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Distribution and risk assessment of hexachlorobutadiene, pentachloroanisole, and chlorobenzenes in sediment and wild fish from a region affected by industrial and agricultural activities in South China

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ABSTRACT

Hexachlorobutadiene, pentachloroanisole, and chlorobenzenes are regulated to control their release into the environment. There is little information regarding the distribution and risks of these pollutants in Chinese rivers. Therefore, we selected a prosperous agricultural and industrial region in South China as our study area and investigated the contamination profiles and risks of these pollutants in sediment and fish tissue samples. The results showed that, when compared with their levels in sediment, these lipophilic pollutants tended to accumulate in fish tissues in the following order: liver > brain > muscle. Some trichlorobenzene was found to be the result of reductive dechlorination of higher chlorinated benzenes. Hexachlorobutadiene and hexachlorobenzene could pose medium risks at certain sampling sites, but in general, almost no risk was found to the ecosystem. When the estimated daily human intakes of analytes through fish consumption were calculated for different age groups, the results suggested the analytes were unlikely to be a serious health concern for human. Our results could be used to update the existing data on the occurrence of these pollutants in the aquatic environment and to provide information for further pollution control by the local government.

1. Introduction

The Stockholm Convention is an international environmental treaty to protect human health and the environment from persistent organic pollutants (POPs). Hexachlorobutadiene (HCBD) and pentachloroanisole (PCA) were listed in the Stockholm Convention in 2015 (UNEP, 2015a, 2015b) and have received increasing attention in recent years. HCBD was most commonly used as a solvent for chlorine-containing compounds (UNEP, 2013a). The estimated production of HCBD was approximately 10,000 metric tons in 1982, but HCBD is no longer intentionally produced in the region of the United Nations Economic Commission for Europe. In China, HCBD occurs only as a by-product during the production of chlorinated hydrocarbons and the high-temperature incineration of acetylene or chlorine residues (Wang et al., 2018). Currently, PCA is not used as a commercial chemical or pesticide. However, under aerobic microbial metabolism in sediment or soil (UNEP, 2013b), PCA is a methylated metabolite of pentachlorophenol (PCP), which was extensively used as a pesticide and biocide for wood preservation (Seiler, 1991). Although PCP was listed in the Stockholm Convention (UNEP, 2015b) and was reported to have higher developmental toxicity than PCA, PCA was suggested as a proxy for PCP to be included in Swedish long-term monitoring programs, rather than listing PCP itself (Cousins et al., 2012). In addition to PCP, hexachlorobenzene (HCB) is considered a possible precursor for PCA formation (UNEP, 2013b). Chlorobenzenes (CBs) were widely used in pesticides and chemical products for a long time. Due to their

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persistence, bioaccumulation, and toxicity, HCB and pentachlorobenzene (PeCB) were listed in the Stockholm Convention in 2001 and 2009 (UNEP, 2001, 2009), while tetrachlorobenzenes and trichlorobenzenes are considered to be priority pollutants by the European, American, and Canadian environmental organizations (CEPA, 1993; EU, 2013; USEPA, 2014). Therefore, HCBD, PCA, and CBs are the target analytes in the present study. Although regulated by certain environmental treaties, these pollutants are still found in the environment and should be of concern.

There are several studies regarding the environmental levels of HCBD, PCA, and CBs. Berger and Schwarzbauer (2016) found that HCBD concentrations were 6–15 ng/g dry weight in sediment from highly contaminated water downstream of the Mulde River in Germany, but HCBD was absent in the upper stream. However, HCBD was not detected in most of the fish samples from English (Jürgens et al., 2013), French (Azimi and Rocher, 2016), German (Fliedner et al., 2016), and Bulgarian rivers (Georgieva et al., 2015). PCA was found in atmospheric and fine particle samples with maximum concentrations of 223 and 11.6 pg/m^3, respectively (Chen et al., 2020; Rauert et al., 2018). HCB was widely detected in sediment, fish, and even in orcas (*Orcinus orca*) (Dahlberg et al., 2020; Lawson et al., 2020), but reports of CBs in most environmental compartments are limited.

The presence of these pollutants could lead to adverse effects on organisms (Cheng et al., 2015; Gustafson et al., 2000; Lock and Ishmael, 1979; Molnár et al., 2015; Starek-Swiechowicz et al., 2017). Chronic exposure to low levels of HCBD is known to induce renal tubular necrosis (Lock and Ishmael, 1979). Microgram per liter levels of PCA will cause tail malformation and pericardial edema of zebrafish embryos and will alter thyroid hormone levels through the induction of messenger ribonucleic acid (mRNA) expression of thyroid hormone-related genes (Cheng et al., 2015). HCB, PeCB, and 1,2,4,5-tetrachlorobenzene (TeCB) can promote the formation of glutathione *S*-transferase π-positive preneoplastic foci in the liver (Gustafson et al., 2000). In addition, HCB and 1,2,4-trichlorobenzene (TCB) are potential hormone disruptors that directly and indirectly affect the hypothalamus–hypophysis–adrenal axis (Molnár et al., 2015; Starek-Swiechowicz et al., 2017). Therefore, it is necessary to elucidate the contamination profiles and ecological and human health risks of these pollutants in the environment.

The Beijiang River is an important drinking water source in southern China. It flows through Qingyuan, a developing city with 3.83 million inhabitants (Yearbook, 2016). Since Qingyuan contains many agriculture, aquaculture, and industrial facilities, substantial treated or untreated wastewater enters the receiving environment. The Beijiang River has abundant fish resources, so human health risk through fish consumption is of great concern. HCBD, PCA, and CBs are hydrophobic and can accumulate in wild fish. However, there is a lack of information on these substances in sediment and fish tissues from the Beijiang River basin.

