

Residues of Polychlorinated Biphenyls (PCBs) in Sediment from CauBay River and Their Impacts on Agricultural Soil, Human Health Risk in KieuKy Area, Vietnam

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Abstract An evaluation of the PCB residues from CauBay River and KieuKy area, Vietnam was carried out. CauBay River has been playing an important role in irrigated water supply for agriculture activities at KieuKy area in the downstream. The PCBs concentrations of sediment, soil samples were analyzed and obtained results indicated the wide extent of contamination of PCBs in CauBay River (from 30.74 to 167.35 ng g⁻¹ dry weight) and KieuKy area (from 21.62 to 60.22 ng g⁻¹ dry weight). This clearly reflected the effect of PCB residues from CauBay River to the quality of agricultural soil of the KieuKy area. The PCBs composition analyses in the samples reflect their long-time release. The total cancer risk of PCBs in the soil of KieuKy fell into the very low range suggesting low risk. However, since PCBs were the species of POPs with more concern in this area, ecological risk assessment should be further investigated.

Keywords PCBs · Sediment · Residue · Human health risk

PCBs belong to the group of Persistent Organic Pollutant which constitutes a global environmental health hazard of a solely anthropogenic origin. PCBs are industrial products and total commercial PCBs produced are estimated to be about 2 million tons globally. PCBs 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 provided supporting evidence for potential carcinogenic effects of PCBs. Thus, PCBs usage has been banned in most places in the world. However, until now, a large amount of PCB oil still exists in the infrastructure of Electric of Vietnam. To enhance national capacity in PCB management in Vietnam, the Global Environment Fund provided financial support for PCB projects during the period from 2010 to 2014. That project was implemented by the Vietnam Ministry of Natural Resources. Thus, PCB contamination is receiving special attention in Vietnam. From the viewpoint of PCB contamination, several places in Vietnam are found to have PCB residues in sediment such as Tam Giang-Cau Hai Lagoon (Frignani 2007) and the Mekong River (Carvalho et al. 2008). Several studies have focused on the contamination of PCBs in industrialized or urbanized areas, while information on agricultural areas is limited.

Hanoi city, the capital of Vietnam, is the center of the economy for the whole country. The CauBay River is a very important channel used to discharge various wastewaters from households and industries in Hanoi. The upstream of CauBay River is enclosed within the LongBien district and its downstream runs through the KieuKy area. KieuKy has typical agricultural production and CauBay River is the only source to supply irrigated water to that area. Possible PCBs sources from CauBay River can seriously affect the soil quality of KieuKy. However, to our knowledge, no data are available for the contamination of PCBs in this river as well as the impact of PCB residues on agricultural soil and human health risk in the downstream agricultural areas. The objectives of this research are to assess the levels and distribution of PCBs in the surficial sediments from the CauBay River and in the agricultural soil of KieuKy area to fill this gap.

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Materials and Methods

The sampling was carried out in April 2014. Ten sediment samples along the CauBay River (from M1 to M10) and ten soil samples (from D1 to D10) in KieuKy area were collected. The sampling locations were chosen at random, with an attempt to get them evenly distributed over the selected region. At each sample location in KieuKy area, five soil samples were collected from a 100 m² square plot (located on the crossing diagonals: four in the corners and one in the crossing point), and then thoroughly mixed to form a composite sample. The soil samples were taken with solvent-rinsed stainless steel scoops from the upper 5 cm. The surficial sediment was collected with a stainless steel grab. The collected samples were homogenised, air dried at room temperature, ground and sieved through a steel mesh (1 mm grid size). All samples were maintained at 4°C until analysis. The concentration of 84 PCBs (PCB 4, 5, 6, 7, 8, 9, 10, 12, 13, 15, 16, 17, 19, 21, 22, 26, 28, 31, 32, 37, 41, 42, 44, 45, 47, 48, 49, 52, 53, 56, 60, 61, 64, 66, 70, 71, 74, 77, 81, 83, 84, 85, 86, 87, 89, 91, 92, 95, 99, 100, 101, 105, 110, 114, 118, 119, 123, 126, 128, 131, 132, 135, 138, 144, 149, 153, 156, 157, 163, 167, 169, 170, 171, 172, 174, 180, 189, 194, 199, 200, 202, 205, 206 and 207) in soil and sediment samples were

analysed following the method described elsewhere by Toan et al. (2007) with slightly modification (Fig. 1).

