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Occurrence and distribution of hexabromocyclododecane in sediments from seven major river drainage basins in China

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Abstract

The concentrations and geographical distribution of hexabromocyclododecane (HBCD) were investigated in 37 composite surface sediments from seven major river drainage basins in China, including Yangtze River, Yellow River, Pearl River, Liaohe River, Haihe River, Tarim River and Ertix River. The detection frequency of HBCD was 54%, with the concentrations ranged from below limit of detection (LOD) to 206 ng/g dry weight. In general, the geographical distribution showed increasing trends from the upper reaches to the lower reaches of the rivers and from North China to Southeast China. Compared to other regions in the world, the average concentration of HBCD in sediments from Yangtze River drainage basin was at relatively high level, whereas those from other six river drainage basins were at lower or similar level. The highest HBCD concentration in sediment from Yangtze River Delta and the highest detection frequency of HBCD in Pearl River drainage basins suggested that the industrial and urban activities could evidently affect the HBCD distribution. HBCD diastereoisomer profiles showed that γ-HBCD dominated in most of the sediment samples, followed by α- and β-HBCD, which was consistent with those in the commercial HBCD mixtures. Further risk assessment reflected that the average inventories of HBCD were 18.3, 5.87, 3.92, 2.50, 1.77 ng/cm^2 in sediments from Pearl River, Haihe River, Tarim River, Yellow River and Yangtze River, respectively.

Key words: HBCD; surface sediment; Chinese river drainage basin; distribution

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Introduction

As the third most used brominanted flame retardant (BFR) after tetrabromobisphenol A (TBBPA) and polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) was primarily applied in polystyrene (PS) insulation foam boards in constructions, back coating of textiles and high impact polystyrene (HIPS) in electrical and electronic equipments. The global production of HBCD was 16,700 metric tons in 2001 (Covaci et al., 2006), in which 9500 metric tons (57%) were sold in Europe (Watanabe and Sakai, 2003). China is one of the main manufacturing countries of HBCD. In 2007, the product capacity of HBCD reached 7500 metric tons (Luo et al., 2010) in China. As additive BFR, HBCD is not chemically bond to materials and can be easily released into environment during production, use, disposal and recycling process. During the past decade, HBCD was found ubiquitous in various environmental media and regions, even in the remote arctic areas (Verreault et al., 2005). Due to its persistency, bioaccumulative and toxic properties, the occurrence of HBCD in environment has aroused growing concern in recent years. Due to its hydrophobic characteristic and low volatility, HBCD is easily adsorbed on organic matters and enter aquatic environment through deposition of atmospheric particles, soil erosion, surface runoff, and discharge of municipal and industrial wastewater (Remberger et al., 2004). Thus, sediment is one of the important sinks and reservoirs of this kind of pollutant. The investigation of contaminations in the sediment can reveal the historical input process of pollutants and provide important information for general contamination status in the local region. In the last decade, studies on HBCD in sediments were mostly conducted in Europe (Morris et al., 2004; Remberger et al., 2004) and North America (Marvin et al., 2006), whereas data in Asia were very scarce, and systematical studies are unavailable on HBCD in sediment from major river drainage basins in

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China.

In this study, sediment samples from seven major river drainage basins in China were collected. Tarim River (inland river), Ertix River and the upper reaches of Yellow River and Yangtze River are situated in the underdeveloped and sparsely populated West and Northwest China. Pearl River, Haihe River, Liaohe River and the lower reaches of Yellow River and Yangtze River are located in the developed East and Southeast China. Yangtze River Delta and Pearl River Delta are the most industrialized and urbanized regions with high population density in China. The aim of this study was to investigate the contamination levels and spatial distribution of HBCD in surface sediments from the seven major river drainage basins, further to better understand the potential sources and estimate the inventory of total HBCD in sediment in Chinese river drainage basins.

