Supporting Information

MANUSCRIPT TITLE: Occurrence of Halogenated Flame Retardants in Sediment off an Urbanized Coastal Zone: Association with Urbanization and Industrialization

AUTHORS: Hui-Hui Liu, Yuan-Jie Hu, Pei Luo, Lian-Jun Bao, Jian-Wen Qiu, Kenneth M.Y. Leung, and Eddy Y. Zeng

ADDRESS: State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China; Department of Biology, Hong Kong Baptist University, Hong Kong SAR, China; the Swire Institute of Marine Science and School of Biological Sciences, The University of Hong Kong, Pokfulam, Hong Kong SAR, China; School of Environment, Jinan University, Guangzhou 510632, China and University of Chinese Academy of Sciences, Beijing 100049, China

NO. OF TABLES: 6

NO. OF FIGURES: 14

NO. OF PAGES: 28

SI Table S1. Nomenclature and Ion Fragment for the Target Analytes Used in this Study

Analyte	**IUPAC nomenclature**	**Log K_{ow} [a]**	**Ion fragments**
TBB	2-ethylhexyl 2,3,4,5-tetrabromobenzoate	8.75 [1]	356.7/358.7/469
TBPH	bis-(2-ethylhexyl)-tetrabromophthalate	11.95,[1] 10.08 [2]	463.7/514.7/512.7
BTBPE	1,2-bis(trbromophenoxy)-ethane	7.88,[2] 9.15 [3]	250.8/252.8/330.6
DBDPE	1,2-bis(2,3,4,5,6-pentabromophenyl)ethane	13.24,[1] 11.10 [2]	81/79/810.3
DP	bis(hexachlorocyclopentadieno)cyclooctane	11.27 [1]	617.8/653.8
TBBPA	tetrabromobisphenol A	4.5 [4]	542.6/554.7/550.7
HBCD	hexabromocyclododecane	7.74,[1] 6.16 [5]	640.6/652.7
TDBPP	tris(2,3-dibromopropyl) phosphate	4.29 [3]	496.6/498.6
PBCCH	pentabromochlorocyclohexane	4.72 [3]	115.8/79/81
HCDBCO	hexachlorocyclopentadienyldibromocyclooctane	7.91 [1]	539.7/541.6

[a] The superscripts are the reference numbers for log K_{ow}

SI Table S2. Quality Assurance and Quality Control Results

Analyte	Matrix spiking blank	Procedural blank	Solvent spiking blank	Sample
ΣBDE	66 ± 3.2%−78 ± 8.7%		77 ± 6%−89 ± 4%	
BDE-209	85 ± 15%		96 ± 10%	
TBB	55 ± 18%		61 ± 16%	
TBPH	58 ± 20%		59 ± 18%	
BTBPE	82 ± 6.2%		86 ± 4.3%	
DBDPE	87 ± 10%		91 ± 12%	
DP	71 ± 9.6%		80 ± 6.3%	
TBBPA	62 ± 15%		76 ± 11%	
HBCD	76 ± 9.5%		78 ± 8.8%	
TDBPP	65 ± 14%		66 ± 12%	
PBCCH	75 ± 11%		80 ± 8.4%	
HCDBCO	79 ± 14%		76 ± 9.8%	
BDE-51	86 ± 18%	104 ± 9.7%	92 ± 10%	90 ± 15%
BDE-115	77 ± 12%	88 ± 6.2%	80 ± 8.4%	86 ± 14%
^{13}C-BDE-138	71 ± 16%	81 ± 6.2%	80 ± 12%	82 ± 9.0%
^{13}C-BDE-209	85 ± 17%	110 ± 8.3%	93 ± 7.2%	89 ± 17%
HBCD-d_{18}	67 ± 19%	80 ± 13%	87 ± 16%	81 ± 14%

SI Table S3. Coordinates of Sampling Sites, Concentrations of Target Analytes (ng g^{-1}) and Contents of Total Organic Carbon (%) with the Surface Sediments from Daya Bay and Hong Kong

Site	Latitude	Longitude	ΣBDE [a]	BDE-209	TBB	TBPH	BTBPE	DBDPE	DP [b]	TBBPA	HBCD [c]	TDBPP	PBCCH [d]	HCDBCO	TOC
							Daya Bay								
D1	22º 43.264′	114º 34.132′	2.6	47	0.54	0.57	2.1	35	1.8	6.1	14	0.051	1.4	0.21	0.62
D2	22º 43.894′	114º 35.249′	1.1	33	0.36	0.27	1.1	22.	0.90	3.4	9.0	0.028	0.77	0.14	0.82
D3	22º 42.672′	114º 34.373′	2.3	44	0.50	0.68	1.6	28	1.8	4.7	17	0.066	2.0	0.18	1.1
D4	22º 42.188′	114º 34.617′	1.4	50	0.18	0.16	1.1	24	1.1	3.6	11	0.034	0.88	0.065	1.2
D5	22º 41.935′	114º 32.975′	1.9	24	0.18	0.14	1.4	16	0.56	4.1	7.6	—[e]	0.97	0.087	1.0
D6	22º 42.492′	114º 32.257′	1.3	15	0.31	0.36	1.6	11	2.5	3.1	11	—	0.63	0.16	1.1
D7	22º 39.510′	114º 33.065′	0.57	19	0.09	0.17	0.94	9.3	0.34	2.1	6.7	—	0.38	0.13	1.5
D8	22º 45.950′	114º 41.867′	0.39	11	0.054	0.14	0.51	3.6	2.2	0.91	1.6	—	0.24	0.093	1.0
D9	22º 45.550′	114º 43.633′	0.25	8.4	0.16	0.056	0.61	6.0	0.15	1.1	3.2	0.040	0.15	0.088	1.3
D10	22º 45.517′	114º 39.667′	0.066	2.6	0.15	0.047	0.88	6.6	1.1	0.49	4.2	0.039	0.16	0.061	1.0
D11	22º 43.470′	114º 37.519′	0.21	4.0	0.081	0.084	0.63	2.6	0.24	0.50	6.8	—	0.28	0.056	0.9
D12	22º 41.252′	114º 35.505′	0.57	15.	0.15	0.19	1.26	9.1	0.90	1.4	4.1	0.026	0.37	0.084	1.1
D13	22º 38.050′	114º 36.950′	0.091	6.1	0.096	0.15	0.73	5.3	0.48	0.92	5.8	0.024	0.32	0.038	0.93
D14	22º 36.450′	114º 41.633′	0.40	13	0.065	0.15	0.68	1.6	0.33	0.23	5.7	—	0.26	0.053	0.56
D15	22º 39.400′	114º 41.850′	0.12	1.9	0.062	0.085	0.96	4.0	0.56	0.70	4.6	0.007	0.13	—	0.81
D16	22º 43.217′	114º 42.267′	0.33	9.5	0.050	0.10	0.48	1.9	0.32	0.53	3.8	—	0.15	0.018	1.1
D17	22º 34.200′	114º 37.433′	0.14	6.8	0.12	0.096	0.21	3.8	0.96	0.32	3.7	0.036	0.23	—	0.90
D18	22º 34.717′	114º 37.633′	0.25	5.2	0.044	0.052	0.11	2.4	0.33	0.29	6.3	—	0.13	—	0.78
							Hong Kong								
H1	22º 29.930′	113º 59.265′	1.2	34	0.24	0.21	0.64	33	1.4	2.4	7.3	0.033	—	0.020	0.54