In this study, we investigate the occurrence and potential sources of HCBD, PCA, and CBs in the sediment of the Qingyuan section of the Beijiang River and its main tributaries, clarify the bioaccumulation characteristics of target analytes in the muscle, liver, and brain tissues of wild fish, and assess the ecological and human health risks posed by these substances. Our results provide better understanding of the contamination profiles and risks of HCBD, PCA, and CBs in the aquatic environment in areas with intensive agricultural and industrial activities.

2. Materials and methods

2.1. Sampling

The sampling sites were located in three districts of Qingyuan, including Qingcheng, Yingde, and Fogang. Detailed information on the sampling sites can be found in Fig. 1 and Tables S1 and S2. Samples were collected in August 2015 (summer). Since the investigated analytes are lipid-soluble (Table S3), water samples were not included as part of this study. A total of 22 sediment and 73 fish samples were collected. Sediment samples (three replicates per sampling site) were collected in 200-mL clean amber bottles, combined with 1 g sodium azide/L sediment to inhibit microbial activity, freeze-dried, homogenized, and stored at 4 °C for further pretreatment. We recorded the species, length, and weight of fish captured by fishing and netting (Table S4). The fish were anaesthetized on ice for several minutes and sacrificed by rapid dissection in the field. Muscle samples were cut into pieces after skin removal. All obtained tissue samples, including fish muscle, liver, and brain, were stored at − 20 °C before extraction. All experiments were performed ethically and complied with the guideline of the Ethics Committee of

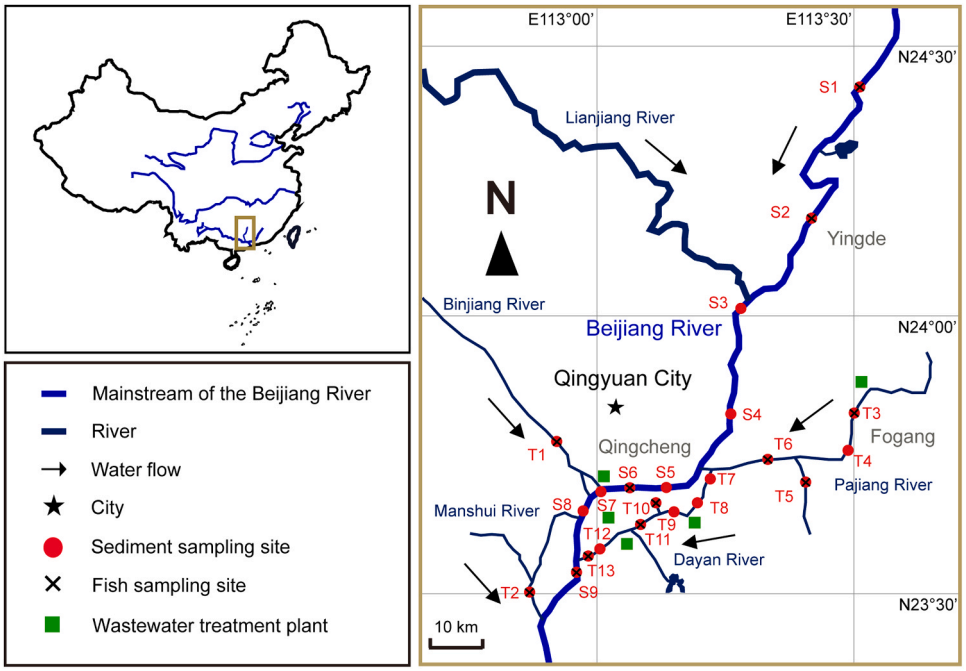

Fig. 1. Sampling locations in the Beijiang River, South China.

South China Normal University for the Care and Use of Laboratory Animals.

2.2. Sample pretreatment and instrument analysis

Six target analytes, including hexachlorobutadiene (HCBD), pentachloroanisole (PCA), hexachlorobenzene (HCB), pentachlorobenzene (PeCB), 1,2,4,5-tetrachlorobenzene (TeCB), and 1,2,4-trichlorobenzene (TCB), were selected as target analytes in this study (Fliedner et al., 2016; Jürgens et al., 2013). Information on the target analytes and suppliers of chemicals and reagents is provided in Table S3 and Text S1. Target analytes in sediment and fish samples were extracted and analyzed using a slightly modified version of a method from a previous study (Chen et al., 2020). In brief, 2.0 g (dry weight, dw) of sediment was placed into a glass centrifuge tube and combined with 20 mL of dichloromethane and 1 ng of phenanthrene-d_{10} (Phe-d_{10}) as a surrogate standard. The solution was spun for 30 s and placed in an ultrasonic bath for 20 min, after which the supernatant was transferred into a 100-mL flat-bottom flask. The above extraction steps were repeated twice. All supernatants from a given sample were combined and concentrated to 1 mL using a rotary evaporator at 40 °C and 300–800 MPa. A column clean-up method was then used to remove potential matrix interference. The glass column was filled from bottom to top with glass wool, 2 g of activated Florisil, 1 g of activated silica gel, and 2 g of anhydrous sodium sulfate. The filled column was preconditioned with 3 × 5 mL of n-hexane and loaded with 1 mL of the concentrated extracts, after which the target analytes were eluted with 40 mL of a dichloromethane and n-hexane mixture (1:1, *v/v*). Finally, the eluate was gently dried with nitrogen and redissolved in 50 μL of n-hexane.

