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Polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and dibenzofurans in marine and lacustrine sediments from the Shandong Peninsula, China

Jing Pan[a], Yongliang Yang[a,*], Cunzhen Geng[b], L.W.Y. Yeung[c], Xinde Cao[d], Tianyou Dai[e]

[a] National Research Center for Geoanalysis, Key Laboratory of Eco-geochemistry, Chinese Academy of Geological Sciences (CAGS), Beijing 100037, People's Republic of China
[b] College of Chemical and Environmental Engineering, Qingdao University, Qingdao 266071, People's Republic of China
[c] Centre for Coastal Pollution and Conservation, Department of Biology and Chemistry, City University of Hong Kong, People's Republic of China
[d] School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China
[e] Chinese Research Academy of Environment Sciences, Beijing 100012, People's Republic of China

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ABSTRACT

Concentrations of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in sediments from Bohai Sea and Yellow Sea coastal waters and lakes in Shandong Peninsula were determined. The total PCB concentrations of the measured 50 congeners ($\sum$50PCBs) in the sediments ranged from 273.7 to 644.5 pg g^{-1} dw (dry weight). The PCB congener profiles in the lacustrine sediments were different from those in the marine sediments. TriCBs and TetraCBs were the dominant homologues in marine sediments, whereas in the sediments from the Nansi Lakes, contributions of PCB homologues were similar. The total concentrations of 2,3,7,8-PCDD/Fs ranged from 6.2 to 27.4 pg g^{-1} dw. The congener profiles of 2,3,7,8-sustituted PCDD/Fs for the sediments were generally similar for both the lakes and the coastal sea areas in Shandong Peninsula. They were characterized by high OCDD, followed by 1,2,3,4,6,7,8-HpCDD and OCDF. The congener profiles of PCDD/Fs in the sediments were consistent with the profiles of main dominant PCDD/Fs in pentachlorophenol and sodium pentachlorophenate products in China. PCDD/F-TEQ ranged from 0.11 to 0.80 pg TEQ g^{-1} dw. The dioxin-like PCB-TEQ had concentrations ranging from 0.03 to 0.08 pg TEQ g^{-1} dw, mainly from PCB126. PCBs and PCDD/Fs concentrations found in the sediments were from background to low polluted levels.

1. Introduction

Polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are three families of global contaminants. Some dioxins have highly toxic carcinogenic, or endocrine disrupting effects [1]. The most toxic member of these families, 2,3,7,8-TCDD is known to have potential health effects at very low doses [2]. Concentrations of 17 PCDD/F congeners substituted with chlorines at 2, 3, 7, 8 positions of benzene rings are routinely converted to TCDD equivalents (TEQs) using the World Health Organization (WHO) toxic equivalency factors (TEFs) [3,4]. The WHO has identified 12 PCBs including 4 non-*ortho* (IUPAC Nos. 77, 81, 126 and 169) and 8 mono-*ortho* (IUPAC Nos. 105, 114, 118, 123, 156, 157, 167 and 189) as dioxin-like PCBs that could have similar toxicity to PCDD/Fs [5]. The 7 PCB congeners (IUPAC Nos. 28, 52, 101, 118, 138, 153 and 180) belong to the US EPA priority pollutants in the environment [6].

PCDD/Fs can be released to the environment either as impurities of chemical products or by-products of incomplete combustion processes. The sources of PCBs are coming from commercial products as coolants and insulators in transformers and capacitors in electrical industries and as anti-corrosion materials as well as in effluents from paper mills, chloralkali industry and products of combustion processes [7]. Sediments become the sinks of PCDD/Fs and PCBs due to their lipophilic property and easy adsorptions on particulate materials [8]. PCDD/Fs and PCBs can be taken up by aquatic biological species and transferred through food chains and deposited by sedimentation processes.