82	H2	22º 28.399′	113º 57.798′	0.91	29	0.17	0.14	0.64	37	0.86	3.4	7.7	—	—	0.088	0.98
83	H3	22º 26.800′	113º 55.600′	0.49	28	0.41	0.13	1.5	28	1.2	2.7	13	0.0081	—	0.039	1.0
84	H4	22º25.298′	113º 53.497′	0.32	14	0.37	0.20	1.2	39	0.71	2.0	5.7	—	0.45	0.11	0.61
85	H5	22º23.801′	113º 53.500′	1.1	44	0.38	0.31	5.6	26	2.1	1.3	11	0.030	0.85	0.021	1.0
86	H6	22º21.402′	113º 54.801′	0.33	36	0.077	0.22	3.4	12	1.5	2.2	5.9	—	—	0.094	0.66
87	H7	22º21.401′	113º 57.304′	0.34	14	0.15	0.13	1.5	26	0.94	1.8	10	—	0.55	0.056	0.90
88	H8	22º20.803′	114º 02.290′	0.59	7.9	0.34	0.56	3.9	14	2.4	3.6	4.3	0.11	—	0.18	1.2
89	H9	22º17.302′	113º 52.597′	0.080	11	0.30	0.46	0.88	9.9	0.56	1.6	3.0	0.040	0.40	0.041	1.0
90	H10	22º09.200′	113º 56.204′	0.11	2.8	0.14	0.35	0.90	12	0.28	0.83	1.7	—	—	0.082	0.70
91	H11	22º09.201′	114º 02.694′	0.29	4.7	0.27	0.21	2.2	14	0.93	1.4	4.3	0.15	0.57	0.10	0.82
92	H12	22º12.203′	114º 04.296′	0.065	7.7	0.26	0.55	2.9	25	2.0	2.1	8.1	—	0.84	0.060	1.2
93	H13	22º15.203′	114º 07.398′	0.80	22	0.56	0.43	4.2	45	2.9	5.7	15	0.12	1.3	0.25	0.84
94	H14	22º16.493′	114º 03.498′	0.80	35	0.80	0.49	3.2	37	2.2	4.9	19	0.058	0.95	0.42	1.0
95	H15	22º18.604′	114º 06.301′	1.9	43	0.58	0.59	6.2	62	3.3	7.6	26	0.14	2.4	0.34	0.67
96	H16	22º17.500′	114º 09.500′	1.1	44	0.53	0.37	5.1	56	4.2	9.0	30	0.082	1.9	0.25	—
97	H17	22º18.102′	114º 11.898′	1.3	53	0.64	0.74	5.3	76	3.7	8.5	27	0.20	2.3	0.49	0.93
98	H18	22º09.196′	114º 07.394′	0.12	5.5	0.16	0.10	1.4	26	0.78	2.4	9.8	0.11	—	0.049	0.69
99	H19	22º09.202′	114º 14.399′	0.29	5.3	0.28	0.15	0.55	7.5	0.65	0.90	7.9	—	0.57	0.11	0.70
100	H20	22º09.200′	114º 23.401′	0.28	7.3	0.12	0.11	0.27	3.8	0.41	1.2	6.0	—	0.42	0.029	0.64
101	H21	22º13.799′	114º 15.903′	0.13	1.5	0.047	0.11	1.3	2.3	1.7	4.4	7.2	0.024	1.1	0.020	1.2
102	H22	22º13.795′	114º 23.400′	0.29	3.8	0.094	0.24	0.88	9.4	0.53	1.4	6.6	—	—	0.086	0.78
103	H23	22º17.500′	114º 15.596′	1.3	23	0.48	0.38	3.1	24	2.4	3.5	17	0.076	2.1	0.22	1.1
104	H24	22º17.501′	114º 20.900′	0.12	2.8	0.082	0.13	1.0	15	0.67	2.4	8.1	—	0.55	0.13	0.51
105	H25	22º20.902′	114º 17.099′	0.30	3.1	0.080	0.15	0.50	18	0.98	0.54	12	0.063	0.17	0.052	1.7
106	H26	22º23.700′	114º 25.900′	0.22	6.6	0.23	0.12	0.53	2.8	0.35	1.5	3.4	—	—	0.11	0.52
107	H27	22º28.295′	114º 25.507′	0.15	5.1	0.047	0.062	1.3	9.3	0.42	1.2	3.2	—	—	0.051	0.36
108	H28	22º26.299′	114º 13.001′	1.2	17	0.084	0.19	2.2	12	2.1	3.5	10	—	0.13	—	0.76
109	H29	22º26.800′	114º 15.600′	0.30	3.1	0.13	0.067	3.9	8.6	1.1	2.8	8.0	0.014	—	0.041	1.8
110	H30	22º28.299′	114º 18.000′	0.53	8.4	0.12	0.12	3.3	15	1.4	1.4	5.4	0.004	—	0.039	2.2
111	H31	22º29.300′	114º 19.502′	0.16	4.5	0.29	0.10	0.74	12	0.93	1.2	5.4	—	—	0.039	1.9

H32	22º30.496′	114º 22.802′	0.32	9.1	0.14	0.078	1.1	6.2	0.42	2.5	1.9	—	—	0.019	1.2
H33	22º31.501′	114º 17.999′	0.24	2.2	0.22	0.071	0.38	4.3	0.42	0.82	2.9	0.010	0.13	0.042	1.9
H34	22º33.600′	114º 19.499′	0.50	6.0	0.19	0.12	0.50	23	0.96	1.4	6.7	0.073	1.0	0.11	1.2
H35	22º33.200′	114º 21.699′	0.19	5.4	0.078	0.051	1.1	6.3	0.61	0.53	5.2	0.016	0.52	0.044	1.1

[a] Sum of BDE-15, -17, -47, -71, -85, -99, -100, -126, -153, -154, -181, -183, -190, -196, -203, -204, -206, -207 and -208. [b] Sum of anti-DP and syn-DP. [c] Sum of β-HBCD and γ-HBCD, and α-HBCD was not detected. [d] PBCCH-D. [e] Not detected.

SI Table S4. Comparison of Global Sediment Concentrations (ng g^{-1}) of Halogenated Flame Retardants

Analyte	Concentration	Sampling site	Reference
ΣBDE [a]	0.12−5.5	Qingdao coast, China	[6]
	0-0.55	Yangtze River Delta, China	[7]
	0.04-6.3	The Great Lakes, North America	[8]
	0.04-95	Pearl River Delta, China	[9]
	0.09-2.6	Daya Bay, China	present study
	0.06-1.9	Hong Kong, China	present study
BDE209	0.16-95	Yangtze River Delta, China	[7]
	21-240	The Great Lakes, North America	[8]
	0-7300	Pearl River Delta, China	[9]
	240-1700	Scheldt estuary, The Netherlands	[10]
	1.9-50	Daya Bay, China	present study
	1.5-53	Hong Kong, China	present study
DBDPE	39-360	Zhujiang estuary, China	[11]
	23-430	Dongjiang river, China	[12]
	0-24	Western Scheldt, The Netherlands	[3, 13]
	0.11-2.8	The Great Lakes, North America	[14]
	1.6-34.8	Daya Bay, China	present study
	2.3-76	Hong Kong, China	present study
HBCD [b]	0.2-6.9	North Sea, The Netherlands	[15]
	0.04-3.1	The Great Lakes, North America	[14]
	0.43-3.9	Lake Ellasjøen, Norway	[16]
	0.06-2.3	Tokyo Bay, Japan	[17]
	1.6-17	Daya Bay, China	present study
	1.7-30	Hong Kong, China	present study
TBBPA	3.8-230	Dongjiang River, China	[12]
	330-3800	English Lakes, England	[18]
	0.3-1.3	Western Scheldt, The Netherlands	[19]
	0.8-4.0	Dutch rivers, The Netherlands	[19]
	0.23-6.1	Daya Bay, China	present study
	0.53-9.0	Hong Kong, China	present study
BTBPE	0.05-2.07	Pearl River Delta, China	[11]
	0.27-21.9	Pearl River Delta, China	[11]
	0.13-8.3	The Great Lakes, North America	[14]
	0-0.3	Western Scheldt, The Netherlands	[3]
	0.10-2.1	Daya Bay, China	present study
	0.27-6.2	Hong Kong, China	present study

DP [c]	5-590	The Great Lakes, North America	[20-23]
	0.04-0.11	Songhua River, China	[24]
	0.25-0.70	Yellow Sea, China	[25]
	0-4.9	Jing-Hang Grand Canal, China	[26]
	0.15-2.5	Daya Bay, China	present study
	0.28-4.2	Hong Kong, China	present study
PBCCH [d]	0.03-0.72	Western Scheldt, The Netherlands	[3]
	0.13-2.0	Daya Bay, China	present study
	0-2.4	Hong Kong, China	present study
HCDBCO	0.21-2.3	The Great Lakes, North America	[14]
	0-0.21	Daya Bay, China	present study
	0-0.49	Hong Kong, China	present study
TDBPP	7.8-89	Baltic Sea (Vistula river)	[27]
	0-0.066	Daya Bay, China	present study
	0-0.20	Hong Kong, China	present study
TBB	0.044-0.55	Daya Bay, China	present study
	0.047-0.80	Hong Kong, China	present study
TBPH	0.047-0.68	Daya Bay, China	present study
	0.051-0.74	Hong Kong, China	present study

[a] Sum of BDE-15, -17, -47, -71, -85, -99, -100, -126, -153, -154, -181, -183, -190, -196, -203, -204, -206, -207 and -208. [b] Sum of β-HBCD and γ-HBCD, and no α-HBCD was detected in our samples. [c] Sum of anti-DP and syn-DP. [d] the isomer PBCCH-D.

SI Table S5. Assignment of Sampling Sites to the Council Districts of Hong Kong, the Corresponding Average Concentrations of all-HFRs (ng g^{-1}), Concentration Deviation and Population Density (person km^{-2})

Council district	**Sampling site**	**Concentration** [a]	**Deviation**	**Population** [b]
South	H21	20	4.0 [c]	6160
North	H33, 34	26	20 [d]	1946
Tai Po	H27, 28, 29, 30, 31, 32	29	10 [d]	1807
Sai Kung	H20, 22, 23, 24, 25, 26	34	23 [d]	2813
Tsuen Wan	H8	38	7.5 [c]	4330
Islands	H9, 10, 11, 12, 13, 14, 18, 19	53	35 [d]	693
Tuen Mun	H4, 5, 6, 7	69	17 [d]	5096
Yuen Long	H1, 2, 3	78	2.5 [d]	3652
Central & Western	H13	98	29 [c]	17950
Yau Tsim Mong	H16	152	30 [c]	39593
Kwai Tsing	H15	154	31 [c]	20158
Kowloon City	H17	180	36 [c]	33278

[a] Average concentration of HFRs for all sampling sites in each council district, and the HFRs in each site include PBDEs and alternative HFRs. [b] The data were calculated with values of district area [28] and population size.[29] [c] Estimated using an instrumental analysis uncertainty of 20% i.e., deviation = $C_{\mathrm{HFR}} \times 20\%$. [d] Estimated as the standard deviations of HFR concentrations at all sampling sites within the same district (i.e., deviation =