For fish samples, the muscle (5.0 g, wet weight, ww), liver (0.12–0.5 g, ww), and brain (0.06–0.5 g, ww) samples were placed into a glass centrifuge tube to which 4 g of anhydrous sodium sulfate, 20 mL of dichloromethane and 1 ng of Phe-d_{10} as a surrogate standard were added. The sample were homogenized using an ultra-turrax homogenizer (IKA, Germany) at 30,000 rpm. Another 20 mL of dichloromethane was used to rinse the ultra-turrax, and the cleaning fluid was combined with the original fish samples. The extraction and purification procedures for the fish samples were the same as those for the sediment samples.

Target analytes were analyzed by a Thermo TRACE™ 1300 gas chromatograph coupled to a TSQ 8000 Evo mass spectrometer (Thermo, USA) with an electron impact (EI) ionization source. A Thermo TG-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used for the chromatographic separation of the target analytes. Quantitative analysis was performed using the selected reaction monitoring (SRM) mode. The optimized instrument operating parameters are presented in Tables S5 and S6.

2.3. Quality control

For recovery tests, sediment or fish tissue samples were spiked with a mixed standard solution (20 ng/g of each analyte) in three replicates. The method detection or quantitation limit (MDL or MQL) of each analyte was calculated as three or ten times the signal-to-noise ratio (S/N), depending on the spiked samples. The recoveries, MDLs, and MQLs of all target compounds in sediment were 83.3–101%, 0.04–0.24 pg/g, and 0.12–0.80 pg/g, while those of fish tissues were 67.8–84.0%, 0.06–0.28 pg/g, and 0.20–0.94 pg/g, respectively (Table S7). A solvent blank and a standard solution were also analyzed during all sample runs. The results suggest that the method used in this study is sensitive and effective for the determination of target analytes in the sediment and fish tissue samples of the Beijiang River. All concentrations were expressed as nanogram per gram, on a dry-weight basis for sediment (ng/g, dw) and a wet-weight basis for fish tissue (ng/g, ww).

2.4. Data processing

Prior to statistical analysis, the concentration value below the MDL was set at zero, while the value below the MQL but above the MDL was assigned a value that was half of the corresponding MQL. Principal component analysis was conducted to compare the variance in contaminant data sets among samples. Spearman correlation analysis was used to explore the correlation between the analyte concentration and the basic information of fish or different investigated regions. The data x were log (x + 1) transformed before principal component analysis. The significance level was set to $p < 0.05$.

Pollutant residues in sediment and fish tissue samples represent a risk to aquatic organisms and humans. Therefore, the risk and hazard quotients of analytes were calculated based on the measured concentrations and estimated daily intakes. Detailed procedures of the risk assessment are provided in Texts S2–S3. All data analysis was performed using SPSS and Origin software for Windows.

3. Results and discussion

3.1. Contaminant frequency and concentration in different environmental matrices

Six target analytes, HCBD, PCA, TCB, TeCB, PeCB, and HCB, were detected in the sediment and wild fish of the Qingyuan section of Beijiang River. Detection frequencies were 82–100% for the sediment and 79–100% for fish tissue samples (Table S8). The concentrations of target analytes in sediment and fish tissue samples are presented in Tables S9–S13. For sediment, the maximum concentration of HCBD was 0.11 ng/g, while the maximum concentrations of CBs ranged from 0.15 ng/g to 0.48 ng/g. These concentrations are two orders of magnitude lower than the concentrations of HCBD and CBs in marine sediment from the Kaohsiung coast (Lee et al., 2005). It should be noted that the marine sediment samples were collected in 1997, which corresponds with a period of extensive use of these target analytes worldwide. PCA was detected in sediment from all sampling sites at mean, median, and maximum concentrations of 0.05, 0.04, and 0.13 ng/g, respectively. These residue levels are the same order of magnitude as those found in a remote alpine area, the Yamzho Yumco Lake on the Tibetan Plateau (Sun et al., 2018).

For wild fish, the dominant contaminant was PCA. The mean concentrations of PCA in muscle, liver, and brain tissues were 3.12, 30.1, and 47.2 ng/g, respectively. These results are one to two orders of magnitude higher than those found in a previous study on marine fish (*Collichthys niveatus*) collected from the Yellow Sea in which mean concentrations of 0.45 ng/g and 0.08 ng/g were measured in the muscle and liver, respectively (Oh et al., 2005). In comparison to PCA, lower levels of HCBD were found in fish muscle, liver, and brain tissues, with mean concentrations of 0.06 ng/g (muscle), 1.29 ng/g (liver), and 0.59 ng/g (brain). Other reports found that the residue of HCBD in fish tissues was lower than the MDL (de Boer et al., 2001; Fliedner et al., 2016; Jürgens et al., 2013). HCBD is reported to be highly bioaccumulative in the tissue of aquatic organisms (BCF_{max} = 19, 000 L/kg). However, it is readily biotransformed into polar metabolites (CEPA, 1999), which explains its low concentrations in the fish tissue samples. HCB was found at higher levels than the other CBs (maximum concentration of 4.88 ng/g for muscle, 71.2 ng/g for liver, and 24.0 ng/g for brain tissue). A similar phenomenon was observed by Kannan et al. (2010). For the most part, the HCB residues in the muscle and liver of fish in this study were higher than those from other regions, such as the Glen, Nene, Kennet, and Thames rivers (de Boer et al., 2001), Vaccarès Lagoon (Roche et al., 2000), Mediterranean coast (Stefanelli et al., 2002), and the Yellow Sea (Kannan et al., 2010; Oh et al., 2005), but lower than those from the German Environmental Specimen Bank (Fliedner et al., 2016). A previous report found lower concentrations of HCB and PCA in the muscle of mandarin fish from a fishpond in

Guangdong Province than those from a fishpond connected to Taihu Lake in Jiangsu Province (Qiu et al., 2012), where a large amount of wastewater was discharged from chemical industrial plants. Although the usage of HCB is banned by the Stockholm Convention (UNEP, 2001), its unintentional emission could occur.