PCB14, PCB 65 and PCB166 were spiked to samples prior to extraction as surrogate standards while PCB 30 and PCB 204 were used as internal standards. In short, about 20 g of dry sample was Soxhlet extracted for 24 h with 400 mL solvent (*n*-hexane/acetone, 1:1 v/v). After that, the extract was dried by passing through anhydrous sodium sulphate and concentrated to around 5 mL. The concentrated extract was filtered through 8 grams of activated Florisil packed in a glass column, which was then eluted by 45 mL of *n*-hexane. The resulting solution was de-sulphurated using activated copper chips and finally treated with concentrated sulphuric acid. Final extracts were concentrated to 5 mL using a rotary vacuum evaporator and then to around 300 µL under a gentle stream of purified nitrogen. All chemicals used were of analytical grade purchased from Fluka Chemical Co., Switzerland. The samples were analysed with the gas chromatography (Varian Star 3400Cx)/mass spectrometry (Varian Saturn 2000). Three groups of PCB standards [Accustandard, Inc. (New Haven, CT)] were used containing a total 84 PCB congeners. The recoveries were from 75 % to 112 % for PCBs congeners. The method detection limits were calculated from real samples as being 3 times the

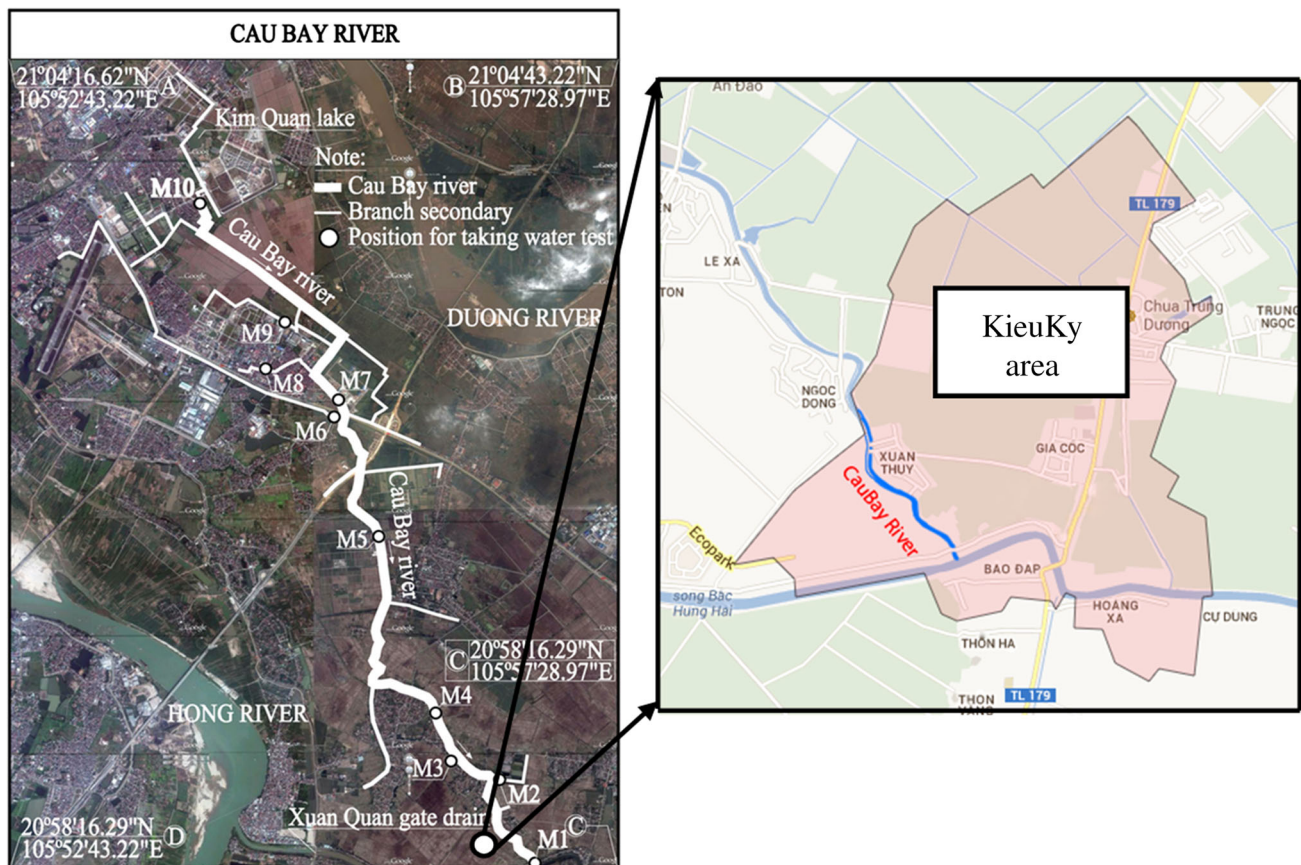


Fig. 1 Study area and sampling locations

Table 1 PCBs concentrations and TOC (%) in the sediment samples from CauBay River and soil samples from KieuKy area

Compound	Sediment samples	Soil samples
<i>A. 6 PCB indicator (ng g⁻¹ dw)</i>		
PCB 28	0.04–0.35 (0.16 ± 0.12)	0.05–0.14 (0.09 ± 0.04 ^d)
PCB 52	0.72–4.15 (1.61 ± 1.26)	0.28–1.66 (0.82 ± 0.56)
PCB 101	1.22–6.13 (2.51 ± 1.82)	0.54–2.79 (1.52 ± 0.86)
PCB 138	2.04–11.59 (4.45 ± 3.62)	1.22–3.44 (2.44 ± 0.90)
