

Levels and distribution of hexabromocyclododecanes in surface waters and sediments from Mihe basin of Shandong Province, China

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Introduction

Levels and distributions of three hexabromocyclododecane diastereoisomers (α -, β -, γ -HBCD) were investigated in surface waters and sediments collected from several rivers in Weifang City, Shandong Province, East China. Individual isomer could be detected in all samples. The total concentrations (Σ_3 HBCDs) in waters were 8.13-156 ng L⁻¹, with largest value in Danhe River, followed by Mihe River and Bailanghe River. Σ_3 HBCDs in sediments ranged from 4.89 ng g⁻¹ dw to 157 ng g⁻¹ dw, with median concentrations of 17.3 ng g⁻¹ dw. Compared to similar studies around the world, HBCDs levels in this region were generally high, indicating the exposure of contamination sources. γ -HBCD dominated in all samples, accounting for 72.3%±8.5% of Σ_3 HBCDs in waters and 73.2%±11.7% in sediments, which corresponded with the commercial profiles. Higher levels of HBCDs could increase ecological risks of local environments. Therefore, more attentions should be paid on geographical distribution of HBCDs in multimedial and bioaccumulation/magnification in food chains/webs.

Materials and methods

Chemicals and standards

Dichloromethane (DCM) and n-hexane were of pesticide residue grade, methanol and acetonitrile were HPLC-grade reagents. Both were obtained from Honeywell (Morristown, NJ). Analytically pure ammonium acetate (>98%) was purchased from Acros Organics (Belgium, USA), and anhydrous sodium sulfate was of guaranteed grade from Sinopharm Chemical Reagent Co., Ltd. Ultrapure water was produced by a Milli-Q system (Millipore, USA) in the laboratory. SupelcleanTM LC-Florisil SPE columns (1.0 g, 6 mL) were bought from Supelco Inc. (Bellefonte, PA, USA). Native HBCD mixture (α -HBCD, β -HBCD and γ -HBCD, > 98%) was obtained from AccuStandard Inc. (New Haven, CT, USA), ¹³C-labeled surrogate standard solutions (¹³C₁₂- α -HBCD, ¹³C₁₂- β -HBCD, ¹³C₁₂- γ -HBCD) and D₁₈- α -HBCD were purchased from Wellington Laboratories (Guelph, Ontario, Canada).

Materials

Paired surface water and sediments samples were collected in three river basins, in Weifang City, Shandong Province, East China.

Residue analysis methods

Sample preparation

For water samples one liter of water sample was transferred to separatory funnel. ^{13}C -labeled surrogate standards ($^{13}\text{C}_{12}$ - α -HBCD, $^{13}\text{C}_{12}$ - β -HBCD, $^{13}\text{C}_{12}$ - γ -HBCD) and 50 mL of dichloromethane were added for liquid-liquid extraction with five-minute oscillation. Extraction cycles repeated three times. The merged organic phases were concentrated to 1-2 mL, and purified by Florisil SPE column. The column was conditioned by passing 10 mL of hexane/dichloromethane (v: v, 4:1) and 10 mL of hexane. After loading the extracts, the cartridges were eluted with 12 mL hexane/dichloromethane (v: v, 4:1). Then eluate was evaporated to dryness under a gentle N_2 stream and re-dissolved in 1 mL of methanol. Finally, the eluate was filtered through a 0.22 μm filter membrane, and the internal standard (D_{18} - α -HBCD) was added prior to instrumental analysis.

For sediment samples 2 g of sediment was mixed with 10 g of anhydrous sodium sulfate and spiked with surrogate standards. Then the sample was performed by accelerated solvent extractor (ASE300, Dionex, USA). The conditions were as follows: extracting solvent hexane/dichloromethane (v: v, 1:1), temperature 120 $^\circ\text{C}$, static extraction 8 min, purge time 120 s, cycle 3 times. The extract was concentrated to about 1-2 mL, then cleaned up by Florisil SPE column. The following procedures were the same as those for waters.