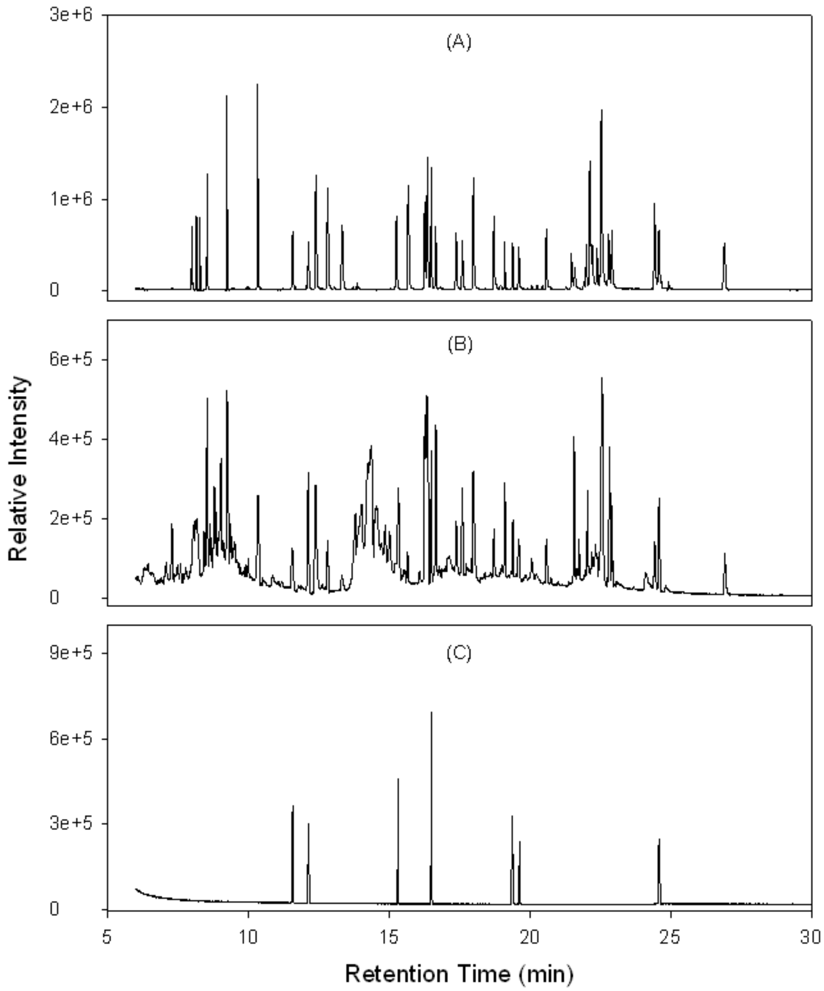
$$\sqrt{\frac{\sum_{i=1}^{n}\left(C_{\mathrm{HFR},i}-\overline{C}_{\mathrm{HFR}}\right)^{2}}{n-1}}$$

; where i represents the ith sampling site, n is the number of sampling sites within the same council district, and $\overline{C}_{\mathrm{HFR}}$ is the average HFR concentration for all sampling sites within the same district.

SI Table S6. Doubling Time (t_2) for PBDEs [a] and Alternative HFRs in Two Sediment Cores and Three Socioeconomic Indices (Production Volume, Production Value and Population Size) in Huizhou, Fitted with a First-Order Kinetic Model

Analyte	**t_2 (yr)**	**r^2**	**p**
	sediment core D13		
Penta-BDE	87 ± 7.9	0.80	< 0.0001
Octa-BDE	82 ± 8.7	0.75	< 0.0001
Deca-BDE	23 ± 2.3	0.75	< 0.0001
TBB+TBPH	23 ± 2.3	0.85	< 0.0001
BTBPE	27 ± 2.9	0.81	< 0.0001
DBDPE	55 ± 8.3	0.65	< 0.0001
DP	43 ± 4.1	0.79	< 0.0001
HBCD	27 ± 3.3	0.71	< 0.0001
	sediment core D16		
Penta-BDE	89 ± 9.6	0.69	< 0.0001
Octa-BDE	107 ± 11	0.47	< 0.0001
Deca-BDE	32 ± 2.8	0.81	< 0.0001
TBB+TBPH	18 ± 1.4	0.91	< 0.0001
BTBPE	21 ± 5.5	0.72	< 0.0001
DBDPE	59 ± 7.3	0.70	< 0.0001
DP	29 ± 2.8	0.79	< 0.0001
HBCD	59 ± 10	0.47	< 0.0001
	socioeconomic index		
Production volume [b]	5.2 ± 0.49	0.90	< 0.0001
Production value [c]	4.2 ± 0.12	0.99	< 0.0001
Population Size	24 ± 0.93	0.97	< 0.0001

[a] Considering the complex compositions of technical products with different predominant constituents,[30] BDE-71, -47, -100, -99, -85, -126, -154 and -153 were classified as the constituents of Penta-BDE product, BDE-183, -181, -190, -203, -204 and -196 of Octa-BDE product, and BDE-209 of Deca-BDE product. In addition, the detectable rates of BDE-15 and -17 are extremely low in these PBDE-technical products,[30] thus the two components were not included in any tech product. BDE-206, -207 and -208 were also not classified, because they may be derived from Octa-BDE tech product, as well as from the degradation of BDE-209 in the environment. [b] Production volume of electronic devices in Huizhou. [c] Production value of electronic industries in Huizhou, with the historical data being obtained from the Statistics Bureau of Guangdong Province, Huizhou Statistics Information Network.[31]



Analyte	Retention time
PBCCH-A	7.983
PBCCH-B	8.153
PBCCH-C	8.277
PBCCH-D	8.527
BDE-15	9.237
BDE-17	10.323
BDE-69	11.568
BDE-51	12.129
BDE-71	12.396
BDE-47	12.810
TDBPP	13.327
^{13}C-PCB-208	15.263
BDE-100	15.683
BDE-99	16.263
HCDBCO	16.360
BDE-115	16.493
TBB	16.650
BDE-85	17.380
BDE-126	17.597
BDE-154	17.991
BDE-153	18.720
BDE-183	19.103
^{13}C-BDE-139	19.387
^{13}C-BDE-138	19.613
BTBPE	20.587
BDE-181	21.474
BDE-190	21.603
TBPH	22.007
syn-DP	22.130
BDE-203	22.213
BDE-204	22.380
BDE-196	22.430
anti-DP	22.538
BDE-208	22.800
BDE-207	22.907
BDE-206	24.432
(^{13}C-)BDE-209	24.584
DEDPE	26.913

Figure S1. Chromatograms of (A) a standard mixture of halogenated flame retardants, (B) a sediment sample, and (C) a solvent blank. The retention time of each analyte is presented on the right.

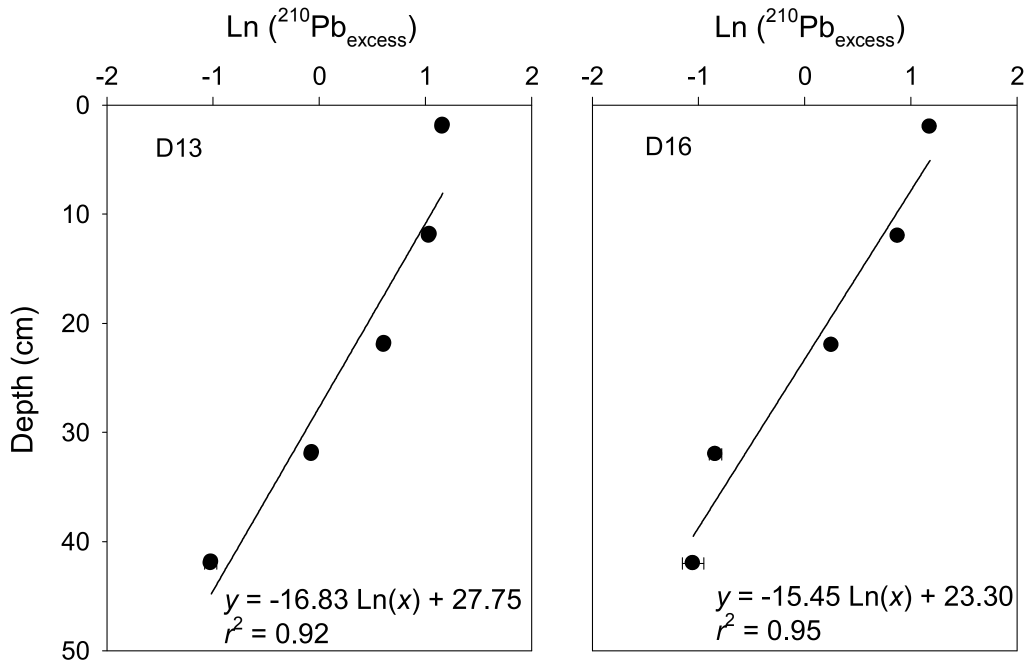


Figure S2. ^{210}Pb age dating of sediment cores D13 and D16 in Daya Bay.