1 Materials and methods

1.1 Reagents and standards

Dichloromethane (DCM) and *n*-hexane were pesticide-grade and purchased from Fisher (Fair Lawn, USA). Methanol and acetonitrile were HPLC-grade and from J. T. Baker (Phillipsburg, USA). Pure water was produced by Milli-Q system (Millipore, USA). Silica gel was supplied by Merck (Darmstadt, Germany) and baked at 600°C for 12 hr before cleanup. Anhydrous sodium sulfate (Na_2SO_4) was purchased from Beijing Chemical Factory (China) and backed at 450°C for 6 hr before extraction and cleanup. Sulfuric acid (H_2SO_4) (analytically pure) and sodiun hydroxide (NaOH) (analytically pure) obtained from Beijing Chemical Factory (China) were used to prepare acid silica and basic silica. The detailed method was provided in our previous study (Wang et al., 2010). Native HBCD mixtures (α-, β-, and γ-HBCD, > 98% purity) were from Accustandard Inc. (New Haven, USA). $^{13}C_{12}$-γ-HBCD and d_{18}-γ-HBCD (> 98% purity) were supplied from Wellington Laboratories (Guelph, Ontario, Canada).

1.2 Sample collection and preparation

A total of 261 original individual surface sediment samples collected during 2003–2004 were from the Specimen Bank of China Institute of Water Resources and Hydropower Research, including 84 samples from Yangtze River drainage basin, 52 from Yellow River drainage basin, 88 from Pearl River drainage basin (the rivers in southeast coast and Hainan Island were included), 12 from Haihe River drainage basin, 7 from Liaohe River drainage basin, 16 from Tarim River drainage basin and 2 from Ertix River drainage basin. All the samples were freeze-dried and sieved by a 16-mesh sieve to removed pebbles, sticks and other inclusions. According to the principle of proximity and same water source, the 261 samples were combined to 37 composite samples. The composite sample was thoroughly homogenized and treated as a single sample, then ground into fine powder in a mortar, sealed in the polyethylene bag and stored at –18°C prior to analysis. The sampling sites of 37 composite samples are shown in **Fig. 1**.

Sediment sample of 3 g and 10 g anhydrous Na_2SO_4 were homogenized and spiked with 10 ng surrogate standard of $^{13}C_{12}$-γ-HBCD, then extracted by accelerated solvent extractor (ASE 300, Dionex, USA) with *n*-hexane:DCM (1:1, *V*/*V*) at 150°C and 1500 psi. The extracts were concentrated to 2 mL using a rotary evaporator (Heidolph, Germany), and then eluted through multilayer silica gel column packed with (from bottom up) neutral silica gel (1 g), basic silica gel (4 g; NaOH:silica gel, 1.2:100, *m*/*m*), neutral silica gel (1 g), acid silica gel (8 g; H_2SO_4:silica gel, 40:100, *m*/*m*), anhydrous Na_2SO_4 (2 cm). The first fraction eluted with 70 mL of *n*-hexane was discarded, and the following elute with 80 mL of *n*-hexane:DCM (1:1, *V*/*V*) containing HBCD diastereoisomers was evaporated to dryness under a gentle N_2 stream. At last, the solvent was exchanged into methanol and spiked with d_{18}-γ-HBCD as recovery standard prior to HPLC-MS/MS analysis.

1.3 Analytical methods

Samples were analyzed on Micromass Quattro Premier XE triple quadrupole MS spectrometer (Micromass, Manchester, UK) equipped with an Alliance 2695 LC system (Waters, Milford, USA). The analytical method was modified based on the previous study (Feng et al., 2010). Briefly, separation of three HBCD diastereoisomers was achieved on Zorbax ODS reversed-phase HPLC column (150 mm × 3.0 mm i.d. 5.0 μm, Agilent, USA). The mobile phase was methanol/acetonitrile/water (30:30:40, *V*/*V*/*V*) at a flow rate of 400 μL/min initially, changed linearly to 70:30:0, *V*/*V*/*V*) over 10 min and held for 13 min, then reversed back to 30:30:40, *V*/*V*/*V*) in 0.1 min and held for 6.9 min. The injection volume was 20 μL. Mass spectrometer was operated in atmospheric pressure chemical ionization (APCI) negative ion mode with multiple reaction monitoring (MRM) for $[M\text{-}H]^- \rightarrow Br^-$ transition at *m*/*z* 640.6→79.0 and 81.0 (native HBCD diastereoisomers), 652.6.6→79.0 and 81.0 (^{13}C-labeled diastereoisomer) and 657.6→79.0 and 81.0 (d_{18}-labeled diastereoisomer). The optimized MS/MS conditions were as follows: corona current 3.0 μA, cone voltage 30 V, source temperature 120°C, probe temperature 150°C, desolvation gas flow 450 L/hr, cone gas flow 50 L/hr and collision energy 11 eV.