Compared with Western Europe, Japan and the United States, relatively few studies on PCDD/Fs and dioxin-like PCBs in sediments from lakes and coastal seas have been reported in China, especially in northern China. Most studies focused on the large lakes in southern China, such as Dongting Lake and Taihu Lake in which sediments might be affected by pentachlorophenol (PCP) and sodium pentachlorophenate (Na-PCP) since it had been widely used during the period of 1960s–1990s to control snail-borne schistosomiasis in South China [9,10]. High concentrations of OCDD, followed by much less OCDF, and 1,2,3,4,6,7,8-HpCDD were found in PCP and Na-PCP samples [9–13]. In the present study, four areas were

* Corresponding author. Tel.: +86 10 6899 9582; fax: +86 10 6832 0365.
E-mail addresses: ylyang2003@yahoo.com.cn, ylyang2003@163.com (Y. Yang).

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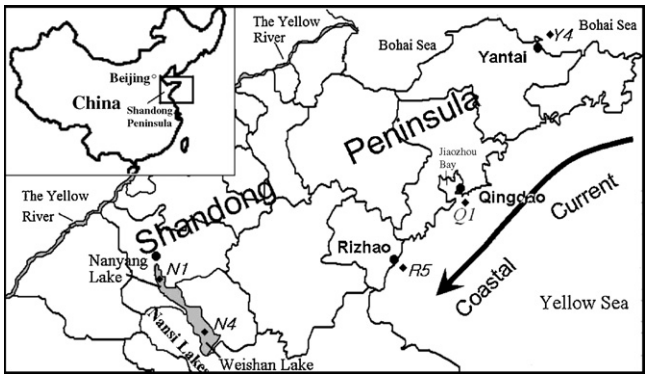

Fig. 1. Sampling locations in the Nansi Lakes (N1 and N4), the coastal waters of the Bohai Sea (Y4) and the Yellow Sea (Q1 and R5). The arrow shows the Yellow Sea Coastal Current.

chosen, including the Nansi Lakes in the southwest of Shandong Peninsula, the coastal seas in Yantai (the Bohai Sea), Qingdao, and Rizhao (the Yellow Sea) (Fig. 1). The Nansi Lakes are well-known river-originated shallow-water lakes in northern China. It is formed by four connected lakes (i.e., from north to south, Nanyang Lake, Zhaoyang Lake, Dushan Lake, and Weishan Lake). The Nansi Lakes are the relay in the eastern network of the "Southern Water to North China Project" which is based on the Grand Canal linking Beijing and southeastern China.

The objectives of the present study were to measure and compare the concentrations of PCBs, PCDD/Fs, WHO-TEQ in marine and lacustrine sediments in Shandong Peninsula to understand the background pollution levels of these contaminants in North China, and to evaluate the possible sources of these contaminants to the regions.

2. Materials and methods

2.1. Sample collection

Surface sediment samples were collected using a grab sampler in Yantai, Rizhao and Qingdao coastal seas, and the north (Nanyang Lake) and the south (Weishan Lake) of the Nansi Lakes (Fig. 1). The sampling locations are shown in Fig. 1 (Q1—Qingdao coastal sea: 35°58.62′N, 120°27.13′E, water depth: 9 m; R5—Rizhao coastal sea: 35°27.31′N, 119°58.82′E, water depth: 10 m; Y4—Yantai coastal sea: 37°06.08′N, 121°27.57′E, water depth: 9 m; N1—Nanyang Lake: 35°04.43′N, 116°43.19′E, water depth: 1.3 m; and N4—Weishan Lake: 34°38.47′N, 117°16.00′E, water depth: 1.5 m). The selection of sampling sites avoided the navigation routes to ensure the samples were not disturbed due to marine traffic. Immediately after collection, samples were stored in a freezer at −20 °C.