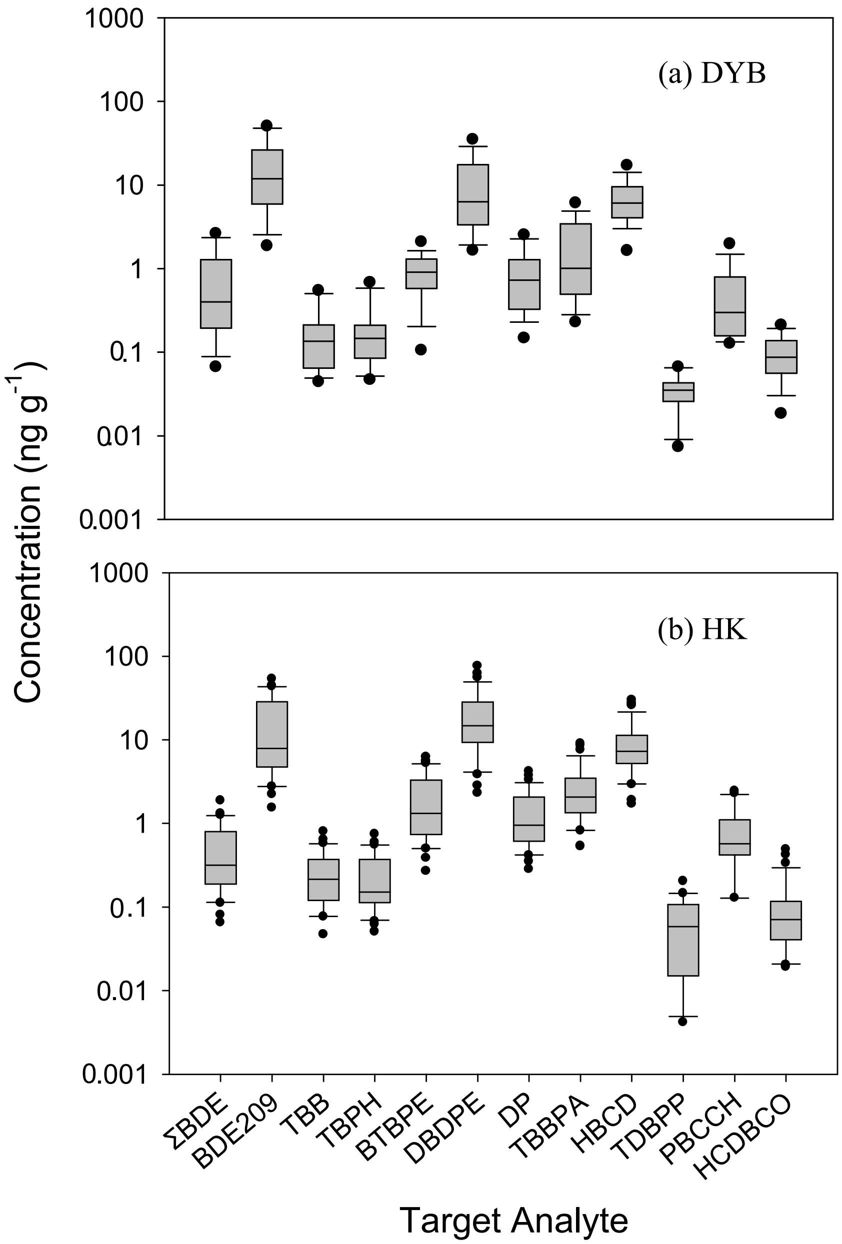


Figure S3. Box plots (10th, 25th, 50th, 75th, 90th and mean) of the concentrations of PBDEs and alternative halogenated flame retardants in surface sediment collected from (a) Daya Bay (DYB) and (b) Hong Kong (HK) waters.

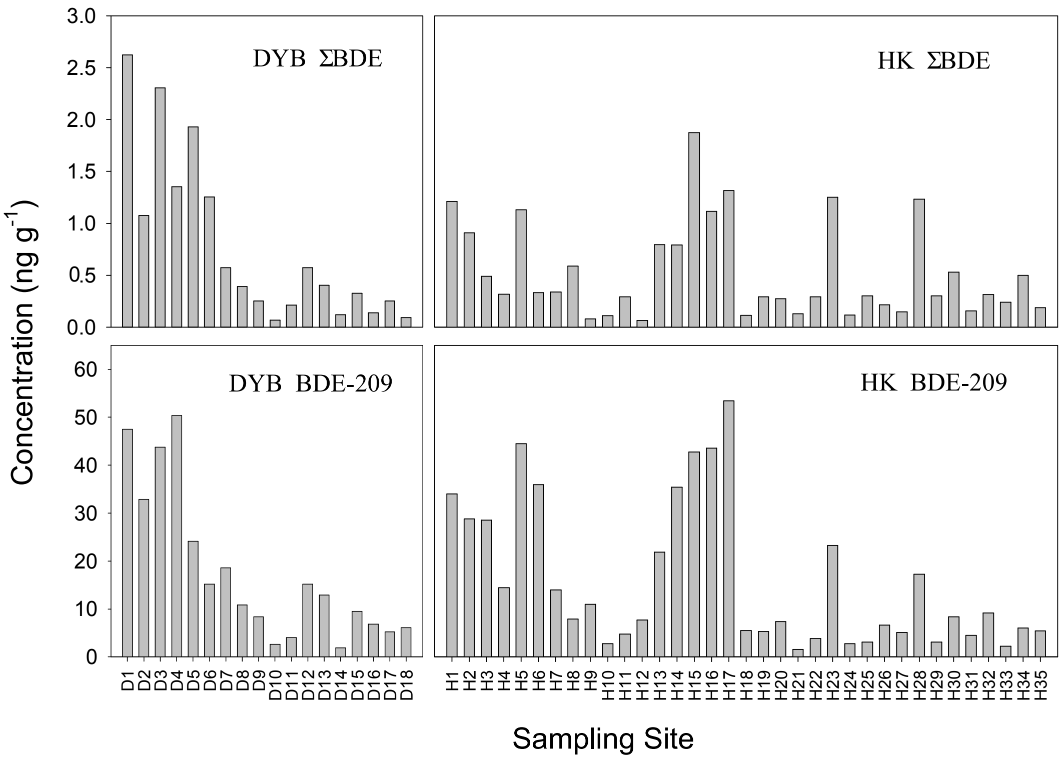


Figure S4. Spatial distribution of ΣBDE and BDE-209 in surface sediment collected from Daya Bay (DYB) and Hong Kong (HK) waters.

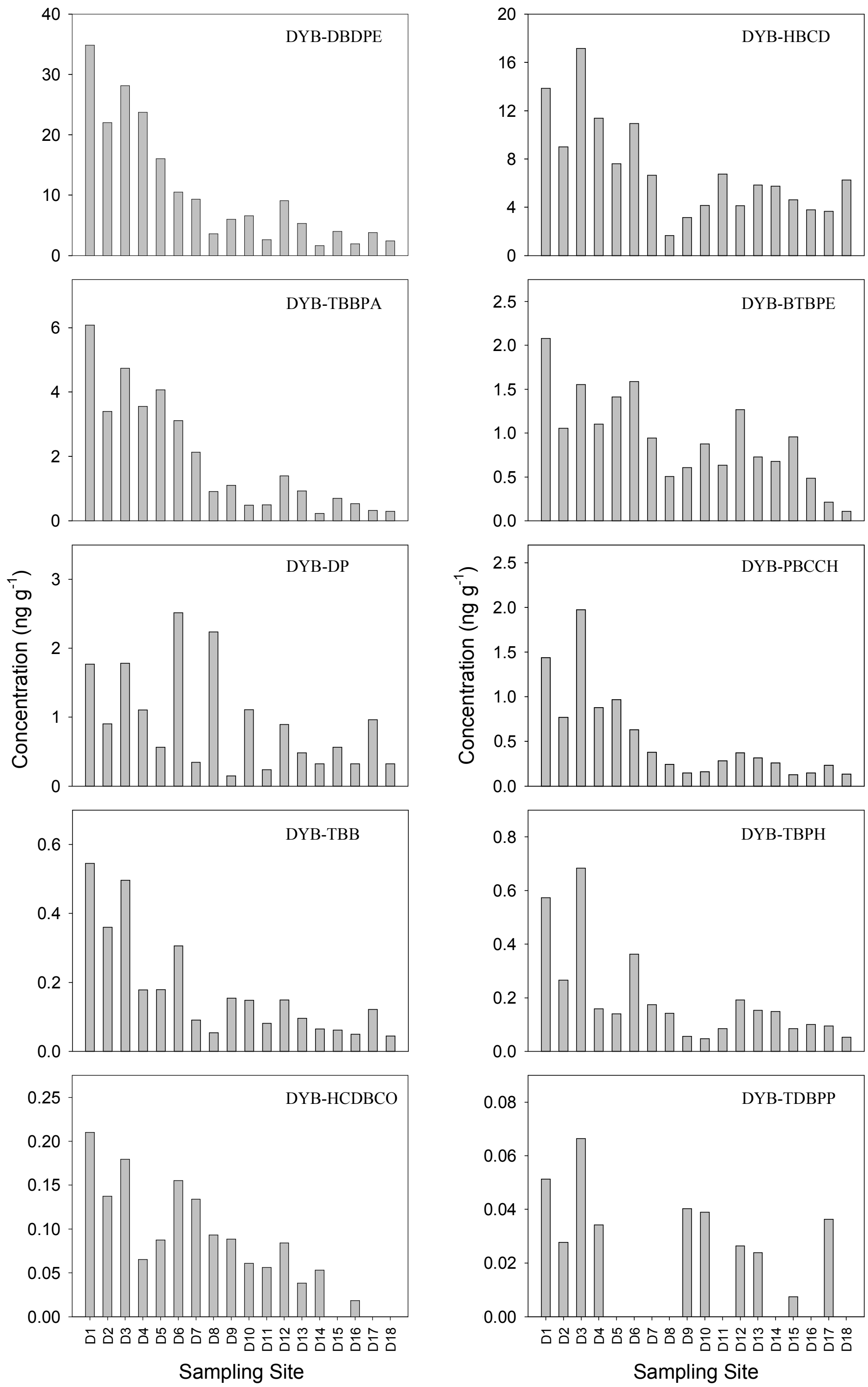


Figure S5. Spatial distribution of individual alternative halogenated flame retardants in surface sediment collected from Daya Bay (DYB) waters.