PCB 153	1.16–9.72 (3.28 ± 2.77)	2.19–5.72 (3.52 ± 1.26)
PCB 180	0.15–4.13 (0.96 ± 1.16)	0.08–0.62 (0.29 ± 0.28)
Σ6PCBs ^a	5.58–36.18 (12.28 ± 10.48)	4.39–12.86 (8.82 ± 3.32)
<i>B. 12 DL-PCBs (ng kg⁻¹ dw)</i>		
PCB 77	386–668 (459 ± 86)	179–240 (122 ± 76)
PCB 81	8–34 (18 ± 8)	2–10 (6 ± 3)
PCB 105	1780–5090 (3446 ± 1018)	580–1480 (1140 ± 308)
PCB 114	118–316 (202 ± 58)	41–108 (62 ± 24)
PCB 118	5790–8180 (6145 ± 715)	1780–2780 (2119 ± 265)
PCB 123	102–318 (185 ± 69)	29–98 (62 ± 22)
PCB 126	46–96 (56 ± 12)	12–29 (19 ± 6)
PCB 156	650–1260 (778 ± 212)	298–422 (324 ± 62)
PCB 157	78–376 (182 ± 98)	26–118 (62 ± 29)
PCB 167	102–356 (212 ± 88)	32–106 (78 ± 24)
PCB 169	3–22 (12 ± 7)	2–8 (5 ± 2)
PCB 189	8–32 (19 ± 9)	3–12 (8 ± 4)
ΣDL-PCBs ^b	9125–16,112 (10,954 ± 2118)	3026–5028 (3788 ± 748)
<i>C. ΣPCBs (ng g⁻¹ dw) and TOC</i>		
PCBs ^c	30.74–167.35 (64.25 ± 47.16)	21.24–60.22 (43.17 ± 14.14)
TOC	2.30–4.20 (3.18 ± 0.66)	0.71–2.32 (1.25 ± 0.86)

^a Σ6PCB – sum of 6 selected PCB congeners; ^b PCB – sum of all PCB isomers and congeners in sediment sample; ^c ΣDL-PCBs: sum of all DL-PCBs congeners; ^d SD: standard deviation

signal/noise ratio and range from 2 to 33 pg g⁻¹. One blank sample was run for every set of five samples to check for secondary contamination. PCB concentrations were not corrected for recoveries. Duplicates of samples were performed and relative standard deviations were less than 10 %. All concentrations were calculated with respect to dry weight (dw). Total organic carbon (TOC) contents of all samples were determined using Apollo 9000 TOC analyzer (Tekmar–Dohrmann Co., USA). Methods to estimate the PCBs cancer risks via ingestion, dermal contact and inhalation of soil particles in KieuKy area were developed by the US. Environmental Protection Agency (USEPA 1997, 2009).

