Supplementary Information

Levels and distribution of Hexabromocyclododecane (HBCD) in environmental samples near manufacturing facilities in Laizhou Bay area, East China

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1. Materials and methods

1.1 Sample extraction and cleanup

Approximately 1 g homogenized samples were mixed with 10 g of anhydrous Na_2SO_4 and spiked with 10 ng $^{13}C_{12}$-γ-HBCD as internal standard, then extracted with n-hexane : DCM (1 : 1, v/v) using accelerated solvent extractor (ASE 300, Dionex, USA). For the samples with very high concentrations of HBCD, a duplicate one was re-analyzed using the diluted solution from 1 g extract to obtain the final HBCD concentration in the sample. The extraction condition was as follows: temperature: 150 ^{o}C for soil and sediment samples, 130 ^{o}C for plants and aquatic species; pressure: 1500 psi; static time: 8 min; purge time: 120 s; flush volume: 60%; two static cycles. Lipids were removed from the ASE extracts with acidic silica gel (40% H_2SO_4). After filtration, the extracts were concentrated to 2 mL using rotary evaporator (Heidolph, Germany), then loaded to multilayer silica gel column (10 mm i.d.) for cleanup, which was packed as from bottom up: neutral silica gel (1 g), basic silica gel (4 g; 1.2% (w/w) NaOH (1 mol L^{-1} solution)), neutral silica gel (1 g), acid silica gel (8 g; 30% (w/w) concentrated H_2SO_4), anhydrous Na_2SO_4 (2 cm). The first eluate with 70 mL n-hexane was discarded, the succeeding fraction with 80 mL of n-hexane : DCM (1 : 1, v/v) was collected and concentrated to 2 mL, then evaporated to dryness under N_2 stream, reconstituted to 0.2 mL in methanol, 10 ng d_{18}-γ-HBCD was added as injection standard finally. For lipid determination, the sample was extracted independently by gravimetric analysis.

1.2 Instrumental analysis

HBCD diastereoisomers were separated on Zorbax ODS reversed-phase HPLC column (150 mm × 3.0 mm i.d. 5.0 μm, Agilent, USA). The injection volume was set as 20 μL and the flow rate was 0.4 mL min^{-1}, the mobile phase consisted of methanol (A), acetonitrile (B) and water (C), the gradient program started at a composition of 30 : 30 : 40 (A : B : C, v/v), then changed linearly to 70 : 30 : 0 (A : B : C, v/v) in 10 min and held for 13 min, finally it returned to 30 : 30 : 40 (A : B : C, v/v) within 0.1 min, the column was equilibrated for 6.9 min between injections. Mass spectrometric analysis was performed on triple quadrupole MS spectrometer operated in atmospheric pressure chemical ionization (APCI) negative ion mode with multiple reaction monitoring mode (MRM), $[M-H]^- \rightarrow Br^-$ transition at m/z 640.6→79.0 and 81.0 for native α-, β-, and γ-HBCD isomers, m/z 652.6.6→79.0 and 81.0 for $^{13}C_{12}$-γ-HBCD, m/z 657.6→79.0 and 81.0 for d_{18}-γ-HBCD were monitored for quantitative determination. The source parameters were as follows: Corona current 3.0 μA, Cone voltage 30 V, Source temperature and the APCI probe temperature were 120 ^oC and 150 ^oC, respectively. Desolvation gas flow and Cone gas flow were 450 L h^{-1} and 50 L h^{-1} respectively. Collision energy was 11 eV. Total organic carbon (TOC) content in soil and sediment were analyzed using Solids TOC Analyzer (OI Analyzer, USA), which was described previously.[1]

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Table S1

Sampling details and concentrations of HBCD diastereoisomers and ∑HBCD (sum of α-, β-, and γ-HBCD) in soil, sediment, plant samples (ng g^{-1} dw) and aquatic species (ng g^{-1} lw) from Laizhou Bay area, East China.