Determination

High performance liquid chromatography-tandem mass spectrometry (8040, Shimadzu, JP) equipped with an ESI source was used to analyze α -HBCD, β -HBCD and γ -HBCD. Agilent Zorbax Extend C_{18} (100 mm \times 3.0 mm i.d. \times 1.8 μm , Agilent, USA) was used to separate isomers. The mobile phase included acetonitrile and 2 mmol $^{-1}$ ammonium acetate aqueous solution. The qualitative and quantitative analysis was based on negative ESI mode and multiple reaction monitoring (MRM). The MRM transitions were $[\text{M}-\text{H}]^- \rightarrow \text{Br}^-$: m/z 640.8 \rightarrow 81/79 for native HBCDs, m/z 652.8 \rightarrow 81/79 for surrogate standards and m/z 657.8 \rightarrow 81/79 for D_{18} - γ -HBCD.

Results and Discussion

Quality control and quality assurance (QC/QA)

Procedural blanks were analyzed concurrently with every batch of ten samples. Duplicate standards (5 ng mL $^{-1}$ for individual HBCD isomer) were intermittently analyzed to check instrument's performance. $^{13}\text{C}_{12}$ - α -, β -, γ -HBCD were used to calculate concentrations of individual HBCD, while D_{18} - α -HBCD was selected to estimate the recoveries. The results showed that no target compounds were detected in blanks. Relative standard deviations of α -HBCD, β -HBCD and γ -HBCD in duplicate standards were less than 15%, indicating the stable instrument conditions. The mean recoveries for $^{13}\text{C}_{12}$ -labeled surrogate standards were 92% \pm 21%. Limits of detection (LODs) were defined as three times of signal to noise. In the present study, LODs of three isomers in waters were 0.02, 0.05, 0.01 ng L $^{-1}$, while 0.02、0.05、0.01 ng g $^{-1}$ dw in sediments.