Results and Discussion

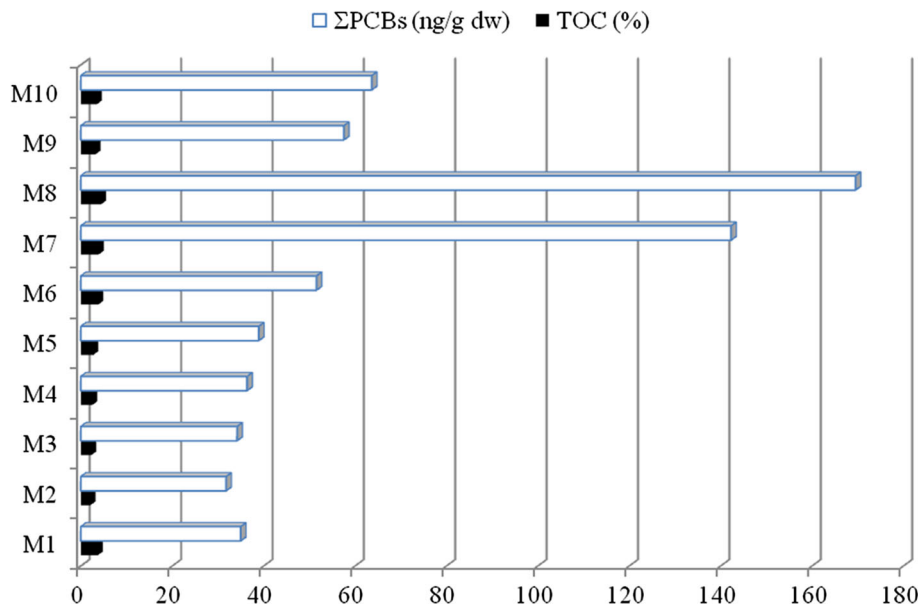
The PCBs concentrations in the collected samples from CauBay River are all shown in Table 1. ΣPCB was detected in all sediment and soil samples.

In industrial and urban sampling sites, PCB concentrations ranged from 50.98 to 167.35 ng g⁻¹ dw (from M6 to M10), while those in agricultural sampling sites ranged

from 30.74 to 37.64 ng g⁻¹ dw (from M1 to M5). It is observed that the highest value corresponded with the site near wastewater lake from resident area of SaiDong ward, (site M8, 167.35 ng g⁻¹ dw). The main source of PCB contamination in industrial and urban sampling sites could originate from the dielectric oil used in old hanging transformers and capacitors, which were widely used in Hanoi. PCBs could have penetrated into the environment by mechanical damage, electrical accidents and retro-filling of dielectric oil (Fig. 2).

Among the reported locations in Vietnam, the levels of PCBs in sediment of the CauBay river are lower than those in Kim Nguu River (237–328 ng g⁻¹ dw) but higher than in TamGiang – CauHai lagoon (2.03–24.7 ng g⁻¹ dw), HaiPhong harbor (0.11–18.7 ng g⁻¹ dw) and Hochiminh City canals (0.12–9.2 ng g⁻¹ dw) (Frignani 2007, Hong et al. 2008, Minh et al. 2007, Giger et al. 2010). From the upstream to downstream, total PCB concentration have a decreasing trend. The Pearson's coefficient between total PCB concentration and downstream distance is 0.39. This result can be explained by the fact that there has been a greater possibility to find PCB contamination sources in the

Fig. 2 Distribution of PCBs and TOC in the sediment from CauBay River, Hanoi



urban and industrial areas in the upstream than agricultural ones in the downstream of CauBay river. Besides, the Pearson's coefficient between TOC and total PCB concentration in sediment samples is 0.58 which indicated the positive correlation at medium level. TOC may have an impact on the PCB accumulation in sediment as these compounds are highly sorptive with high K_{OC} values.

In industrial and urban sampling sites, ΣDL -PCBs concentrations ranged from 13,928 to 16,112 ng kg^{-1} dw (from M6 to M10), while those in agricultural sampling sites ranged from 9125 to 12,492 ng kg^{-1} dw (from M1 to M5). When compared with other regions in Vietnam, the levels of DL-PCBs in sediment of CauBay river are highest followed by the West Lake which are located in the centre of Hanoi (Kishida et al. 2010). 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. However, the levels of DL-PCBs in CauBay river are still lower than those in sediment of urban areas in Osaka, Japan and higher than residues found in Taiwan (Chi et al. 2007; Kishida et al. 2010).