The contamination patterns of target analytes in different environmental matrices are shown in Fig. 2 and Table S8. POPs were reported to accumulate primarily in the fatty tissues of fish (Kodavanti et al., 2014). Our results show higher analyte levels in the liver and brain than in muscle, suggesting that they accumulated mainly in lipid tissues. Xu et al. (2011) indicated that the lipid content of different tissues of four Chinese commonly seen fish species, including silver carp, crucian carp, snakehead fish, and grass carp, followed the order of brain > liver > muscle. However, in the present study, the concentrations of target analytes followed the order of liver > brain > muscle. These findings reveal that the lipid content may not be related to the analyte concentration in fish. Similarly, most field or exposure experiments have concluded that levels of pollutants such as antibiotics and organophosphate flame retardants were lowest in muscle and highest in the liver (Bekele et al., 2018; Zhao et al., 2015). The liver is an organ that plays a key role in modifying or breaking down xenobiotic pollutants for detoxification. The higher concentrations of target analytes in liver tissues could indicate their low rates of degradation or metabolism (Wang et al., 2016), which occurs by oxidation, hydrolysis, or glucuronidation. In the case of PCA, its residues in the environment may be the result of structure-like pollutant transformation, since PCA is not manufactured commercially. Earlier reports have shown that PCA could originate from PCP methylation by bacteria in sediment rather than by enzymes in the liver of rainbow trout (Glickman et al., 1977; UNEP, 2013b). PCA in fish tissues may be attributed to release from sediment. The presence of polychlorinated compounds in brain samples proves that they can cross the blood–brain barrier, suggesting high-affinity binding of these substances to brain tissues.

3.2. Spatial distribution in the Qingyuan section of Beijiang River

As shown in Table S14, the mean and median levels of all analytes in fish muscle and brain samples were higher in Qingcheng than in Yingde or Fogang, while the levels in sediment samples were similar among the three districts. Spearman correlation analysis was conducted to determine the correlation between analyte concentrations and basic information about the investigated regions collected from the 2016 Qingyuan Statistical Yearbook (Yearbook, 2016). HCBD and HCB concentrations were weakly associated with the sown area of fruits, the sown area of crops, the number of chemical manufacturing plants, and the total emission of industrial gases ($R = 0.309–0.445$, $p < 0.01$) (Table S15). Fang et al. (2017) indicated that HCBD and HCB were detected in the soil, air, and vegetation at and around a typical pesticide-contaminated site. Additionally, there was a weak correlation between the number of textile enterprises and the levels of PCA ($R = 0.177$, $p < 0.05$) (Table S15). PCP, a precursor of PCA in the environment, was used as a preservative treatment for textiles and leather to prevent microbiological attack by fungi and bacteria (Alcock and Jones, 1997). However, the input of target analytes in the study area could not be confirmed because of the weak Spearman correlation.

A component matrix followed by principal component analysis was used to compare the variance in contaminant data sets among samples. Based on Bartlett's test of sphericity ($p < 0.001$), the results of the principal component analysis are reliable. Two principal components (PC), PC1 and PC2, accounted for 67.6% and 17.4%, respectively, of the total variance identified. Based on the component matrix (Table S16), PC1 was related to the sum of TeCB, PeCB, HCB, PCA, and HCBD, while PC2 was associated with TCB. The score plot indicates that the highest concentrations of these substances were found in fish liver and brain tissues, further indicating their high bioaccumulation in fish organs (Fig. 3a). On the other hand, the loading plot displays the obvious separation between TCB and other target analytes (Fig. 3b). These