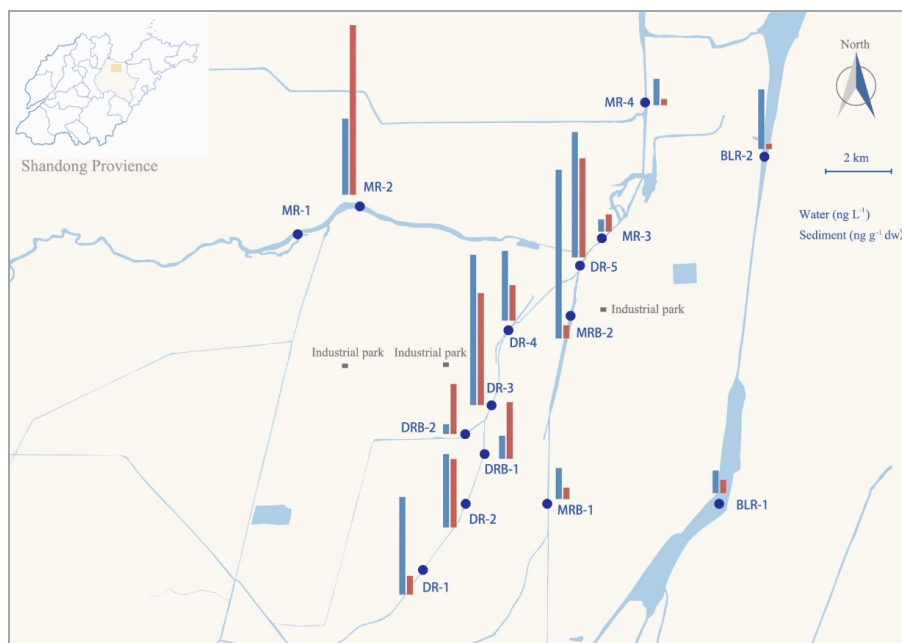
HBCD in water and sediment

Three HBCD diastereoisomers were detected in every water samples from three river basins of Shandong Province, East China, and their concentrations were shown in Table 1. The total HBCD concentrations (Σ_3 HBCDs) in surface water ranged from 8.13 ng L⁻¹ to 156 ng L⁻¹. The largest levels existed in Danhe River (mean value 72.6, range of 8.95-139 ng L⁻¹), followed by Mihe River (mean value 49.8, range of 8.13-156 ng L⁻¹) and Bailanghe River (mean value 38.1, range of 21.0-55.2 ng L⁻¹). Three HBCD diastereoisomers were also detectable in sediments, as shown in Table 1. The concentrations range was 4.89-157 ng g⁻¹ dw, but most of sampling sites had lower levels, with median concentrations of 17.3 ng g⁻¹ dw. HBCDs in Danhe River were higher than those in other rivers. γ -HBCD was the dominated isomer in both water and sediment samples, followed by α -HBCD and β -HBCD, which accorded with the commercial products. γ -HBCD accounted for 72.3% \pm 8.5% and 73.2% \pm 11.7% of Σ_3 HBCDs in water and sediment, and there was no statistically significant difference. These values were comparable to those in industrial products, indicating that the effects of HBCDs production extended the rate of degradation, migration, or conversion. This study systematically investigated concentrations and distributions of HBCDs in surface waters and sediments from several rivers in Weifang City, East Chin. In general, HBCDs levels were relatively higher due to the existence of pollution sources. Danhe river had slightly larger concentrations than Mihe and Bailanghe rivers. Both gradually decreased along flow direction owing to the current dilution, pollutants degradation and various environmental factors, etc. Their concentrations near estuary reached comparable levels with those found in other nonproductive regions, indicating . Isomers profiles were dominated by γ -HBCD, in accordance with the composition of commercial products.

Table 1 Concentrations of HBCD diastereoisomer in water and sediment

Sampling sites	Surface water (ng L ⁻¹)				Sediment (ng g ⁻¹ dw)			
	α -HBCD	β -HBCD	γ -HBCD	Σ_3 HBCDs	α -HBCD	β -HBCD	γ -HBCD	Σ_3 HBCDs
MR-1	1.50	0.38	6.25	8.13	0.65	0.47	6.16	7.28
MR-2	15.3	9.23	45.9	70.5	32.6	58.0	66.5	157
MR-3	2.22	0.51	8.51	11.2	2.75	1.53	11.6	15.9
MR-4	7.22	1.35	15.8	24.4	0.83	0.07	4.91	5.81
MRB-1	6.20	3.76	18.7	28.6	1.61	0.59	8.39	10.6
MRB-2	18.0	11.2	127	156	1.22	0.72	10.3	12.2
DR-1	12.0	6.15	72.2	90.3	2.19	1.67	13.5	17.3
DR-2	8.50	7.81	51.5	67.8	9.32	6.60	47.3	63.2
DR-3	19.9	11.4	108	139	15.6	10.8	77.3	104
DR-4	10.4	6.15	47.8	64.4	9.29	5.22	18.3	32.8
DR-5	18.4	9.28	88.4	116	20.8	14.4	56.6	91.8
DRB-1	4.38	1.68	15.2	21.3	7.73	4.61	40.1	52.4
DRB-2	2.04	1.26	5.66	8.95	8.12	3.99	34.1	46.2
BLR-1	8.23	1.76	11.0	21.0	2.09	1.24	9.04	12.4
BLR-2	6.48	2.16	46.5	55.2	0.56	0.33	4.00	4.89

Figure 1 Distributions of Σ 3HBCDs in surface waters and sediments in Weifang City, Shandong Province, East China



References:

1. Yi S, Liu J G, Jin J, et al. Assessment of the occupational and environmental risks of hexabromocyclododecane (HBCD) in China. *Chemosphere*, 2016, 150:431-7.
2. LETCHER R J, LU Z, CHU S, et al. Hexabromocyclododecane Flame Retardant Isomers in Sediments from Detroit River and Lake Erie of the Laurentian Great Lakes of North America. *Bulletin of Environmental Contamination and Toxicology*, 2015, 95: 31-6.
3. De Wit C A, Herzke D, Vorkamp K. Brominated flame retardants in the Arctic environment - trends and new candidates. *Science of the Total Environment*, 2010, 408(15): 2885-918.
4. Zhu H, Zhang K, Sun H, et al. Spatial and temporal distributions of hexabromocyclododecanes in the vicinity of an expanded polystyrene material manufacturing plant in Tianjin, China. *Environmental Pollution*, 2017, 222(338-47).
5. Anim A K, Drage D S, Goonetilleke A, et al. Distribution of PBDEs, HBCDs and PCBs in the Brisbane River estuary sediment. *Marine pollution bulletin*, 2017, 120(1-2): 165-73.
6. Wang L, Zhang M, Lou Y, et al. Levels and distribution of tris-(2,3-dibromopropyl) isocyanurate and hexabromocyclododecanes in surface sediments from the Yellow River Delta wetland of China. *Marine Pollution Bulletin*, 2017, 114(1): 577-82.