2.2. Chemical analysis

All the reagents used were of HPLC grade: silica gel 60 (0.063–0.200 mm, Merck Co.); anhydrous sodium sulfate (79%, Sigma Co.); alumina (Alumina B–Super I, ICN Biomedicals Co., Germany); Bio-Beads S-X3 (200–400 mesh, Bio-Rad Co.). PCDD/Fs standards and ^{13}C isotope labeled PCDD/Fs and PCBs internal standards were all from Cambridge Isotope Laboratory, USA. The total organic carbon (TOC) of sediment samples was measured by a TOC/TN analyzer (multi-N/C 2000, Analytik Jena AG, Germany).The extractions were performed in Lancaster University, UK and the method details have been previously reported [14]. Briefly, 5 g of freeze-dried samples were weighed and spiked with ^{13}C-labeled PCDD/Fs and PCB internal standards and was Soxhlet-extracted with toluene. After extraction the solution was evaporated and passed through a multi-layer silica gel column, followed by a gel permeable column. The target analytes were further fractionated using an alumina column. PCBs were eluted by 12 mL of 7% DCM–hexane solution, and dioxin-like PCBs were eluted with 6 mL of toluene. Finally, PCDD/Fs were eluted with 30 mL of 1:1 DCM/hexane solution. All the eluants were concentrated to 0.5 mL and the solution was micro-concentrated to 25 μL after adding $^{37}Cl_4$-TCDD injection standard for instrumental analysis.

2.3. Instrumental analysis

PCDD/Fs and dioxin-like PCBs were analyzed by using a HP-6890 high-resolution gas chromatograph coupled with VG AUTOSPEC PLUS high-resolution mass spectrometer. The column was DB-5 MS (60 m × 0.25 mm × 0.1 μm). The measurement was under constant pressure mode with 10 psi. The injection inlet temperature was 280 °C. The GC column temperature program for dioxin-like PCBs and PCDD/Fs was from 110 to 240 °C at a rate of 20 °C min^{-1} and then to 300 °C at 10 °C min^{-1} with a final hold time of 5 min. The ion source temperature was 280 °C. The HRMS was operated in an electron impact (EI) and selected ion monitoring (SIM) mode at resolution R > 10,000 (10% valley). Other PCBs were determined by gas chromatography coupled with electron impact mass spectrometry (GC–EI-MS, Fisons MD-800) using a DB-5MS column (30 m × 0.25 mm × 0.25 μm).

Qualification was carried out using retention times and mass ratios. The retention time of a component peak should be exactly equal to that of corresponding standard, and the mass ratio between the two single ions of a compound was within 0.8–1.0. Quantification was carried out directly using each ^{13}C-labeled internal standard. As there were no corresponding ^{13}C-labeled internal standard for each PCB isomers, the isomers belonging to the same chlorine-substituted PCB homologues were quantified by the corresponding ^{13}C-labeled internal standard (e.g. ^{13}C-PCB28 for TriCBs, and ^{13}C-PCB52 for TetraCBs). Chlorine natural isotope abundant ratios were used for supervision of congeners in PCB and PCDD/F measurement. All the results were corrected for blanks. The recoveries were in the range of 39.2–93.8% (mean 79.6%), 40.7–93.8% (mean 73.2%) and the blank were <0.39, <15.0 pg g^{-1} for PCDD/Fs and PCBs, respectively.

3. Results and discussion

3.1. PCB concentrations and homologue profiles

The concentrations of individual and total PCBs detected in the sediments are summarized in Table 1. The total PCB concentrations of the measured 50 congeners ($\sum$50PCBs) in the sediment samples ranged from 273.7 to 644.5 pg g^{-1} dry weight (dw). The highest concentration of $\sum$50PCBs was observed at the sampling site N4 at Weishan Lake, which is connected to the Great Canal in the south. The $\sum$50PCBs concentrations in the sediments were in the order of Nansi Lakes (N1 and N4) > Yantai (Y4) > Qingdao (Q1) > Rizhao (R5), suggesting that PCB levels decreased from inland to the Bohai Sea coastal water, and the lowest was in the Yellow Sea coastal waters of the Shandong Peninsula.

$\sum$50PCBs in both the northern (N1) and southern (N4) Nansi Lakes sediments were similar (631.5 and 644.5 pg g^{-1} dw, respectively), whereas those in the marine sediments were lower (347.6, 273.7 and 367.9 pg g^{-1} dw for Q1, R5 and Y4, respectively). The PCB congeners at higher levels were the EPA priority "standard" individual congeners (PCB28, 52, 101, 118, 138, 153 and 180). PCB28 was the highest PCB congener detected in all samples. $\sum$7PCBs (PCB28,

Table 1
Concentrations of PCBs in the marine and lacustrine sediments from the Shandong Peninsula (pg g^{-1} dw).