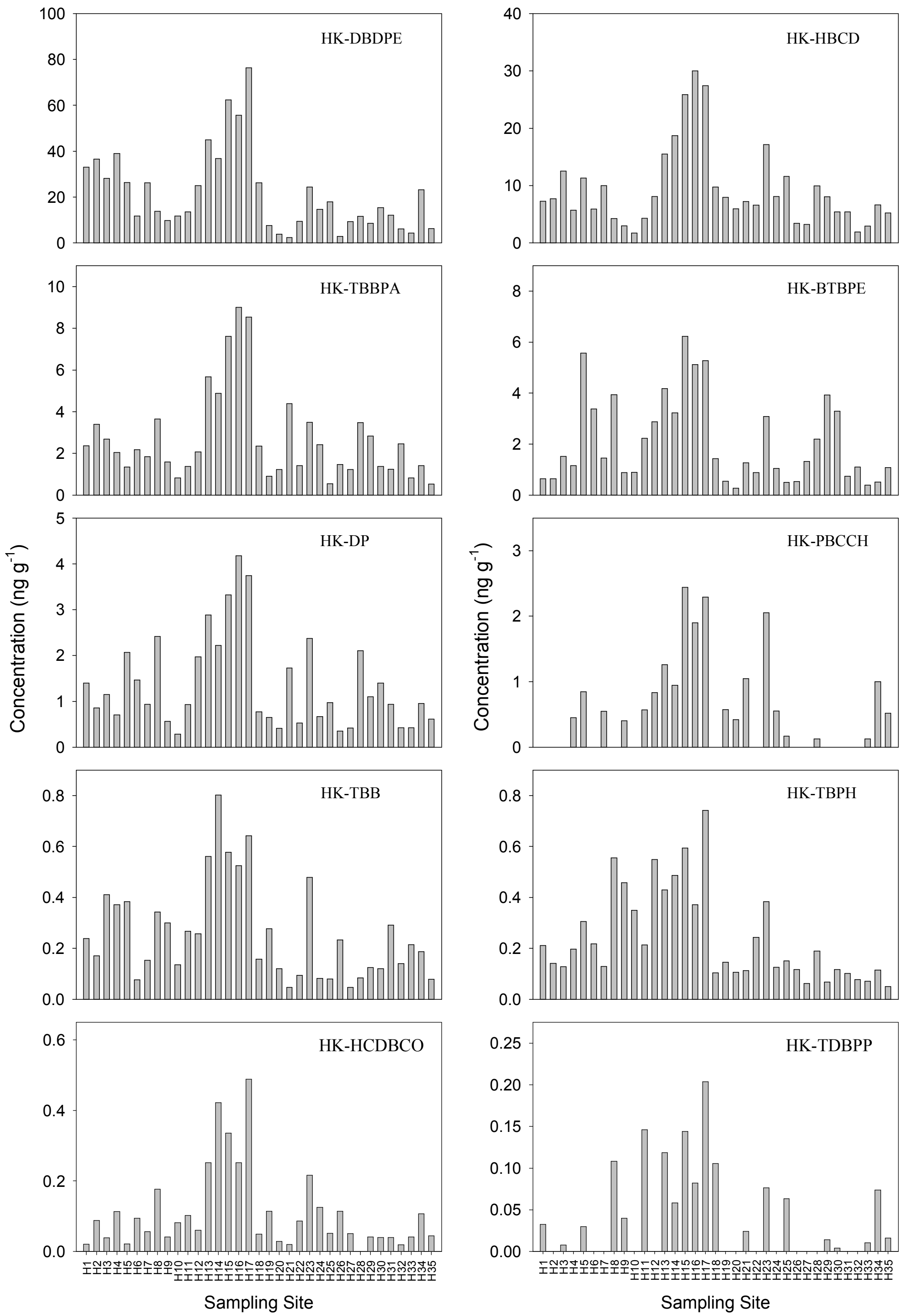


Figure S6. Spatial distribution of individual alternative halogenated flame retardants in surface sediment collected from Hong Kong (HK) waters.

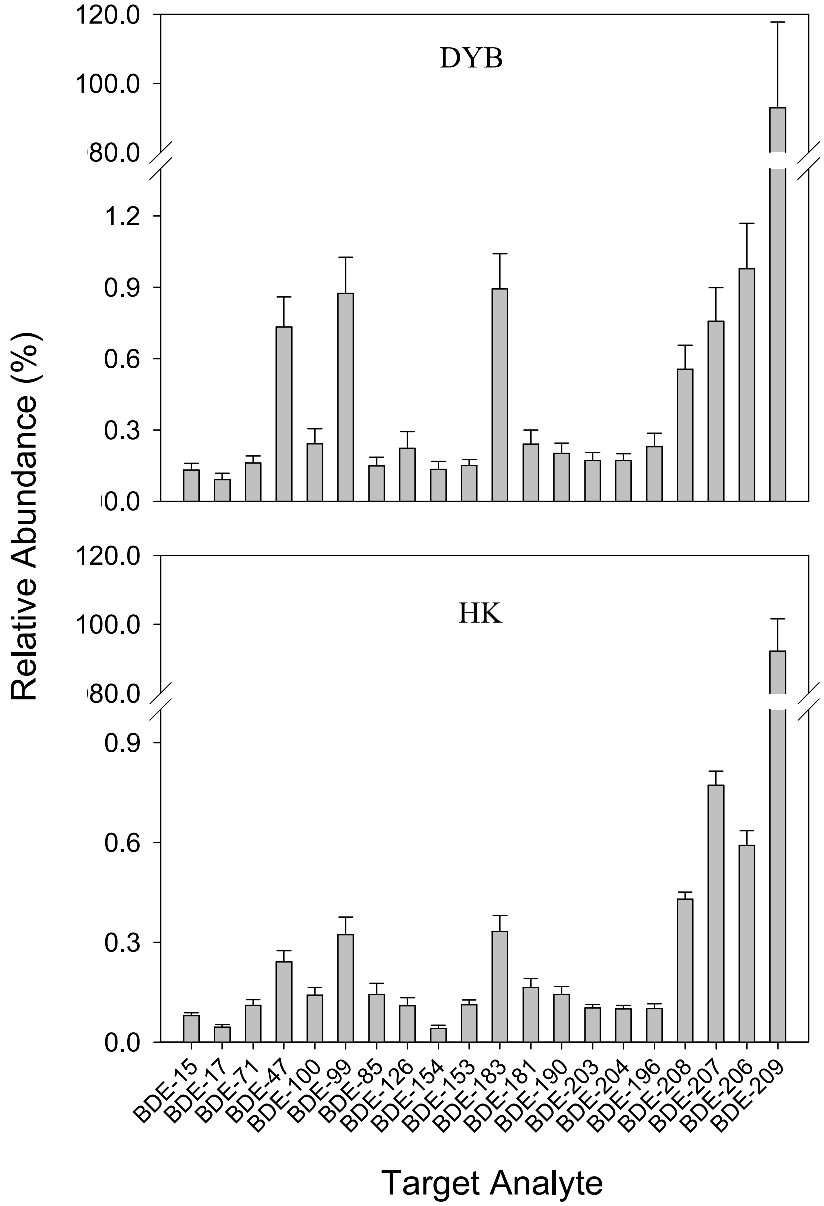


Figure S7. Relative abundances of individual BDE in surface sediment collected from Daya Bay (DYB) and Hong Kong (HK) waters.