Total organic carbon (TOC) analysis was performed on a Solids TOC Analyzer (OI Analytical, College Station, USA) coupled with non-dispersive infrared (NDIR) detection. Approximately 100 mg (dry weight) sediment sample was weighed and phosphoric acid solution (5%, *V*/*V*) was added to remove inorganic carbon at 250°C. The operational parameters were as follows: combustion

temperature was 900°C and detection time was 6 min.

1.4 Quality assurance and quality control

Solvent blank (methanol) was analyzed before sample analysis to ensure no contaminations from the instruments and mobile phase. One procedural blank was processed simultaneously in each batch of 12 samples. All the targets in the blank samples were under limit of detection (LOD). A duplicate sample (10 ng/g of native α-, β-, and γ-HBCD standard mixture) was used to verify the stability of instrument sensitivity and repeatability of analytical method for every 10 samples. The relative standard deviations (RSD, n = 6) of α-, β-, and γ-HBCD concentrations were 11.4%, 6.65% and 8.40%, respectively. Recoveries of surrogate standard $^{13}C_{12}$-γ-HBCD in all samples were 91.8% ± 17.7% (mean ± SD, n = 37). Method detection limits (MDLs) were calculated as three times S/N (signal to noise) in the procedural blanks analysis, and the values were 0.23, 0.088 and 0.085 ng/g for α-, β-, and γ-HBCD, respectively.

2 Results and discussion

2.1 Contamination levels and geographical distribution of HBCD

HBCD could be detected in 54% of all the samples, with the concentrations ranged from below LOD to 206 ng/g dw.

The geographical distribution of total HBCD concentrations in sediments from seven river drainage basins is provided in **Fig. 1**. The concentrations of three HBCD diastereoisomers and total HBCD in 37 composite sediment samples from the seven river drainage basins are given in **Table 1**. In general, HBCD concentrations in sediment samples showed decreasing trends from Southeast China to North China. The residue levels of HBCD increased from the upper reaches to the lower reaches, especially in Yangtze River and Pearl River. In the seven river drainage basins, the highest detection frequency of HBCD (100%) was presented in Pearl River drainage basin and Tarim River drainage basin. In spite of the lowest detection frequency (22%) of HBCD in sediment from Yangtze River drainage basin, the concentration of HBCD could be up to 206 ng/g dw in Yangtze River Delta (sampling site 10 in **Fig. 1**).

Similar geographical distribution of HBCD was also observed in sediments from other regions. The spatial distribution of HBCD in suspended sediments from Detroit River exhibited a strong association with urban and industrial activities and the highest level was found in the industrial areas (Marvin et al., 2006). Studies on sediments from coastal water of Korea (Ramu et al., 2010) and Tokyo Bay (Minh et al., 2007) implied that municipal and industrialized areas were the emission sources of HBCD. The southeast coast area of China (including Yangtze River Delta area, Pearl River Delta area and southeast area of Fujian Province) is the fastest developed region which contributes 33.5% of the gross domestic product (GDP) of the whole country (Tang and Yu, 2006). Statistical data showed that, in this area, the industrial wastewater and municipal sewage accounted for 30.34%, the exhaust gas contributed 20.61% and the solid waste contributed 11.53% of the total in the country (Zhao and Luo, 2000). The excessive emission of pollutants accelerated environmental degradation. Heavy pollutions of persistent organic pollutants (POPs) in the Yangtze River Delta and Pearl River Delta (Qiu et al., 2004; Chen et al., 2006; Zou et al., 2007) suggested that the southeast coast area has been a potential environmental risk region of POPs. In the