IUPAC no.	Q1	R5	Y4	N1	N4
77	3.6	2.8	20.0	7.0	4.8
81	0.11	0.12	0.06	0.29	0.20
126	0.27	0.71	0.48	0.46	0.54
169	0.09	0.26	0.08	0.14	0.21
105	9.2	5.9	3.8	15.9	10.9
114	n.d.	n.d.	n.d.	n.d.	n.d.
118	13.4	11.5	7.5	30.6	24.7
123	4.3	n.d.	n.d.	n.d.	n.d.
156	n.d.	n.d.	n.d.	n.d.	n.d.
157	n.d.	n.d.	n.d.	n.d.	n.d.
167	n.d.	n.d.	n.d.	n.d.	n.d.
189	n.d.	n.d.	n.d.	n.d.	n.d.
18	27.0	19.7	39.0	23.9	22.5
22	20.5	13.2	23.5	16.3	13.8
28	45.3	32.1	58.2	53.6	49.0
31	37.7	23.5	33.3	32.7	34.1
∑TriCBs	130.4	88.5	154.1	126.5	119.4
41/64	17.6	10.3	18.4	25.4	17.9
44	12.9	8.7	11.0	20.5	14.4
49	10.5	6.8	10.0	18.5	13.2
52	15.0	10.0	12.5	31.7	21.6
60/56	18.1	12.3	12.4	25.0	17.2
70	18.1	12.4	42.0	30.1	17.2
74	10.8	8.0	8.7	18.5	13.1
∑TetraCBs	102.9	68.5	114.9	169.7	114.5
87	6.9	4.5	3.1	18.5	10.7
90/101	9.5	7.6	6.6	25.0	25.4
95	7.8	5.7	5.7	15.3	17.9
99	3.5	4.3	3.2	16.7	13.0
110	12.8	11.3	7.7	30.9	29.0
∑PeCBs	40.4	33.4	26.3	106.4	95.9
132	n.d.	4.0	1.7	10.4	6.3
138	16.4	14.9	9.6	31.3	44.7
141	n.d.	n.d.	2.5	2.9	2.6
149	6.9	6.7	6.5	17.9	26.2
151	n.d.	n.d.	n.d.	5.7	10.0
153	14.1	9.7	8.4	26.0	41.1
158	n.d.	n.d.	n.d.	1.9	2.4
∑HxCBs	37.4	35.3	28.6	96.0	133.1
170	n.d.	4.6	2.5	11.3	21.3
174	n.d.	3.7	1.8	9.4	16.3
180	5.5	7.8	3.9	25.0	44.6
183	n.d.	1.4	0.7	4.8	7.5
187	n.d.	3.8	3.1	12.2	21.3
∑HpCBs	5.5	21.3	12.0	62.8	110.9
194	n.d.	2.8	n.d.	8.0	13.7
203	n.d.	2.8	n.d.	7.7	15.6
∑OctaCBs	n.d.	5.6	n.d.	15.7	29.3
∑PCBs	347.6	273.7	367.9	631.5	644.5
∑7PCBs	119.2	93.6	106.7	223.2	251.1
∑Dioxin-like PCBs	30.9	21.3	32.0	54.4	41.4
Dioxin-like PCB-TEQ	0.03	0.08	0.05	0.05	0.06
TOC (%)	0.41	0.72	0.44	5.17	2.28
∑7PCBs (pg g^{-1} TOC)	85,827	37,783	83,363	12,208	28,293

n.d.: not detected.

52, 101, 118, 138, 153 and 180) from the 5 sediments in the present study are in the range of 88–117 pg g^{-1} dw.

Reports on PCB concentrations in sediments samples from lakes in North China are scarce. In comparison, our data for Nansi Lakes were lower than those in surface sediments of Taihu Lake (∑19PCBs: 890–29,700 pg g^{-1} dw) [9] and urban lake sediments from Wuhan city (∑39PCBs: 900–46,000 pg g^{-1} dw) in South China [15]. In Lake Ontario in North America, the average ∑7PCBs concentration in sediment was 64,600 pg g^{-1} dw [16,17]. The less industrial activities in the vicinity of Nansi Lakes might result in low PCB level when compared with those previous studies.