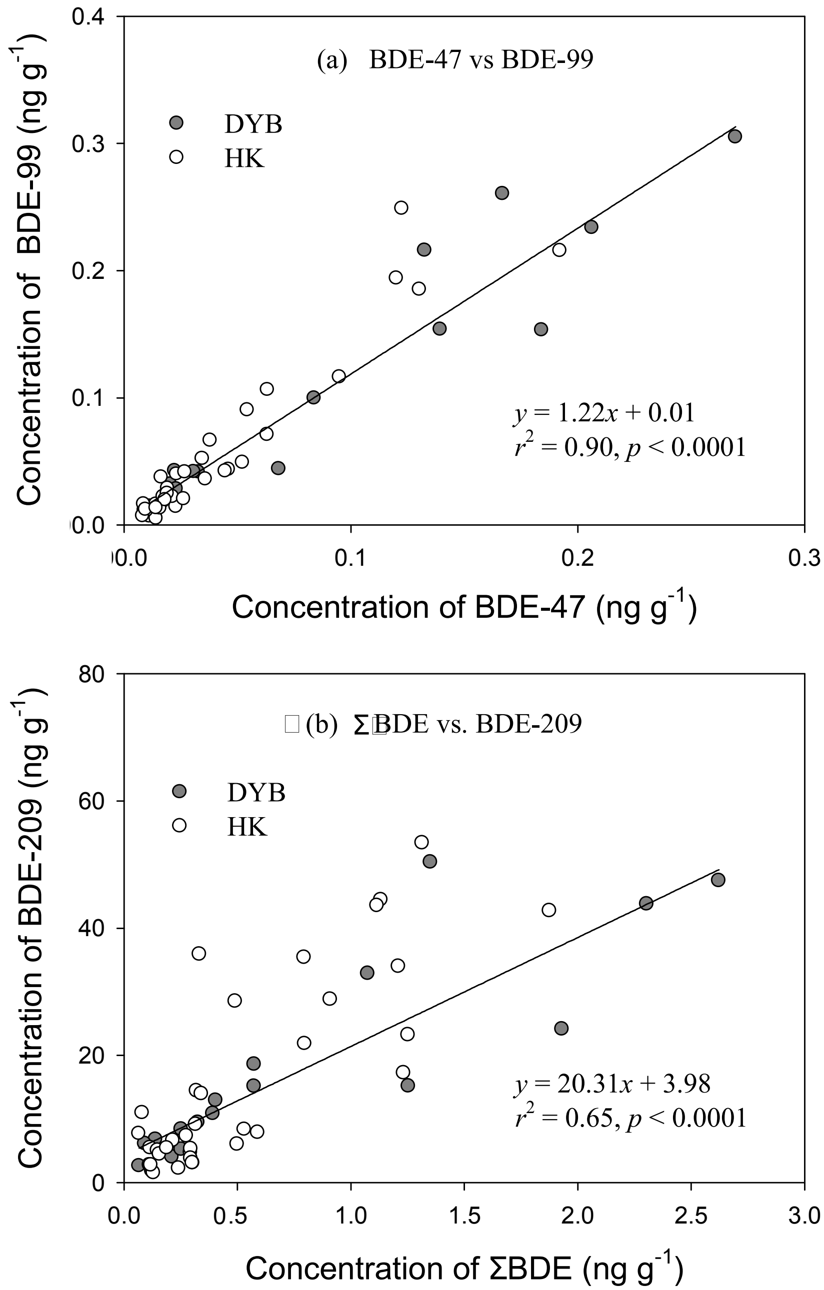
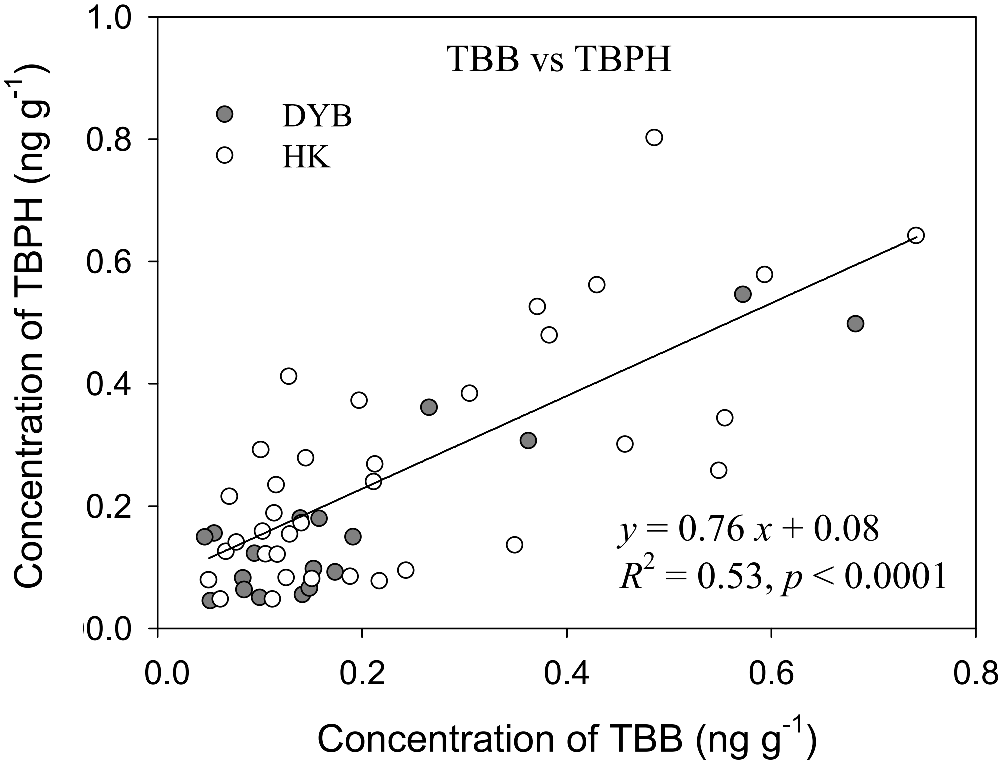


Figure S8. Correlation of the concentrations of BDE-47 and BDE-99, and the concentrations of ΣBDE and BDE-209.

283
284



285 **Figure S9.** Correlation of the concentrations of TBB and TBPH.

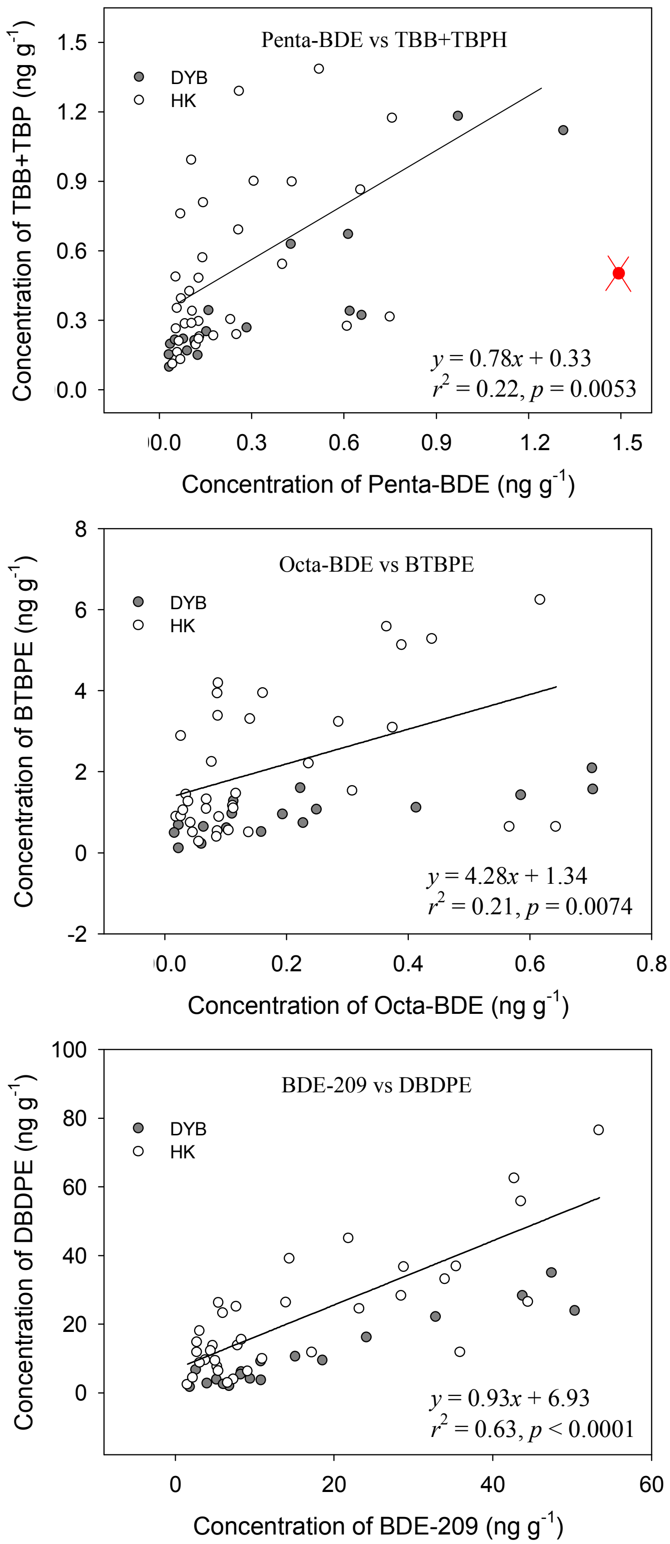


Figure S10. Correlations of the concentrations of Penta-BDE and the sum concentration of TBB and TBPH (TBB+TBPH), the concentrations of Octa-BDE and BTBPE, and the concentrations of BDE-209 and DBDPE. The red point in the first figure was deleted when fitting the linearity. Herein, BDE-71, -47, -100, -99, -85, -126, -154 and -153 were classified into Penta-BDE product, BDE-183, -181, -190, -203, -204 and -196 were classified into Octa-BDE product, and BDE-209 was classified into Deca-BDE product. BDE-15 and -17 generally have very low detection rate in these PBDE-technical products and have high background concentrations in air, the two components were not classified into any tech product. BDE-206, -207 and -208 were also not classified, because they may come from the Octa-BDE tech product, and also may be the degradation products of BDE-209 in environment.

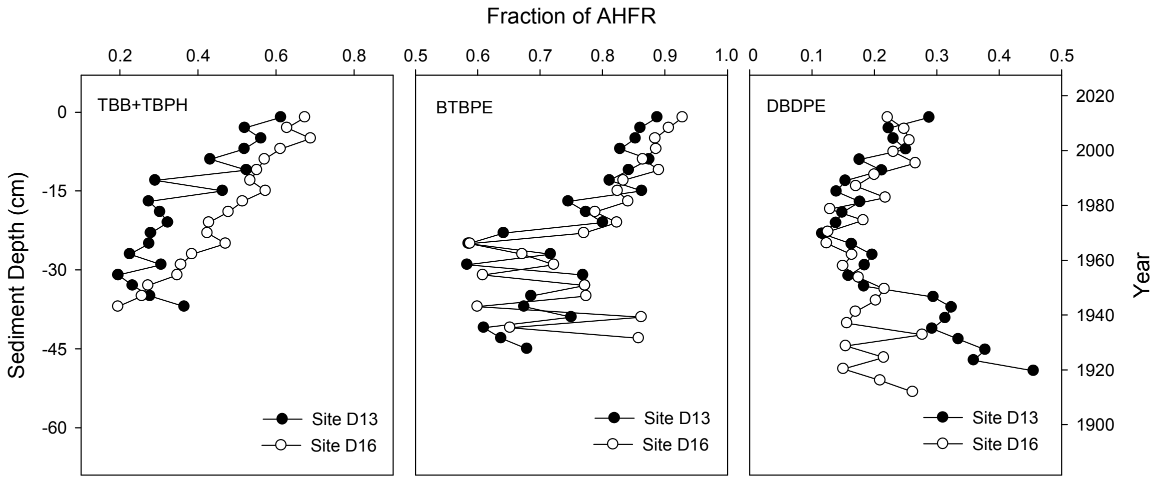


Figure S11. Vertical profiles of the fractions of [TBB+TBPH] in [TBB+TBPH+Penta-BDE], of BTBPE in [BTBPE+Octa-BDE] and of DBDPE in [DBDPE+Deca-BDE] in sediment cores collected from D13 and D16 of Daya Bay.