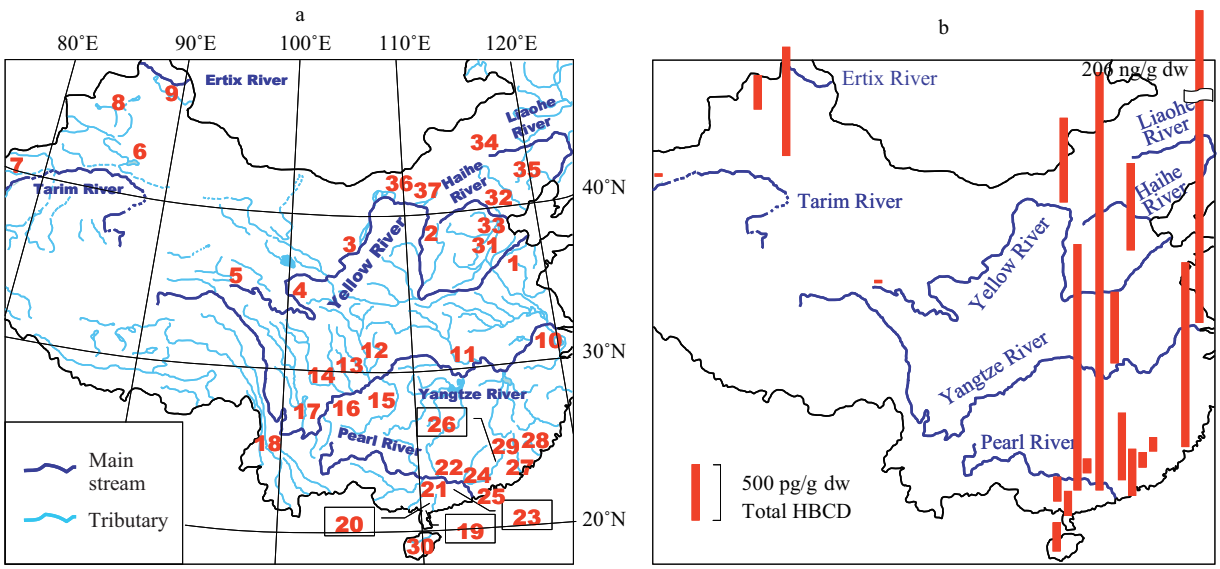

Fig. 1 Sampling sites (a) and geographical distribution (b) of HBCD in sediments from seven river drainage basins in China: Yangtze River, Yellow River, Pearl River, Liaohe River, Haihe River, Tarim River and Ertix River.