Our data on marine sediment samples were lower than those in surface sediments in Jiaozhou Bay, the Yellow Sea (∑50PCBs: 646–32,920 pg g^{-1} dw and ∑7PCBs: 178–9031 pg g^{-1} dw) [18]. ∑27PCBs concentrations in the surface sediments of the southern Yellow Sea were reported as 518–5850 pg g^{-1}, with average value of 1720 pg g^{-1} [19]. The ∑12PCBs in sediment of Bohai Bay was reported as 340–35,000 pg g^{-1} dw (average 4400 pg g^{-1} dw) [20]. Through the above comparisons with the nearby marine sediments, it is apparent that the PCB levels in coastal marine sediments of Shandong Peninsula were comparatively low, while significant differences between the sediments in the bay areas and in the open seas were found.

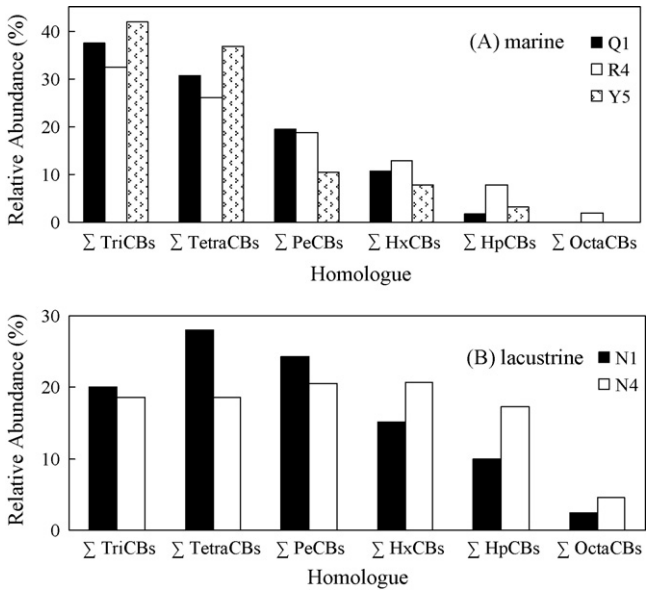

Fig. 2. PCB homologue profiles in (A) marine sediments (Q1, R4, and Y5) and (B) lacustrine sediments (N1, N4).

The total concentrations of dioxin-like PCBs in N1 and N4 were similar (54.4 and 41.4 pg g^{-1} dw, respectively), whereas those in Q1, R5 and Y4 were lower (30.9, 21.3 and 32.0 pg g^{-1} dw, respectively). The results suggested that dioxin-like PCBs in sediments from the lakes were higher than those in the coastal sea sediments of the Shandong Peninsula. Except for Y4 site, the concentrations of mono-*ortho* PCBs were higher than those of the non-*ortho* PCBs that dominated by PCB118 and PCB105. In the case of non-*ortho* PCBs, PCB77 was the dominant congener.

The homologues of PCBs in the marine sediments were also different from those of the lakes (Fig. 2). Locations Q1, R5 and Y4 were dominated by lower chlorinated PCBs. The TriCBs contributed to ∑PCBs in these samples were in the range of 32.3–41.9% and the TetraCBs had contributions ranging from 26.1% to 36.7%. In comparison, in the Nansi Lakes the TriCBs (18.5–20.0%), TetraCBs (18.6–28.0%), PeCBs (20.5–24.3%), HxCBs (15.2–20.7%) and HpCBs (9.9–17.2%) had similar contribution, suggesting that PCBs in the coastal seas and the lakes might originate from different sources.

3.2. PCDD/F concentrations and congener profiles

Concentrations of the total PCDD/Fs (∑PCDD/Fs) and 2,3,7,8-substituted PCDD/Fs congeners (∑2,3,7,8-PCDD/Fs) for the 5 sampling sites are summarized in Table 2. ∑PCDD/Fs varied from 47.7 to 147.0 pg g^{-1} dw and ∑2,3,7,8-PCDD/Fs ranged from 6.2 to 27.4 pg g^{-1} dw.