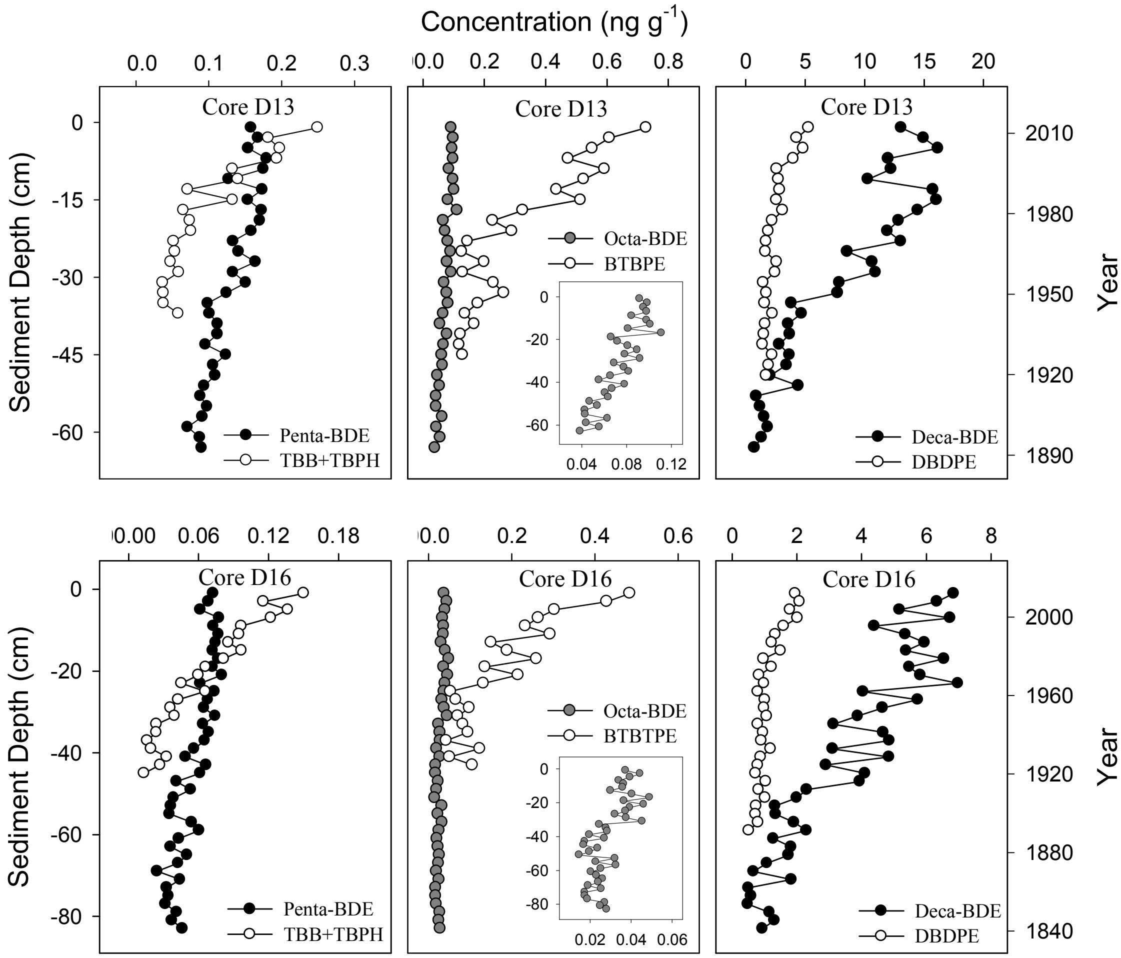


Figure S12. Vertical concentration profiles of Penta-, Octa- and Deca-BDE, the sum of TBB and TBPH (TBB+TBPH), BTBPE and DBDPE in sediment cores collected from D13 (above) and D16 (below) from Daya Bay. The classification of each BDE into three tech product was the same as that in Figure S10.

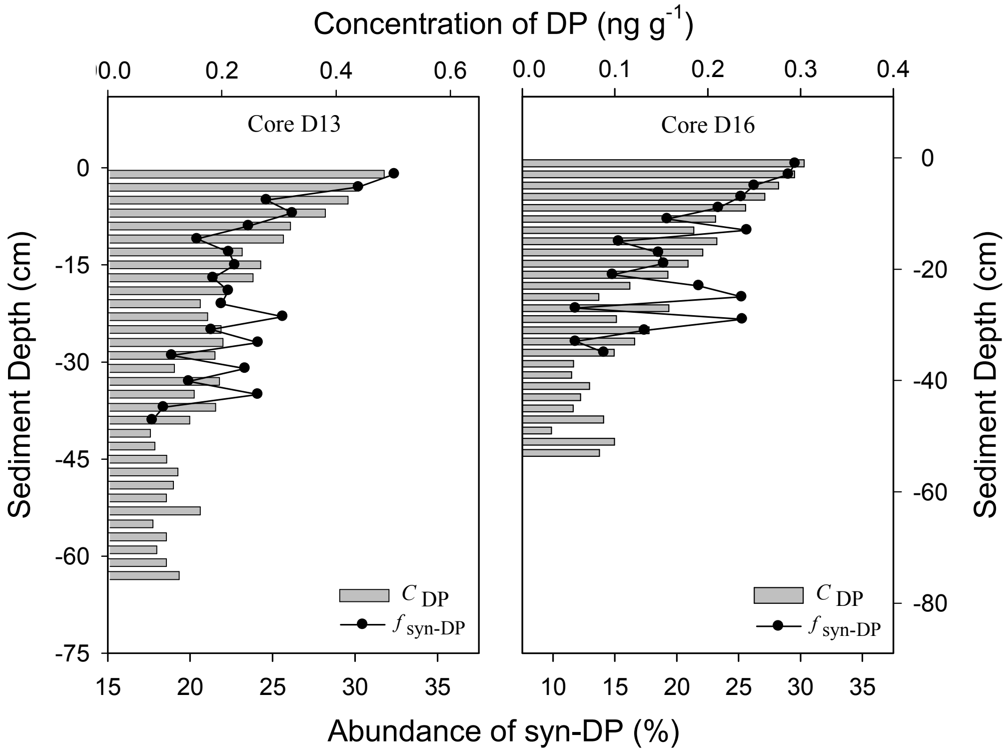


Figure S13. Vertical concentration profiles of DP (sum of anti-DP and syn-DP) and relative abundances of syn-DP in sediment cores collected from D13 and D16 of Daya Bay.

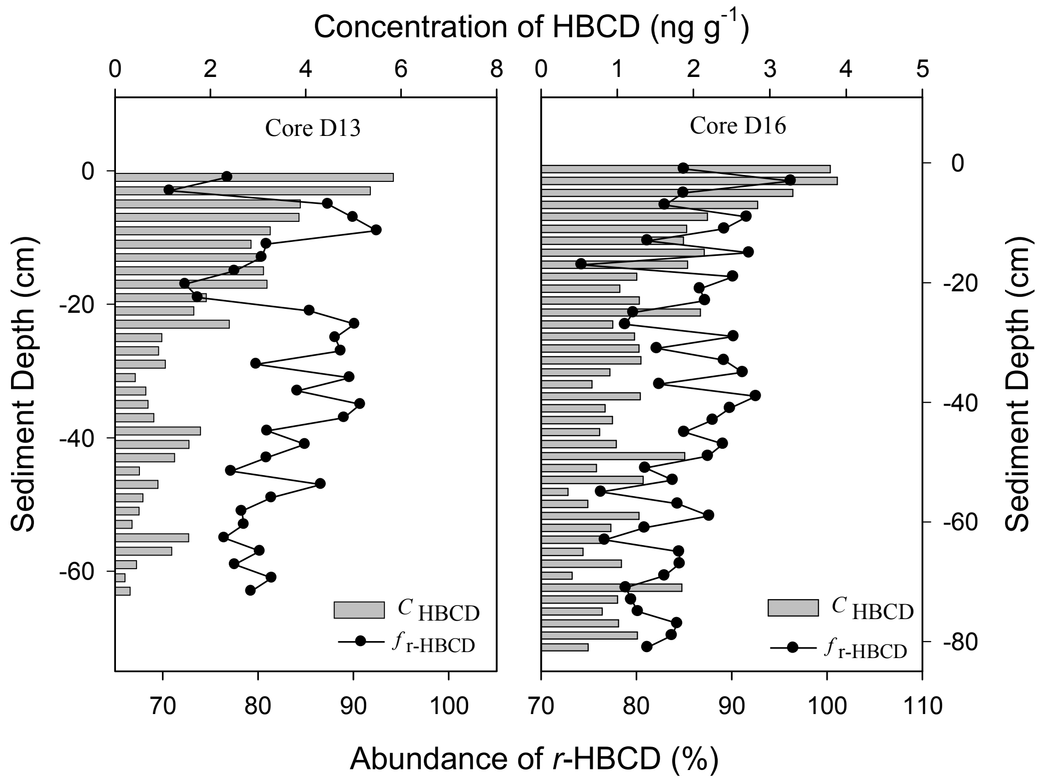


Figure S14 Vertical concentration profiles of HBCD (sum of β-HBCD and γ-HBCD) and relative abundances of γ-HBCD in sediment cores collected from D13 and D16 of Daya Bay.