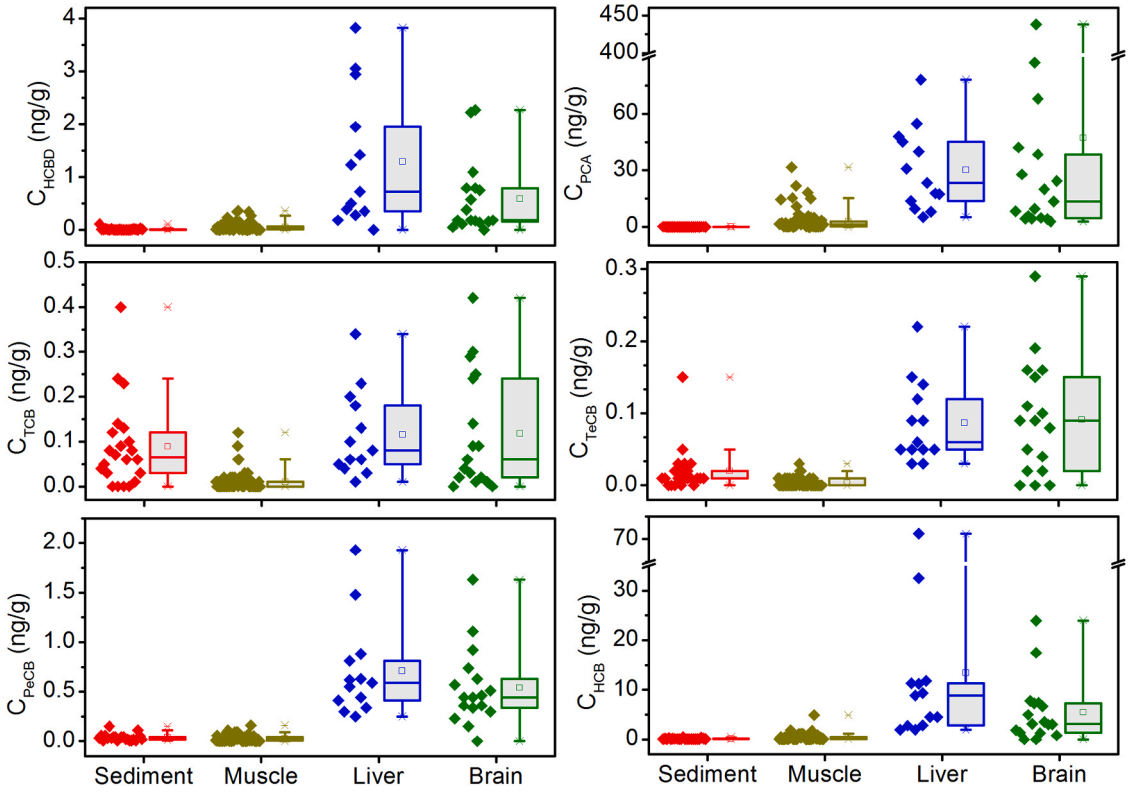

Fig. 2. Box plots of pollutant concentrations in sediment, fish muscle, fish liver, and fish brain samples collected from the investigated region. The box represents the range of the 25th and 75th percentiles, while the whisker is determined by the 5th and 95th percentiles. Median and mean concentrations are displayed as solid lines and hollow squares, respectively, in the box.

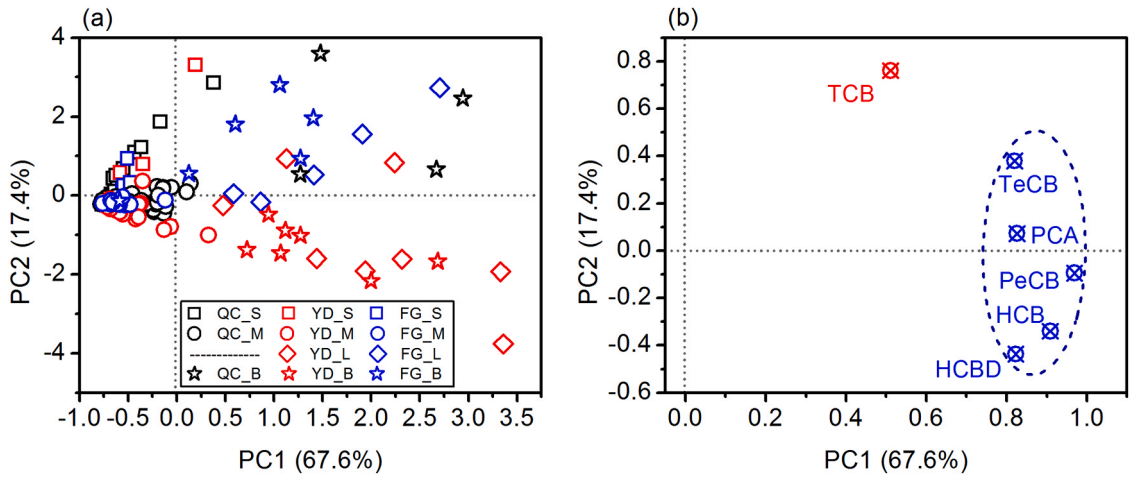

Fig. 3. Score (a) and loading (b) plots derived from principal component analysis based on the pollutant concentrations in all samples from the investigated region. QC, YD, and FG represent the samples collected from the respective Qingcheng, Yingde, and Fogang districts in Qingyuan, while S, M, L, and B indicate the respective sediment, fish muscle, fish liver, and fish brain samples.

patterns are quite different from our earlier study, which demonstrated a relationship between agricultural activity and the distribution of TCB and TeCB in atmospheric fine particle ($PM_{2.5}$) samples (Chen et al., 2020). Accordingly, we could speculate that there was another pollution source of TCB in the investigated zone.

Pollutant concentrations in sediment have been reported to be related to log K_{ow} values (Tian et al., 2014). Pollutants in biological tissues are known to have a relationship with log K_{ow}, fish weight, or fish length (Abalos et al., 2019). In agreement with these previous studies, we found a significant but weak correlation between the log K_{ow} values and the concentrations of each target analyte in sediment samples ($R = 0.22$, $p < 0.05$) (Fig. 4a). Interestingly, because it had the lowest log K_{ow} value but highest concentrations among the target analytes, TCB apparently affected the linearity of the fitting curve. Fig. 4b shows the variation among samples in the proportion of CBs (as a percentage of the total concentrations of chlorobenzenes) in the investigated region. The proportion of TCB increased with decreasing amounts of HCB. No obvious relationship can be seen for the proportion of TeCB or PeCB. Sohn and Haggblom (2016) demonstrated that HCB became dechlorinated via PeCB to TCB in sediment of the Hackensack River, New Jersey. A similar phenomenon of microbial reductive dechlorination of HCB was also found in anaerobic sewage sludge (Fathepure et al., 1988). The fitting bias of the values of log K_{ow} and pollutant concentrations, as well as the apparent separation between TCB and other target analytes, is most likely due to the formation of TCB from higher chlorinated benzenes such as HCB. These higher chlorinated benzenes therefore represent a source of TCB in sediment. With respect to fish tissues, there was no correlation between the log K_{ow} values and pollutant contents ($p > 0.05$). Conversely, the concentration of each analyte was weakly associated with the weight ($R = 0.22$–0.41, $p < 0.05$) or length of the sampled fish ($R = 0.27$–0.42, $p < 0.01$).