Limited number of reports on PCDD/F concentrations in sediments samples from both lakes and coastal seas were available in China [13,21]. In comparison, our data for the Nansi Lakes were lower than those in surface sediments of Taihu Lake (∑2,3,7,8-PCDD/F: 120.1–1315.1 pg g^{-1} dw [9] and Jiaozhou Bay

Table 2
Concentrations of PCDD/Fs in the marine and lacustrine sediments from the Shandong Peninsula (pg g^{-1} dw).

IUPAC no.	Q1	R5	Y4	N1	N4
2,3,7,8-TCDF	0.37	0.67	0.15	0.55	1.3
1,2,3,7,8-PeCDF	0.29	0.60	0.14	0.24	0.73
2,3,4,7,8-PeCDF	0.22	0.22	0.03	0.17	0.49
1,2,3,4,7,8-HxCDF	0.31	1.01	0.14	0.2	0.51
1,2,3,6,7,8-HxCDF	0.27	0.45	0.07	0.29	0.60
2,3,4,6,7,8-HxCDF	0.11	0.23	0.08	0.22	0.15
1,2,3,7,8,9-HxCDF	0.11	n.d.	n.d.	0.05	0.04
1,2,3,4,6,7,8-HpCDF	1.00	2.41	0.48	n.d.	2.86
1,2,3,4,7,8,9-HpCDF	0.17	n.d.	n.d.	0.11	0.21
OCDF	1.82	1.90	0.49	1.11	n.d.
2,3,7,8-TCDD	0.04	0.03	0.01	0.02	0.06
1,2,3,7,8-PeCDD	0.23	0.17	0.01	0.09	0.10
1,2,3,4,7,8-HxCDD	0.17	0.10	0.01	0.08	0.08
1,2,3,6,7,8-HxCDD	0.15	0.29	0.05	0.09	0.13
1,2,3,7,8,9-HxCDD	0.25	0.50	0.12	0.21	0.30
1,2,3,4,6,7,8-HpCDD	0.84	2.63	0.46	0.92	1.56
OCDD	5.55	16.2	3.95	9.24	14.2
$\sum$2,3,7,8-PCDD/Fs	11.9	27.4	6.2	13.6	23.4
$\sum$PCDD/Fs	47.7	141.0	77.8	109.1	147.0
PCDD/F-TEQ	0.59	0.72	0.11	0.39	0.80
$\sum$TEQ	0.62	0.80	0.17	0.44	0.86
PCDD/F-TEQ/$\sum$TEQ(%)	95.0	90.5	68.9	88.0	93.1
OCDD/$\sum$2,3,7,8-PCDD/Fs(%)	46.7	59.0	63.7	68.0	60.9
$\sum$2,3,7,8-PCDD/Fs (pg g^{-1} TOC)	2938	3782	1405	263	1027

n.d.: not detected; $\sum$TEQ = PCDD/F-TEQ + dioxin-like PCB-TEQ.

($\sum$2,3,7,8-PCDD/Fs: 4.1–232 pg g^{-1} dw [11]). The concentrations of PCDD/Fs in sediment cores from Bohai Bay were reported to be 500–3500 pg g^{-1} dw [21]. The concentration range of $\sum$2,3,7,8-PCDD/F was 2.33–253 pg g^{-1} dw in sediments from the Yellow River Estuary and the Yangtze River Estuary [22]. Thus, the PCDD/Fs in sediments of the Shandong Peninsula were at a relatively low level.

Although the levels are different from site to site, the congener profiles of 2,3,7,8-sustituted PCDD/Fs for the sediments were generally similar for both the lakes and the coastal sea areas in Shandong Peninsula. They were characterized by high OCDD, followed by 1,2,3,4,6,7,8-HpCDD and OCDF. The average relative abundance of individual 2,3,7,8-sustituted PCDD/Fs in the sediments and in PCP and Na-PCP products used in China were presented in Fig. 3. The congener profiles of PCDD/Fs in the sediments were consistent with the profiles of dominant PCDD/Fs (OCDD (76%) as well as OCDF (10%) and 1,2,3,4,6,7,8-HpCDD (10%)) in PCP and PCP-Na [23] (Fig. 3).