References

(1)Ruan, T.; Wang, Y.; Wang, C.; Wang, P.; Fu, J.; Yin, Y.; Qu, G.; Wang, T.; Jiang, G. Identification and evaluation of a novel heterocyclic brominated flame retardant tris(2,3-dibromopropyl) isocyanurate in environmental matrices near a manufacturing plant in southern China. *Environ. Sci. Technol.* **2009,** 43 (*9*), 3080−3086.

(2)Covaci, A.; Harrad, S.; Abdallah, M. A. E.; Ali, N.; Law, R. J.; Herzke, D.; de Wit, C. A. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. *Environ. Int.* **2011,** 37 (*2*), 532−556.

(3)López, P.; Brandsma, S. A.; Leonards, P. E. G.; de Boer, J. Optimization and development of analytical methods for the determination of new brominated flame retardants and polybrominated diphenyl ethers in sediments and suspended particulate matter. *Anal. Bioanal. Chem.* **2011,** 400 (*3*), 871−883.

(4)Chu, S. G.; Haffner, G. D.; Letcher, R. J. Simultaneous determination of tetrabromobisphenol A, tetrachlorobisphenol A, bisphenol A and other halogenated analogues in sediment and sludge by high performance liquid chromatography-electrospray tandem mass spectrometry. *J. Chromatogr. A* **2005,** 1097 (*1–2*), 25−32.

(5)Kuromochi, H.; Suzuki, S.; Kawamoto, K.; Osako, M.; Sakai, S. Measurements of water solubility and 1-octanol/water partition coefficient of three hexabromocyclododecane diastereoisomers. In BFR 2010 Proceedings, April 7−9, 2010, Kyoto, Japan; pp 102−105.

(6)Yang, Y. L.; Pan, J.; Li, Y.; Yin, X. C.; Shi, L. Polychlorinated naphthalenes and polybrominated diphenylethers in near-shore sediments of Qingdao. *Chin. Sci. Bull.* **2003,** 48 (*21*), 2244−2251.

(7)Chen, S. J.; Gao, X. J.; Mai, B. X.; Chen, Z. M.; Luo, X. J.; Sheng, G. Y.; Fu, J. M.; Zeng, E. Y. Polybrominated diphenyl ethers in surface sediments of the Yangtze River Delta: Levels, distribution and potential hydrodynamic influence. *Environ. Pollut.* **2006,** 144 (*3*), 951−957.

(8)Li, A.; Rockne, K. J.; Sturchio, N.; Song, W.; Ford, J. C.; Buckley, D. R.; Mills, W. J. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 4. influencing factors, trends, and implications. *Environ. Sci. Technol.* **2006,** 40 (*24*), 7528−7534.

(9)Mai, B. X.; Chen, S. J.; Luo, X. J.; Chen, L. G.; Yang, Q. S.; Sheng, G. Y.; Peng, P. A.; Fu, J. M.; Zeng, E. Y. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environ. Sci. Technol.* **2005,** 39 (*10*), 3521−3527.

(10)Verslycke, T. A.; Vethaak, A. D.; Arijs, K.; Janssen, C. R. Flame retardants, surfactants and organotins in sediment and mysid shrimp of the Scheldt estuary (The Netherlands). *Environ. Pollut.* **2005,** 136 (*1*), 19−31.

(11)Shi, T.; Chen, S. J.; Luo, X. J.; Zhang, X. L.; Tang, C. M.; Luo, Y.; Ma, Y. J.; Wu, J. P.; Peng, X. Z.; Mai, B. X. Occurrence of brominated flame retardants other than polybrominated diphenyl ethers in environmental and biota samples from southern China. *Chemosphere* **2009,** 74 (*7*), 910−916.

(12)Zhang, X. L.; Luo, X. J.; Chen, S. J.; Wu, J. P.; Mai, B. X. Spatial distribution and vertical profile of polybrominated diphenyl ethers, tetrabromobisphenol A, and decabromodiphenylethane in river sediment from an industrialized region of South China. *Environ. Pollut.* **2009,** 157 (*6*), 1917−1923.

(13)Kierkegaard, A.; Bjorklund, J.; Friden, U. Identification of the flame retardant decabromodiphenyl ethane in the environment. *Environ. Sci. Technol.* **2004,** 38 (*12*), 3247–3253.

(14)Yang, R.; Wei, H.; Guo, J.; Li, A. Emerging brominated flame retardants in the sediment of the Great Lakes. *Environ. Sci. Technol.* **2012,** 46 (*6*), 3119–3126.

(15)Klamer, H. J. C.; Leonards, P. E. G.; Lamoree, M. H.; Villerius, L. A.; Akerman, J. E.; Bakker, J. F. A chemical and toxicological profile of Dutch North Sea surface sediments. *Chemosphere* **2005,** 58 (*11*), 1579–1587.

(16)Evenset, A.; Christensen, G. N.; Carroll, J.; Zaborska, A.; Berger, U.; Herzke, D.; Gregor, D. Historical trends in persistent organic pollutants and metals recorded in sediment from Lake Ellasjøen, Bjørnøya, Norwegian Arctic. *Environ. Pollut.* **2007,** 146 (*1*), 196–205.

(17)Tlustos, C.; McHugh, B.; Pratt, I.; Tyrrell, L.; McGovern, E. Investigation into levels of dioxins, furans, polychlorinated biphenyls and brominated flame retardants in fishery produce in Ireland. *Mar. Environ. Health Ser.* **2007,** 26 (*1*), 1–32.

(18)Harrad, S.; Abdallah, M. A.; Rose, N. L.; Turner, S. D.; Davidson, T. A. Current-use brominated flame retardants in water, sediment, and fish from English lakes. *Environmental Science & Technology* **2009,** 43 (*24*), 9077–9083.

(19)Morris, S.; Allchin, C. R.; Zegers, B. N.; Haftka, J. J. H.; Boon, J. P.; Belpaire, C.; Leonards, P. E. G.; Van Leeuwen, S. P. J.; De Boer, J. Distributon and fate of HBCD and TBBPA brominated flame retardants in north sea estuaries and aquatic food webs. *Environ. Sci. Technol.* **2004,** 38 (*21*), 5497–5504.

(20)Qiu, X.; Marvin, C. H.; Hites, R. A. Dechlorane plus and other flame retardants in a sediment core from Lake Ontario. *Environ. Sci. Technol.* **2007,** 41 (*17*), 6014–6019.

(21)Hoh, E.; Zhu, L.; Hites, R. A. Dechlorane plus, a chlorinated flame retardant, in the Great Lakes. *Environ. Sci. Technol.* **2006,** 40 (*4*), 1184–1189.

(22)Tomy, G. T.; Pleskach, K.; Ismail, N.; Whittle, D. M.; Helm, P. A.; Sverko, E.; Zaruk, D.; Marvin, C. H. Isomers of dechlorane plus in Lake Winnipeg and Lake Ontario food webs. *Environ. Sci. Technol.* **2007,** 41 (*7*), 2249–2254.

(23)Sverko, E.; Tomy, G. T.; Marvin, C. H.; Zaruk, D.; Reiner, E.; Helm, P. A.; Hill, B.; Mccarry, B. E. Dechlorane plus levels in sediment of the lower Great Lakes. *Environ. Sci. Technol.* **2008,** 42 (*2*), 361–366.

(24)Qi, H.; Liu, L. Y.; Jia, H. L.; Li, Y. F.; Ren, N. Q.; You, H.; Shi, X. Y.; Fan, L. L.; Ding, Y. S. Dechlorane plus in surficial water and sediment in a northeastern Chinese river. *Environ. Sci. Technol.* **2010,** 44 (*7*), 2305–2308.

(25)Zhao, Z.; Zhong, G.; Moller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R.; Tang, J.; Zhang, G. Levels and distribution of dechlorane plus in coastal sediments of the Yellow Sea, North China. *Chemosphere* **2011,** 83 (*7*), 984–990.

(26)Wang, D. G.; Yang, M.; Qi, H.; Sverko, E.; Ma, W. L.; Li, Y. F.; Alaee, M.; Reiner, E. J.; Shen, L. An Asia-specific source of dechlorane plus: concentration, isomer profiles, and other related compounds. *Environ. Sci. Technol.* **2010,** 44 (*17*), 6608–6613.

(27)Hyötyläinen, T.; Hartonen, K.; Säynädjoki, K.; Riekkola, M. L. Pressurised hot-water extraction of brominated flame retardants in sediment samples. *Chromatographia* **2001,** 53 (*5–6*), 301–305.

(28)Area and population in each administrative district of Hong Kong. http://www.quhua.net/hongkong/238.html. (accessed October 10, 2013).

(29)Census and Statistics Department, Hong Kong Special Administrative Region. The profile of Hong Kong population analysed by district council district, 2012. http://www.statistics.gov.hk/pub/B71306FB2013XXXXB0100.pdf. (accessed October 30, 2013). *Hong Kong Monthly Digest of Statistics*, June 2013.

(30)La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.* **2006,** 40 (*20*), 6247−6254.

(31)Statistics Bureau of Guangdong Province. Huizhou Statistics Information Network. http://www.hzsin.gov.cn/hz09type.asp?typeID=16. (accessed October 1, 2013).