3.3. *Environmental and human health risk assessment in the investigated regions*

This study found residues of target analytes in sediment and fish. Since the influence of residues on aquatic organisms and humans is unclear, a risk assessment was conducted.

The risk quotient (RQ) is used to evaluate the ecological risks posed by chemicals. RQs can be found in the European Commission Technical Guidance Document and are calculated by dividing a measured environmental concentration (MEC) by a predicted no-effect concentration

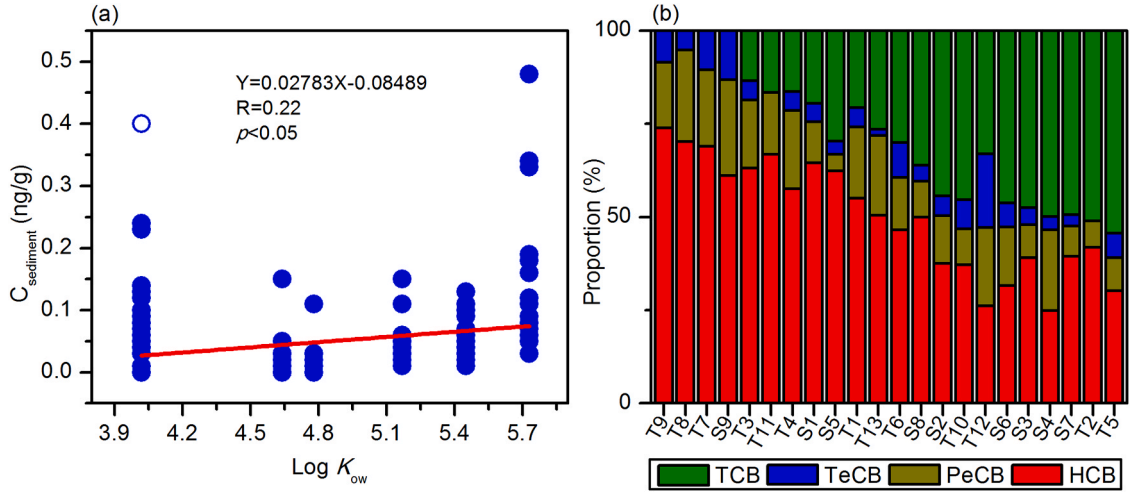

Fig. 4. Correlation analysis (a) between the log K_{ow} values and pollutant concentrations in sediment (n = 22). The hollow square was assumed to be an outlier and was excluded from the regression analysis. The stacked column plot (b) depicts the proportion of each chlorobenzene (as a percentage of the total measured concentration of chlorobenzenes) in sediment from each sampling site.

(PNEC) (EC, 2002). Information about the sediment toxicity of target analytes is limited. Therefore, an indirect approach to risk assessment was used. A measured concentration of a chemical was converted into its corresponding pore water concentration (Text S2 and Table S17) to evaluate its RQ for aquatic organisms (Chen et al., 2018). After collecting and screening aqueous toxicity data for each target analyte, we determined that the chronic toxicity data were insufficient for a statistical extrapolation method, and we decided to use an assessment factor method instead. The derived PNEC values of HCBD, PCA, TCB, TeCB, PeCB, and HCB were 100, 100, 7200, 1800, 680, and 48 ng/L, respectively (Table S18). The RQ values of most analytes were lower than 0.1 (Fig. 5a), indicating their minimal to low risk to ecosystems in the investigated region. HCBD and HCB posed a medium risk to aquatic organisms at certain sampling sites, with frequencies of 4.55% (n = 22). Our results indicate that the residues of HCBD and HCB in sediment should be of concern, although using the indirect approach does increase the uncertainty of the risk evaluation (Chen et al., 2018). More chronic toxicity data on benthic organisms for sediment PNEC derivation are therefore needed.

Fish consumption is considered to be one of the most important human exposure pathways for hydrophobic pollutants. Dietary intake of target analytes via fish consumption will lead to potential health risks, commonly evaluated by a hazard quotient (HQ). The HQ can be calculated by dividing an estimated daily intake (EDI) by an acceptable daily intake (ADI). The maximum EDIs of HCBD, PCA, and CBs for different age groups were 3.72, 426, and 69.3 ng/kg bw/day, respectively (Table 1). The EDIs for different age groups followed the order of adults > children > youth. The dietary intakes of analytes for males were slightly higher than those of females for children (2–5 years) and adults (> 18 years), but the opposite trend was found for the youth group (6–18 years). Since fish liver and brain tissue are popular food items for residents of southern China, fish consumption via the liver and brain was included in the analysis. The mean EDIs of most analytes were higher for fish liver than fish muscle or brain, with the exception of PCA, which had higher EDIs in the fish brain. An earlier study indicated that the mean EDIs of HCBD and HCB were 0.4 and 1.26 ng/kg bw/day, respectively, for adults and 1.23 and 3.92 ng/kg bw/day, respectively, for children (Fernandes et al., 2019). These data agree with our results on fish liver consumption. It must be noted that the EDIs calculated by Fernandes et al. (2019) were based on a large range of commonly consumed dietary items, including eggs, poultry, meat, fish, and vegetables, suggesting that eating patterns affect the dietary intakes of pollutants.