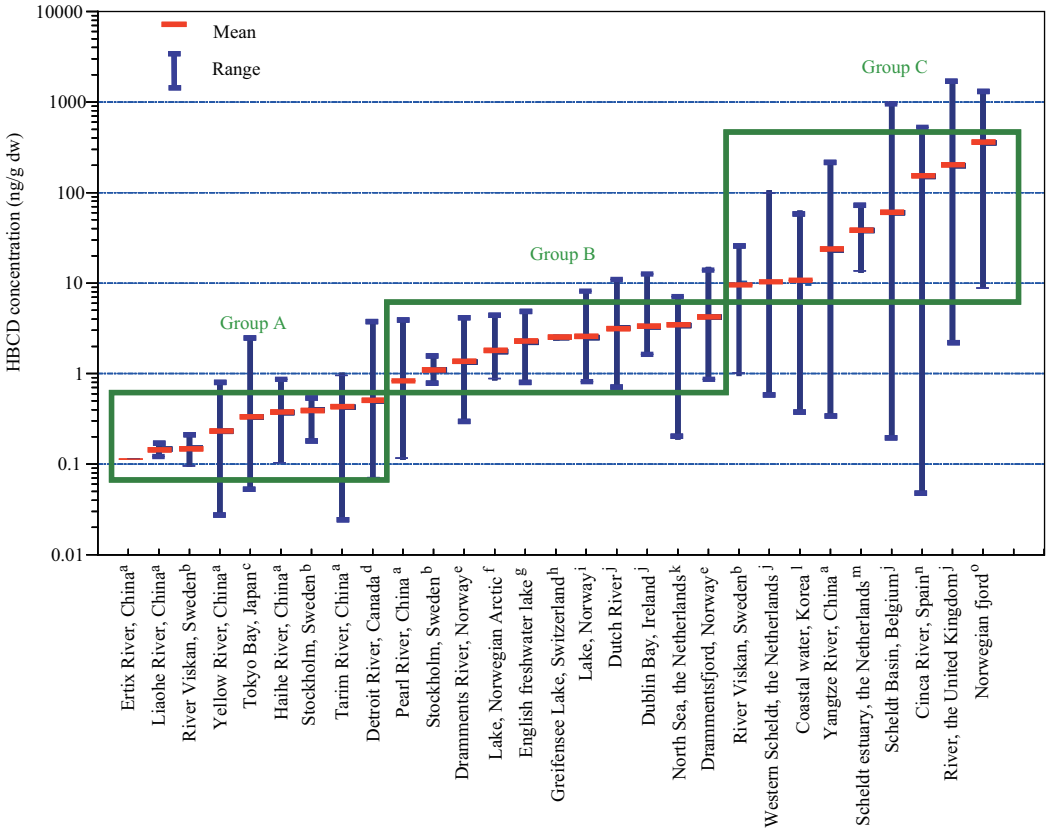

Fig. 2 Worldwide comparison of mean and range of total HBCD concentrations in sediments. Mean and range values below LOD were replaced with LOD. [a] this study; [b] Remberger et al., 2004; [c] Minh et al., 2007; [d] Marvin et al., 2006; [e] Schlabach et al., 2004a; [f] Evenset et al., 2007; [g] Harrad et al., 2009; [h] Kohler et al., 2008; [i] Schlabach et al., 2004b; [j] Morris et al., 2004; [k] Klamer et al., 2005; [l] Ramu et al., 2010; [m] Verslycke et al., 2005; [n] Eljarrat et al., 2004; [o] Haukås et al., 2009.

southeast coast area of China with high population density and high industrialization, PS insulation foam boards, textiles and electrical equipments containing HBCD are commonly used. More HBCD could be released from these products (Morf et al., 2005; Ramu et al., 2010; Abdallah et al., 2008) and then accumulated in sediment through the discharge of industrial wastewater and municipal sewage, atmospheric deposition, etc. A study from Sweden (Remberger et al., 2004) showed that there were indications of elevated levels in air, sediments, and possibly in deposition in the urban area compared to background sites. A recent study in China also showed that HBCD concentrations in atmosphere in urban areas were substantially higher than those in industrial areas, which suggested that urban areas are one major source of HBCD (Yu et al., 2008). In the present study, the highest HBCD concentration found in Yangtze River Delta and the relatively high HBCD concentration found in Pearl River drainage basin suggested that urbanization and industrialization could evidently affect the distribution of HBCD.

It is notable that relatively high concentrations of HBCD were detected in Tarim River drainage basin. Our substantial survey found that sampling site 6 in Tarim River was near the industrial wastewater and municipal sewage discharge site, which might explain the relatively high HBCD concentration in the sediment. However, for the two other sampling sites in Tarim River (site 7 and 8), no potential source was found close to these two sites, the occurrence of HBCD might be associated with atmospheric transport since it has the potential long-range transport ability, which was also mentioned in other studies (Minh et al., 2007; Ueno et al., 2006).

2.2 Worldwide comparison of HBCD levels in sediment

The comparison of HBCD concentrations in sediments collected in 1996–2009 from different regions in the world was summarized, and the mean values and range were plotted in **Fig. 2**. The average concentrations of total HBCD could be divided into three groups (Lam et al., 2009), group A (0–0.5 ng/g dw), group B (0.5–10 ng/g dw) and group C (> 10 ng/g dw). In general, HBCD contaminations in sediments from Chinese river drainage basins were at the relatively low level. Five of the seven rivers including Yellow River, Haihe River, Liaohe River, Tarim River, and Ertix River were included in group A, and HBCD concentrations in sediments from these rivers were comparable to those in Tokyo Bay (Minh et al., 2007), Detroit River (Marvin et al., 2006) and upstream River Viskan in Sweden (Remberger et al., 2004).

Only the HBCD concentrations in sediments from Pearl

Table 1 Concentrations of HBCD in sediments from seven river drainage basins in China.

