁻¹ dw. The mean value of TEQ of DL-PCBs in the CauBay were higher than those in CanGio district (0.2 ng TEQ·kg⁻¹ dw), Hue city (0.1 ng TEQ·kg⁻¹ dw), and TrucBach-West Lake (4.5 ng TEQ·kg⁻¹ dw), but much lower than those in urban locations of Osaka (32.6 ng TEQ·kg⁻¹ dw) [4]. Due to the propensity of DL-PCBs to accumulate in various compartments of environment, further evaluation of the ecotoxicology should be undertaken as a high priority.

Conclusions

This work investigated the contamination status of DL-PCBs in surficial sediments of the CauBay River. The wide occurrence and high residue levels of PCBs have been

found in the study area (from 9,398 to 17,369 ng·kg⁻¹ dw). Composition analyses show that the predominance of heavily chlorinated PCBs, PCB 118, PCB 105, and PCB 156 remained when they penetrated the CauBay sediment. The total TEQ values of DL-PCBs in the sediment samples from CauBay range from 5.3 to 11.9 ng TEQ·kg⁻¹ dw. The main source of DL-PCBs in the CauBay are attributable to both commercial PCBs and pyrogenic sources.

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