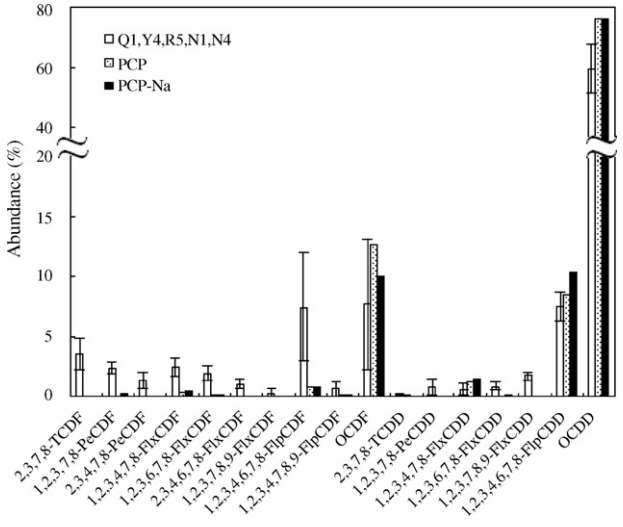

Fig. 3. The average relative abundance of 2,3,7,8-substituted PCDD/Fs in the sediments of Q1, Y4, R5, N1 and N4 and in PCP and PCP-Na reported in Ref. [23]. The error bars denote ±SD (standard deviation) of the average values.

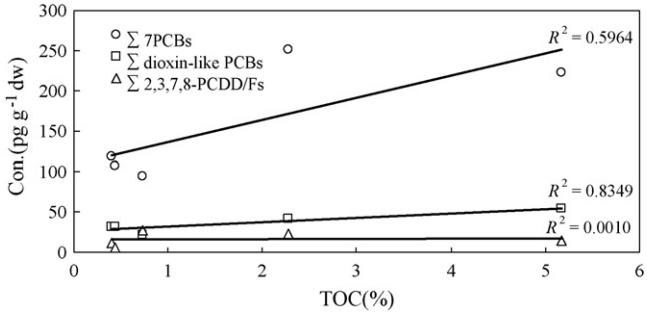

Fig. 4. Linear regression of concentrations (pg g^{-1} dw) of $\sum$7PCBs, $\sum$dioxin-like PCBs and $\sum$2,3,7,8-PCDD/Fs with total organic carbon content (TOC, %).

OCDD was predominant in sites of N1, R5 and the Bohai Sea site Y4 and contributed 68.0%, 60.9% and 63.7% to the $\sum$2,3,7,8-PCDD/Fs (Table 2). The two lake sampling sites were both at the downstream of the Grand Canal flowing from South China, where the PCP and PCP-Na have been used for three decades [24]. PCP and PCP-Na have been manufactured for nearly half a century in the industrial city Tianjin in western coast of the Bohai Sea and similar congener profiles of 2,3,7,8-sustituted PCDD/Fs for the river sediments in Tianjin and sediment cores from Bohai Bay to those in PCP and PCP-Na were reported [21,24]. This observation suggested that PCP and PCP-Na might be possible sources for the sampling sites of the present study.

3.3. TOC normalized concentrations of PCBs and PCDD/Fs

Linear regression concentrations (pg g^{-1} dw) of $\sum$7PCBs, $\sum$dioxin-like PCBs and $\sum$2,3,7,8-PCDD/Fs with total organic carbon content (TOC, %) are shown in Fig. 4. It can be seen that the concentrations of $\sum$7PCBs and $\sum$dioxin-like PCBs were positively correlated with TOC, suggesting that the PCB distribution is mainly governed by the distribution of organic particles. When the concentrations were normalized by TOC, the marine sediments showed higher $\sum$7PCBs and $\sum$dioxin-like PCBs concentration levels (mean 22,177 and 5940 pg g^{-1} TOC, respectively) than those of lake sediments (mean 7669 and 1435 pg g^{-1} TOC, respectively). These results suggested more enrichment of PCBs by the organic matter in the marine sediments than in the lake sediments.