River	Sampling site	*n*	TOC (%)	Concentration (pg/g dw)			
				α-HBCD	β-HBCD	γ-HBCD	Total HBCD[a]
Yellow River	1	4	1.38	< 94.8[b]	< 35.8	< 34.7	< 165
	2	8	1.62	< 81.3	< 30.7	< 29.7	< 142
	3	9	2.31	< 118	< 44.6	< 43.1	< 206
	4	16	2.50	< 85.7	< 32.4	< 31.4	< 150
	5	6	2.25	< 79.5	< 30.0	30.4	30.4
	36	6	3.10	< 95.9	< 36.3	< 35.1	< 167
	37	3	5.88	288	86.1	375	749
Tarim River	6	7	2.56	214	106	636	956
	7	3	1.99	< 72.1	< 27.2	26.4	26.4
	8	4	3.50	< 95.6	< 36.2	321	321
Ertix River	9	4	2.26	< 66.7	< 25.2	< 24.4	< 116
Yangtze River	10	8	0.90	23908	16143	166051	206102
	11	14	2.12	< 234	< 88.5	629	629
	12	11	1.96	< 207	< 78.3	< 75.8	< 361
	13	14	1.77	< 201	< 75.9	< 73.5	< 350
	14	8	1.79	< 201	< 75.9	< 73.5	< 350
	15	2	2.21	< 266	< 101	< 97.4	< 464
	16	12	3.33	< 249	< 94.0	< 91.0	< 434
	17	12	1.97	< 221	< 83.4	< 80.7	< 385
	18	3	1.63	< 277	< 105	< 101	< 483
Pearl River	19	6	2.01	79.9	< 26.8	132	212
	20	5	1.57	< 81.8	< 30.9	135	135
	21	5	1.89	1554	269	369	2192
	22	7	1.73	70	< 28.2	131	201
	23	16	1.71	216.6	26.4	3479	3722
	24	12	2.63	276	< 31	303	579
	25	8	1.57	96.5	49.0	268	414
	26	3	0.85	77.7	< 23.2	52.5	130
	27	5	1.52	< 178	68.1	117	185
	28	10	2.25	632	35.4	978	1645
	29	2	1.88	< 83.2	< 31.5	120	120
	30	9	0.61	< 156	< 59.0	244	244
Haihe River	31	7	3.19	455	101	227	783
	32	4	1.88	< 121	< 45.7	< 44.2	< 211
	33	1	2.02	< 68.1	< 25.8	< 24.9	< 119
Liaohe River	34	3	0.04	< 91.6	< 34.6	< 33.5	< 160
	35	4	0.49	< 75.9	< 28.7	< 27.8	< 132

[a] Total HBCD is the sum of α-, β-, γ-HBCD, the values below LOD were not calculated in total HBCD; [b] the LOD value.

River in this study fell into group B. As mentioned above, Pearl River Delta is one of the most industrialized and urbanized regions in China, which could result in the indications of high HBCD concentrations. Nevertheless, HBCD in this area was at the lowest end of level in group B. As the second mostly used BFR in Europe, HBCD has been found in many environmental matrices and aquatic organisms in Europe. In group B, the sediment samples were collected from different regions in Europe with no significant sources, including river, lake, bay, fjord, estuary and sea, etc. Therefore, the concentrations of HBCD in this group could be considered as the general contamination levels in sediments in Europe. The relatively high levels of HBCD in Europe than those in Pearl River drainage basin might imply the larger amounts of consumption of HBCD in Europe than those in Pearl River drainage basin.

In group C, all the sampling sites in Europe were close to HBCD pollution sources such as BFR manufacture plants, textile industries, chemical industries and polystyrene plants. It was particularly worth noting that two Asian sampling areas, coastal water in Korea (Ramu et al., 2010) and Yangtze River in China were included in group C, even though no clear HBCD sources were found near the sampling sites. Similar with the result that the highest HBCD concentration was found in sediment from the developed Yangtze River Delta, in Korea, the highest concentration was also found in the industrialized and urbanized region, Onsan Bay. These results implied that urban and industrial activities might be the potential sources of HBCD, and their impacts on environment could reach or exceed those from point sources and should be concerned.

2.3 Profiles of HBCD diastereoisomers

Diastereoisomer profiles of HBCD in sediments from 20 sampling sites (the values below LOD were not included) are given in **Fig. 3**. Among the three HBCD diastereoisomers, γ-HBCD was predominant, followed by α- and β-HBCD in most of the samples, which was similar to those of commercial HBCD mixtures. This result was

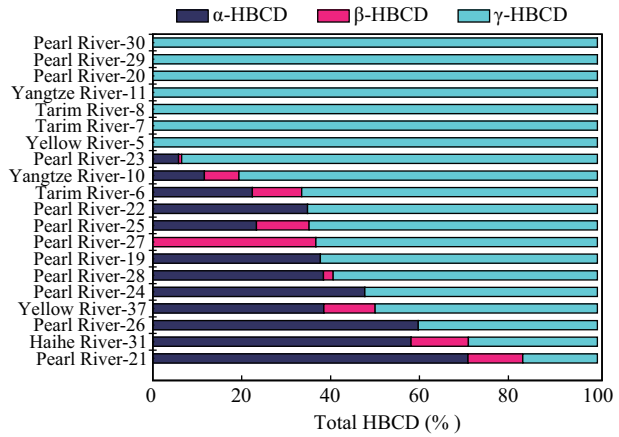

Fig. 3 Diastereoisomer profiles of HBCD in sediments from Chinese river drainage basins, the values below LOD were not included.