Due to the scarcity of information on some pollutants, only pollutants with available reference doses can be used for risk evaluation. The acceptable daily intakes (ADIs) of HCBD, HCB, and PCP are 200, 270, and 6000 ng/kg bw/day, respectively (HC, 2010; UNEP, 2013a, 2013b). It should be noted that PCA concentrations in fish muscle and liver samples in this study were up to two orders of magnitude higher than those found in an earlier study (Oh et al., 2005). Taking into account the high residues of PCA in fish tissues and information on the ADI of PCP, we used a PCA to PCP transformation rate of 50% to calculate the estimated EDIs of PCP (Text S3). As shown in Fig. 5b, the HQ values were all lower than one (< 1), indicating that the exposure scenarios reported in this study are unlikely to result in a serious health concern given our current state of knowledge on toxic effects. These findings are in keeping with other reports of no health risks posed by HCBD and HCB (Fernandes et al., 2019; Zhang et al., 2014). With respect to exposure to humans

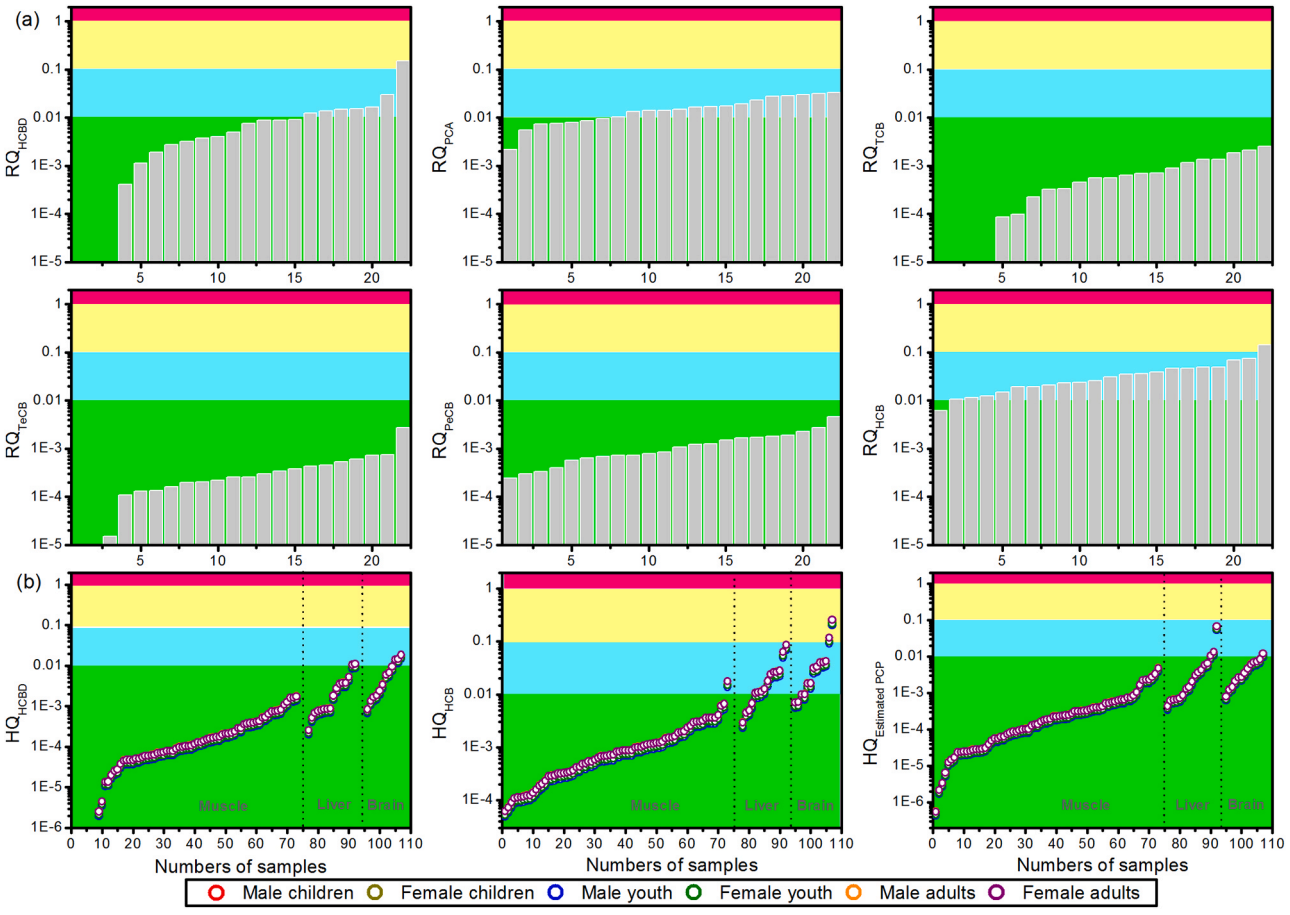

Fig. 5. Calculated risk (a, RQ) and hazard (b, HQ) quotients of pollutants to aquatic organisms and humans for sediment and fish tissue samples. Green, blue, yellow, and red regions represent minimal, low, medium, and high risks, respectively.

Table 1
Estimated daily intakes (ng/kg bw/day) of target analytes via fish consumption for children, youth and adults[a].