Sampling site	Distance from S0 (km)	Species	Body length (cm)[a]	TOC/Lipid (%)[b]	Concentration			
					α-HBCD	β-HBCD	γ-HBCD	∑HBCD
S0	0	soil		1.2	483	250	1562	2295
		reed		5.0	11320	10810	62097	84227
S1	6.95 (south of S0)	soil		2.5	8.24	4.25	23.7	36.2
		reed		3.7	42.4	30.9	166	239
S2	4.99 (south of S0)	soil		1.7	6.87	5.06	27.2	39.1
		reed		5.8	21.2	5.55	222	249
S3	3.16 (south of S0)	soil		1.4	15.4	1.87[c]	38.9	56.2
		reed		5.5	53.1	54.9	295	403
S4	1.21 (south of S0)	soil		2.8	3.51	2.41	39.6	45.5
		reed		6.1	56.7	99.3	265	421
S5	0.35 (south of S0)	soil		1.0	15.4	8.06	79.8	103
		cypress		9.4	10648	10695	86572	107915
S6	0.2 (west of S0)	cypress		6.6	4749	4306	40458	49513
S7	0.28 (west of S0)	soil		2.1	698	303	997	1998
		cypress		8.3	12867	11017	56380	80264
S8	0.97 (west of S0)	soil		2.3	19.4	12.9	62.9	95.2
		reed		5.2	353	272	1337	1962
S9	0.91 (north of S0)	sediment		2.4	155	142	732	1029

S10	1.16 (north of S0)	soil		1.9	316	86.1	1456	1858
		seepweed		2.7	99.8	95.2	515	710
S11	2.18 (north of S0)	soil		4.7	25.4	12.4	33.0	70.8
		seepweed		3.8	31.3	27.8	185	244
S12	4.25 (north of S0)	soil		2.8	1.34	0.90	6.13	8.37
		seepweed		2.1	16.4	17.4	173	207
S13	6.19 (north of S0)	soil		1.9	1.88	0.91	2.14	4.93
		reed		6.3	82.4	71.2	394	548
S14	8.19 (north of S0)	sediment		8.0	0.654	0.25[c]	2.03	2.93
		reed		5.8	74.0	34.5	468	577
S15	23.8 (southeast of S0)	soil		1.8	1167	762	4972	6901
		reed		5.0	12559	17215	130467	160241
		cypress		9.1	14032	13126	121799	148957
S16	18.6 (southeast of S0)	soil		1.0	2.30	3.59	7.27	13.2
		reed		4.6	165	97.4	1031	1293
S17	19.9 (southeast of S0)	sediment		5.4	16.1	7.53	40.6	64.2
S18	29.3 (southeast of S0)	sediment		1.6	1.54	0.87	4.18	6.59
		seepweed		5.1	2.00[c]	6.11	102	110
S19	35.8 (southeast of S0)	sediment		2.0	0.48	0.42	4.99	5.89
		male crab muscle (n = 25)	3.0-4.5	2.6	8.37	22.1	81.8	112
		female crab muscle (n = 28)	2.5-4.0	2.8	13.4	11.7	49.1	74.2
		crab spermary (n = 25)	3.0-4.5	59.	67.1	0.94	6.24	74.3
		crab ovary (n = 28)	2.5-4.0	65	62.6	1.64	8.53	72.8

		male crab gill (n = 25)	3.0-4.5	2.9	117	67.6	261	446
		female crab gill (n = 28)	2.5-4.0	1.6	231	105	479	815
		goby muscle (n = 1)	8.0	6.0	83.0	15.4	75.1	174
		goby roe (n = 1)	8.0	19	184	5.50	13.0	203
		crucian carp muscle (n = 5)	8.0-10	6.6	121	24.0	49.2	194
		stone moroko muscle (n = 1)	8.0	3.8	171	13.6	42.1	227
S20	63.8 (southeast of S0)	sediment		0.39	1.31	1.02	6.36	8.69
		cypress		8.37	13.6	9.41	61.2	84.2
S21	75.7 (southwest of S0)	soil		3.6	N.D.[d]	0.066	0.81	0.88
		reed		4.8	1.54	0.73	6.61	8.88
S22	34.5 (south of S0)	goby（whole body, n > 100）	3.0-5.0	8.8	21.0	1.37	4.34	26.7
		silver carp (whole body, n = 25)	11-14	30	4.92	0.68	1.49	7.09
		loach (whole body, n = 20)	9.0-13	9.0	118	6.35	3.68	128
		freshwater shrimp (whole body, n = 12)	3.0-4.0	5.3	12.2	7.20	26.5	45.9

a: Body length of fish; carapace widths of crabs.

b: Lipid content of plants and species, TOC of soil and sediment.

c: Between LOD and LOQ.

d: Below LOD.