consistent with HBCD profiles in sediments from coastal water of Korea (Ramu et al., 2010) and English freshwater lakes (Harrad et al., 2009). It is noticeable that the compositions of HBCD diastereoisomers varied largely in the sediments from Pearl River, α-HBCD contributions ranged from 0 (sampling site 20, 29, 30) to 70.9% (sampling site 21). The wide variation of α-HBCD contributions was also found in the sediments from other areas. For example, investigation on suspended sediments from Detroit River (Marvin et al., 2006) revealed significant shifts from γ-HBCD to α-HBCD. One-third of the samples were found containing relatively high ratios of α isomer. Study on sediment core from Tokyo Bay also showed high percentage of α-HBCD (Minh et al., 2007). Composition of HBCD diastereoisomers can be influenced by several factors in the environment, such as their different physical-chemical properties, profiles of commercial HBCD mixtures, isomer thermal rearrangement during manufacture process and diastereoisomer-specific processes in abiotic and biotic matrices. In the present study, the sampling sites were widely distributed in all over the country, great differences in geographical conditions, climatic conditions and anthropogenic influence on environment might be the reasons for the complicated composition patterns of HBCD in this study.

2.4 Correlation of HBCD concentrations with TOC content

HBCD is assumed to preferentially partition to organic carbon/matter in environmental matrices and reach partition equilibrium in the end due to its strong hydrophobicities ($\log K_{ow}$ = 5.6) (Covaci et al., 2006). This was supported in a recent study (Ramu et al., 2010) where HBCD concentrations and TOC contents in sediment were positively correlated. However, in the present study, there was no significant relationship observed between HBCD concentration and TOC content in sediment. As Meng et al. (2011) indicated, besides TOC content, land use, wet deposition and degradation in environment were also considered to exert strong influences on HBCD distribution. In addition, the emission source could evidently affect the distribution of contaminants in the surrounding area. In the present study, sediment samples were collected from the whole country, and the natural environment and pollution status around the sampling sites were complicated and changeable, all these factors may have effects on the distribution of HBCD in sediment, which might underestimate the TOC effect.

2.5 Inventory of total HBCD in the sediments

Inventory of contaminations represents the total integrated mass of pollutants per unit area, which provides the important information for risk assessment of sediment. It was calculated using the following equation (Song et al., 2004):

$$\text{Inventory} = \Sigma C_i d_i \rho \quad (1)$$

where, C_i (ng/g dw) is the average contaminant concentration, d_i (cm) is the thickness of sediment segment, ρ (g/cm^3) is the density of dry sediment.

In this study, only surface sediments were obtained. The thickness was about 15 cm with dry sediment bulk density as 1.5 g/cm^3 (Zou et al., 2007). The total HBCD concentrations (**Table 1**) below LOD were set as zero when calculating the average concentrations of HBCD. Considering the high HBCD concentrations in sediments from sampling site No. 6 (near the industrial wastewater and municipal sewage discharge site) and No. 10 (HBCD concentration was far higher than those from other sites) would result in overestimating HBCD inventory, therefore, the two sites were not included when calculating the average concentration of HBCD. The results showed that the average inventories were 18.3, 5.87, 3.92, 2.50, 1.77 ng/cm^2 in Pearl River, Haihe River, Tarim River, Yellow River, and Yangtze River, respectively. Compared with Japan which was the largest HBCD consumer in Asia, HBCD inventory in Pearl River was comparable with those in Tokyo Bay (the inventories of HBCD were 13–38 ng/cm^2) (Minh et al., 2007), whereas for other four rivers, the values were at the relatively low level. Sediment served as the dwelling and food source of aquatic organism (Haukås et al., 2010). Therefore, the ubiquitous contaminations of HBCD in sediment in Chinese river drainage basins, especially in Yangtze River Delta and Pearl River Delta, should be paid more attention. Further monitoring and investigation are necessary and effective regulations are urgent on minimizing emissions to environment.

3 Conclusions

This study revealed that HBCD could be ubiquitously detected in Chinese river drainage basins, while their concentrations were relatively low except for in some regions where enhanced industrial and urban activities exist. The geographical distribution of HBCD concentration showed

increasing trends from North China to Southeast China and from the upper reaches to the lower reaches of the rivers, suggesting that intensive urbanization and industrialization could evidently affect the distribution of HBCD. The high estimated inventory of HBCD in Pearl River may pose a threat to aquatic organisms, thus increase human exposure risk.

Acknowledgments

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