	Children (2–5 years)		Youth (6–18 years)		Adults (> 18 years)	
Gender	Male	Female	Male	Female	Male	Female
Fish muscle						
HCBD	0.31 (0.05, 0.02)	0.31 (0.05, 0.02)	0.28 (0.04, 0.02)	0.30 (0.05, 0.02)	0.35 (0.05, 0.02)	0.35 (0.05, 0.02)
PCA	27.2 (2.69, 1.05)	26.8 (2.65, 1.03)	24.1 (2.38, 0.93)	26.1 (2.58, 1.00)	30.7 (3.03, 1.18)	30.5 (3.01, 1.17)
TCB	0.11 (0.01, 0.004)	0.11 (0.01, 0.003)	0.09 (0.01, 0.003)	0.10 (0.01, 0.003)	0.12 (0.01, 0.004)	0.12 (0.01, 0.004)
TeCB	0.03 (0.003, 0.002)	0.03 (0.003, 0.002)	0.02 (0.003, 0.002)	0.03 (0.003, 0.002)	0.03 (0.004, 0.002)	0.03 (0.004, 0.002)
PeCB	0.13 (0.02, 0.02)	0.13 (0.02, 0.02)	0.12 (0.02, 0.01)	0.13 (0.02, 0.02)	0.15 (0.03, 0.02)	0.15 (0.03, 0.02)
HCB	4.21 (0.35, 0.20)	4.14 (0.35, 0.20)	3.72 (0.31, 0.18)	4.04 (0.34, 0.19)	4.75 (0.40, 0.22)	4.72 (0.39, 0.22)
Fish liver						
HCBD	3.30 (1.12, 0.62)	3.24 (1.10, 0.61)	2.91 (0.99, 0.55)	3.16 (1.07, 0.59)	3.72 (1.26, 0.70)	3.69 (1.25, 0.69)
PCA	67.4 (26.0, 20.1)	66.3 (25.6, 19.8)	59.6 (23.0, 17.8)	64.7 (24.9, 19.3)	76.1 (29.3, 22.7)	75.5 (29.1, 22.5)
TCB	0.30 (0.10, 0.07)	0.29 (0.10, 0.07)	0.26 (0.09, 0.06)	0.28 (0.10, 0.07)	0.33 (0.11, 0.08)	0.33 (0.11, 0.08)
TeCB	0.19 (0.07, 0.05)	0.19 (0.07, 0.05)	0.17 (0.07, 0.05)	0.18 (0.07, 0.05)	0.21 (0.08, 0.06)	0.21 (0.08, 0.06)
PeCB	1.66 (0.61, 0.51)	1.63 (0.60, 0.50)	1.47 (0.54, 0.45)	1.59 (0.59, 0.49)	1.87 (0.69, 0.57)	1.86 (0.69, 0.57)
HCB	61.4 (11.6, 7.60)	60.4 (11.4, 7.48)	54.3 (10.2, 6.72)	58.9 (11.1, 7.29)	69.3 (13.1, 8.57)	68.8 (13.0, 8.51)
Fish brain						
HCBD	1.96 (0.51, 0.16)	1.93 (0.50, 0.16)	1.73 (0.45, 0.14)	1.88 (0.49, 0.15)	2.21 (0.57, 0.18)	2.20 (0.57, 0.18)
PCA	377 (40.7, 11.5)	371 (40.1, 11.3)	333 (36.0, 10.2)	362 (39.0, 11.0)	426 (45.9, 13.0)	423 (45.6, 12.9)
TCB	0.36 (0.10, 0.05)	0.35 (0.10, 0.05)	0.32 (0.09, 0.05)	0.34 (0.10, 0.05)	0.40 (0.12, 0.06)	0.40 (0.11, 0.06)
TeCB	0.25 (0.08, 0.07)	0.24 (0.08, 0.07)	0.22 (0.07, 0.07)	0.24 (0.07, 0.07)	0.28 (0.09, 0.08)	0.28 (0.09, 0.08)
PeCB	1.41 (0.47, 0.38)	1.39 (0.46, 0.38)	1.24 (0.41, 0.34)	1.35 (0.45, 0.37)	1.59 (0.53, 0.43)	1.58 (0.52, 0.43)
HCB	20.7 (4.76, 2.73)	20.3 (4.68, 2.69)	18.3 (4.20, 2.42)	19.8 (4.56, 2.62)	23.3 (5.37, 3.08)	23.2 (5.33, 3.06)

[a] Maximum (Mean, Median).

from fish brain consumption, HCB could pose a medium risk. The intake of complex pollutants through fish consumption might cause inevitable harm to humans and should receive more attention.

4. Conclusions

This study shows that HCBD, PCA, and CBs were found in sediment and fish tissue samples from the Qingyuan section of Beijiang River. These lipophilic pollutants had higher concentrations in fish tissues than in sediment and had residue levels in the order of liver- > brain > muscle ≈ sediment. PCA was the dominant pollutant in fish tissues. The results of Spearman correlation analysis and principal component analysis suggested that microbial reductive degradation of higher chlorinated benzenes was the source of TCB in sediment. The results of an ecological risk assessment showed that, with the exception of the medium risk posed by HCBD and HCB at certain sampling sites, there was minimal to low risk to ecosystems in the investigated region. The estimated daily human intakes of analytes through fish consumption followed the order of adults > children > youth. The HQ values indicated that these pollutants might not pose a risk to human safety under most exposure scenarios. To our knowledge, this study is the first to report contamination profiles and the comprehensive risks of HCBD and PCA in Chinese rivers. The findings could provide important insights into the fate of these priority pollutants in the aquatic environment and might become the basis of further pollution control by the local government.

CRediT authorship contribution statement

ZF Chen, Y Lu, and ZW Cai designed the experiments. ZF Chen and X Dai conducted the sampling. Y Lu, YZ Xu and YJ Chen performed the extraction and clean-up experiments. Y Lu and Y Chen performed the GC-MS/MS analysis. ZF Chen and Y Lu conducted the statistical analysis. ZF Chen, and L Yao conducted the ecological risk assessment. ZF Chen and Z Qi conducted the human health risk assessment. ZF Chen, Y Lu, and ZW Cai wrote the paper. All authors discussed and commented on the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126002.

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