Table S2

Diastereoisomer contributions of two commercial HBCD products from S0 and S15.

Manufacturing site	α-HBCD contribution (%)	β-HBCD contribution (%)	γ-HBCD contribution (%)
S0	17.5	12.6	69.9
S15	26.1	14.2	59.9

Table S3

Bioaccumulation factors (BAFs) for HBCD in reed, seepweed and cypress species.

sampling site	plant species	ΣHBCD concentrations in soil (ng g^{-1} dw)	ΣHBCD concentrations in plants (ng g^{-1} dw)	BAFs
S0	reed	2295	84227	36.7
S1	reed	36.2	239	6.60
S2	reed	39.1	249	6.37
S3	reed	56.2	403	7.17
S4	reed	45.5	421	9.25
S8	reed	95.2	1962	20.6
S13	reed	4.93	548	111
S15	reed	6901	160241	23.2
S16	reed	13.2	1293	98.3
S21	reed	0.88	8.88	10.1
S10	seepweed	1858	710	0.38
S11	seepweed	70.8	244	3.45
S12	seepweed	8.37	207	24.7
S5	cypress	103	107915	1047
S7	cypress	1998	80264	40.2
S15	cypress	6901	148957	21.6

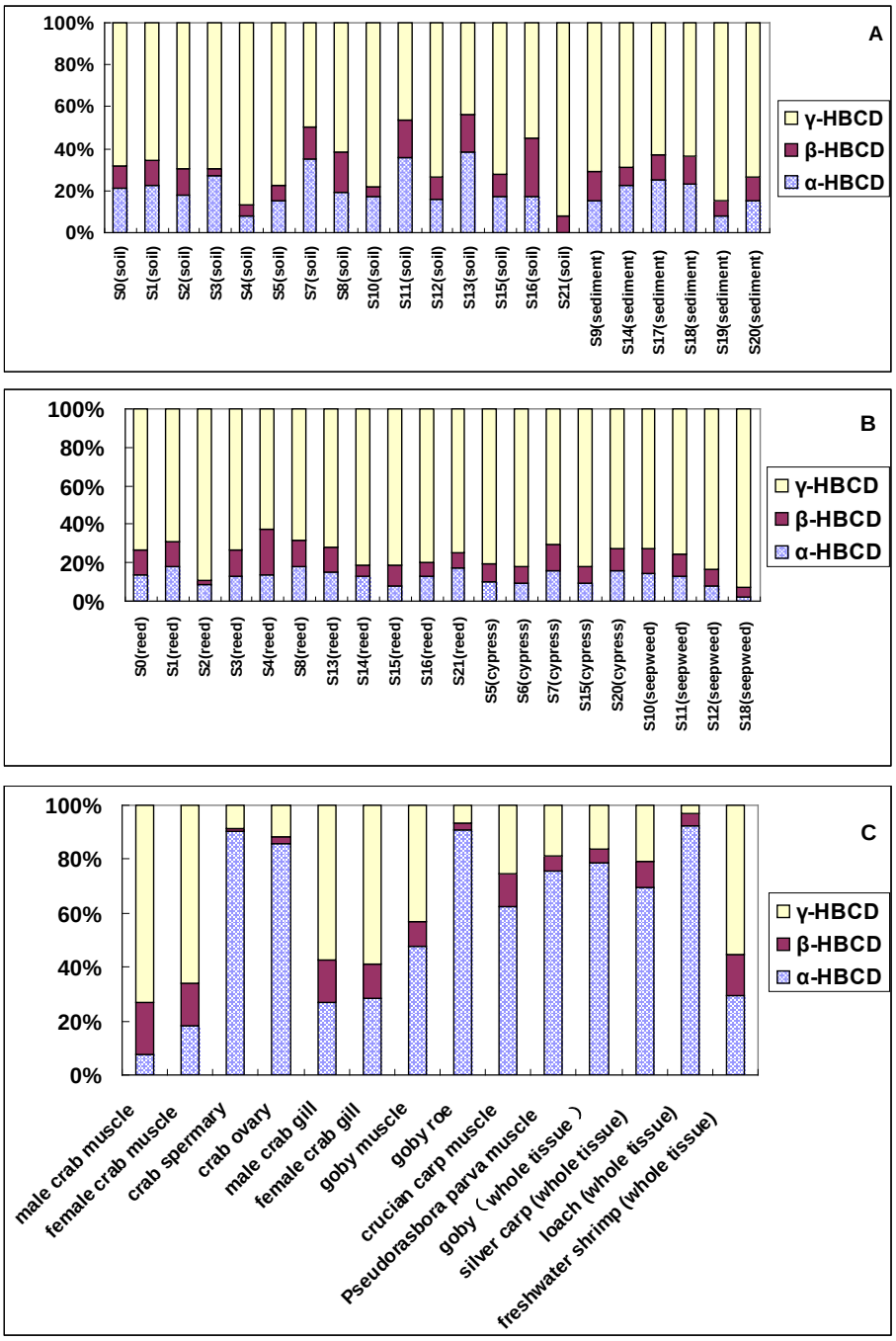

Fig. S1. Diastereoisomer profiles of HBCD in soils and sediments (A), plants (B) and aquatic species (C).

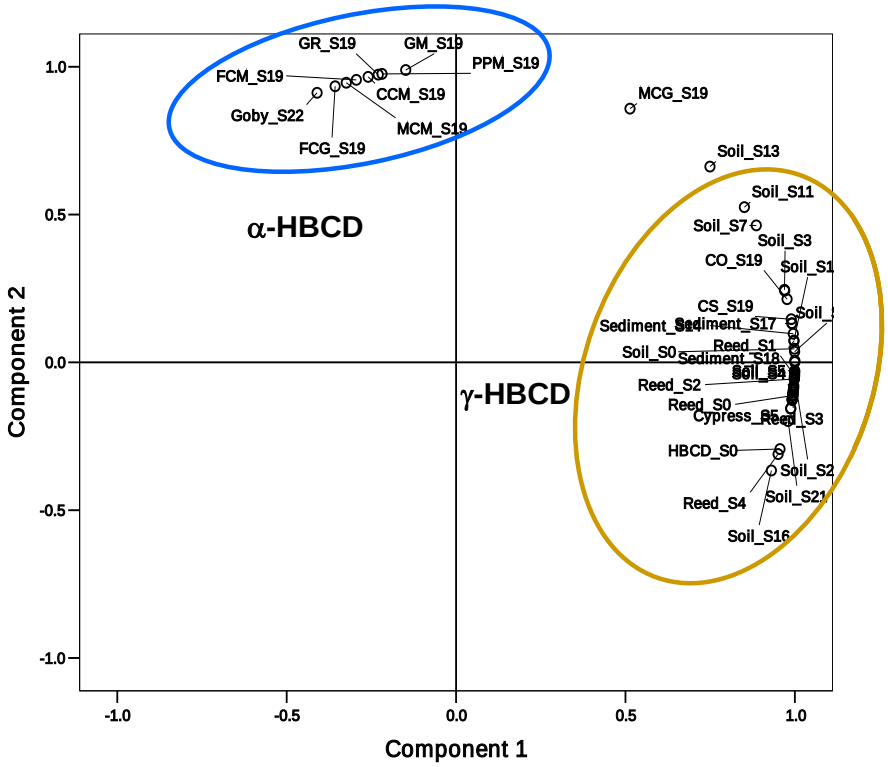

Fig. S2. Principal component analysis of HBCD distribution in the soil, sediment, plant samples and aquatic species from Laizhou Bay area, East China: male crab muscle (MCM), female crab muscle (FCM), crab spermary (CS), crab ovary (CO), male crab gill (MCG), female crab gill (FCG), goby muscle (GM), goby roe (GR), crucian carp muscle (CCM), stone moroko muscle (PPM), silver carp (SC), freshwater shrimp(FS).

Reference

1 P. Wang, Q.H. Zhang, Y.W. Wang, T. Wang, X.M. Li, Y.M. Li, L. Ding, and G.B. Jiang, *Chemosphere*, 2009, 76, 1498–1504.