Concerning the composition analyses, PCBs congeners could be detected from tri-CB to octa-CB in the collected sediment samples. 6 PCB indicators are principal component which account for a high percentages in the samples. The mean percentages of 6 selected PCB congeners comparing with $\Sigma 6$ PCBs in the analyzed sediment samples from CauBay river followed the order PCB138 (34.22 %) > PCB153 (25.39 %) > PCB101 (19.24 %) > PCB52 (12.29) > PCB180 (7.52) > PCB28 (1.35 %). This order can be explained by the fact that lightly chlorinated PCBs are less persistent, have lower $\log K_{ow}$ and are more volatile than heavily chlorinated PCBs. Therefore, heavily chlorinated PCBs are more accumulative in the sediment,

whereas lightly chlorinated PCBs are degraded and volatilized faster than the other PCBs. With regards to DL-PCBs, the ratio of $(\text{PCB126} + \text{PCB169})/(\text{PCB77} + \text{PCB126} + \text{PCB169})$ in CauBay river range from 9.8 % to 14.8 %, with a mean of $11.8 \% \pm 1.4 \%$, suggesting that the DL-PCBs in CauBay river are attributable to both commercial PCBs and pyrogenic sources.

Besides accumulating in sediment, PCBs can be redistributed from sediment to water and be transported along the CauBay River. PCBs can penetrate into the irrigated water and accumulate in the agricultural soil in the downstream. To assess this situation, agricultural soil samples in KieuKy area which have direct contact with irrigated water from CauBay River were analyzed and PCBs were detected in all representative samples (Table 1). The results show that PCBs concentrations in agricultural soil samples ranged from 21.24 to 60.22 ng g^{-1} dw (mean $43.17 \pm 14.14 \text{ ng g}^{-1}$ dw). Similarly with sediment samples, 6 PCB indicators were detected and account for a high percentages in the soil samples.

Principle components analysis (PCA) was employed to compare the PCB composition in soil and sediment samples. The results of PCA are "score" plots in which the samples are plotted in the PCA coordinates. The obtain results show that soil and sediment samples have similar profile and are located in close proximity. The projection of the PCB profile on the plane of the principal components 1 and 2 captures 89 % of the original variance. This clearly shows the impact of PCB residues from the sediment of CauBay River on the quality of agricultural soil in KieuKy area.

PCBs residue in soil samples from KieuKy are comparable to those in soil samples of the Moscow region (2.0–34 ng g^{-1} dw), but higher than in the mineral topsoil of mainly rural areas in the United Kingdom and in

Fig. 3 Principal component plot of PCBs in the CauBay River and KieuKy area

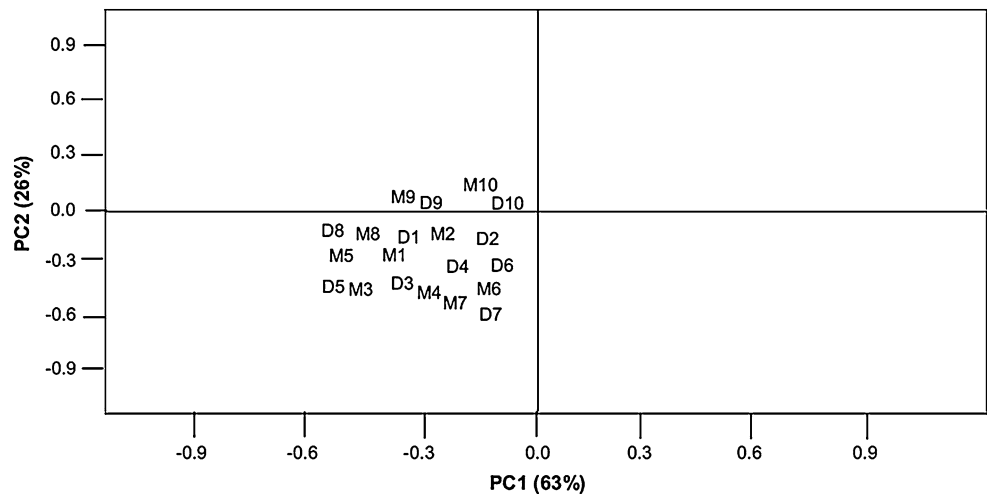


Table 2 Selected values of input parameters to calculate CR for PCBs

Symbol	Meaning of parameters	Selected values
IngR	Soil ingestion rate (mg days ⁻¹)	100
ED	Exposure duration (years)	70
EF	Assumed exposure frequency (days/year)	350
CF	Conversion factor (kg mg ⁻¹)	1 × 10 ⁻⁶
SF _{oral}	Oral slope factor (mg kg ⁻¹ days ⁻¹) ⁻¹	2.0E+00
AT	Upper-bound value of averaging time (days)	25,550
BW	Average body weight (kg)	70
SA	Contact surface area of skin with soil (cm ²)	3300
AF _{soil}	Skin adherence factor for soil (mg cm ²)	0.2 mg cm ²
ABS	Dermal absorption factor (%)	0.14 (for PCBs)*
GIABS	Fraction of contaminant absorbed in gastrointestinal tract	1
AF _{Inh}	Absorption factor for the lungs	1
InhR	Inhalation rate (m ³ days ⁻¹)	15.8 (for adults)
SF _{oral}	Oral slope factor (mg kg ⁻¹ days ⁻¹) ⁻¹	2.0E+00
PEF	Particle emission factor (m ³ kg ⁻¹)	1.36 × 10 ⁹
IUR	Inhalation unit risk (mg m ³) ⁻¹	(5.7E-01)

* Data from Health Canada (2004)

Switzerland (3.5–17 ng g⁻¹ dw) (Wilcke et al. 2006) (Fig. 3).

Human risk assessment was evaluated via inhalation of soil particles, dermal contact and ingestion. According to the Human Health Evaluation Manual, the PCBs cancer risk in agricultural soil can be calculated by using Eq. (1), (2) and (3) (USEPA 1997, 2009).

$$CR_{ingest} = \frac{C_{soil} \times IngR \times EF \times ED \times CF \times SF_{oral}}{BW \times AT} \quad (1)$$

$$CR_{dermal} = \frac{C_{soil} \times SA \times AF_{soil} \times ABS \times EF \times ED \times CF \times SF_{oral} \times GIABS}{BW \times AT} \quad (2)$$

$$CR_{inhale} = \frac{C_{soil} \times InhR \times EF \times ED \times IUR \times AF_{Inh}}{PEF \times AT} \quad (3)$$

whereas: CR_{ingest} is the cancer risk (CR) via accidental ingestion of soil; CR_{dermal} is the cancer risk via dermal contact of soil; CR_{inhale} is the cancer risk via inhalation of soil; C_{soil} is the concentration of the contaminant in soil (mg kg⁻¹).

The meaning of other parameters in these equations and their selected values of input parameters are listed in Table 2. PCBs CR via exposure pathways are calculated by using selected values of input parameters and levels of PCBs concentrations in soil samples from KieuKy area. As shown in Table 3, the calculated total cancer risks for PCBs of all sampling locations range from 1.16E-07 to 3.18E-07.

Table 3 PCBs CR via exposure pathways

PCBs CR via exposure pathways	Minimum	Maximum	Mean
Ingestion	6.18E–08	1.62E–07	1.19E–07
Dermal contact	5.68E–08	1.52E–07	1.09E–07
Inhalation	1.39E–10	3.82E–010	2.79E–10
Total CR	1.16E–07	3.18E–07	2.28E–07

According to the Human Health Evaluation Manual (USEPA 2009), the following qualitative ranking of cancer risk estimates was used to rank the risk: very low (value $\leq 10^{-6}$); low ($10^{-6} < \text{value} \leq 10^{-4}$); moderate ($10^{-4} < \text{value} \leq 10^{-3}$); high ($10^{-3} \leq \text{value} < 10^{-1}$); and very high (value $\geq 10^{-1}$). Thus, the obtain total CR is at the very low cancer risks rank. For different exposure pathways, the increasing trend in risks of cancer for PCBs was as follows: inhalation < dermal contact < ingestion. Since PCBs were the species of POPs with more concern in this area, ecological risk assessment should be further investigated.

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