The $\sum$2,3,7,8-PCDD/F concentrations were not correlated with TOC, suggesting that the PCDD/F distribution might not be governed by the distribution of organic particles. Just as the case of $\sum$7PCBs and $\sum$dioxin-like PCBs, the marine sediments showed higher TOC normalized $\sum$2,3,7,8-PCDD/F concentration levels (averaging 2710 pg g^{-1} TOC) than those of lake sediments (averaging 645 pg g^{-1} TOC).

3.4. TEQ contributions of dioxin-like PCBs and PCDD/Fs

Total WHO-TEQ ($\sum$TEQ = PCDD/F-TEQ + dioxin-like PCB-TEQ) values were calculated using WHO 1998-TEF for dioxin-like PCBs and PCDD/Fs [3,4]. The $\sum$TEQ levels ranged from 0.17 to 0.86 pg TEQ g^{-1} dw with a mean value of 0.52 pg TEQ g^{-1} dw (Table 2). The lowest and highest $\sum$TEQ were found from Y4 in the Bohai Sea coastal water and N4 in Weishan Lake, respectively. In comparison, the concentrations of total WHO-TEQ were 0.83–17.7 pg TEQ g^{-1} dw in sediments from Taihu Lake [9] and 0.11–1.01 pg TEQ g^{-1} dw in sediments from Yellow River Estuary and Yangtze River Estuary [22].

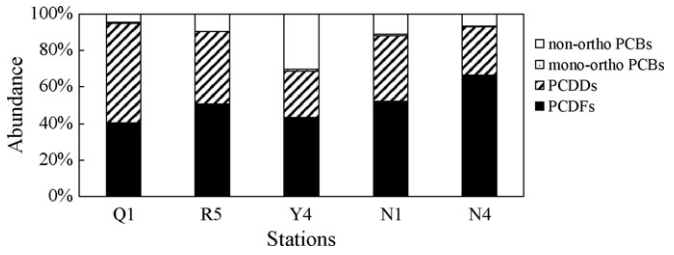

Fig. 5. The contribution of non-*ortho* PCBs, mono-*ortho* PCBs, PCDDs and PCDFs to the $\sum$TEQ.

The dioxin-like PCB-TEQ levels ranged from 0.03 to 0.08 pg TEQ g^{-1} dw. PCB126 had the highest contribution to dioxin-like PCB-TEQ (88.1–93.3%). The highest dioxin-like PCB-TEQ was observed at R5 (0.08 pg TEQ g^{-1} dw), followed by N4 (0.06 pg TEQ g^{-1} dw), N1 and Y4 (both 0.05 pg TEQ g^{-1} dw) and Q1 (0.03 pg TEQ g^{-1} dw), respectively.

The PCDD/F-TEQ concentrations were in the range of 0.11–0.80 pg TEQ g^{-1} dw. 1,2,3,7,8-PeCDD (8.71–38.9%) and 2,3,4,7,8-PeCDF (13.1–30.5%) were the dominant contribution compounds to PCDD/Fs-TEQ. The ratios of PCDD-TEQ/PCDF-TEQ ranged from 0.4 to 1.4, with a mean value of 0.8. Generally, the ratio in sewage sludge samples was more than 1.0 [25,26]. However, in the present study, only the sediment from Qingdao (Q1) presented the ratio >1.0. Our previous work on PCDD/Fs in sediments from Jiaozhou Bay in Qingdao City showed that the sewage sludge from the Haibo River was a major PCDD/F source inside Jiaozhou Bay [11].

The contributions of dioxin-like PCBs and PCDD/Fs to the $\sum$TEQ were shown in Fig. 5. The contributions of dioxin-like PCBs were similar in sediments from Yellow Sea (Q1 and R5) and the Nansi Lakes (N1 and N4). In contrast, dioxin-like PCB-TEQ in sediments from the Bohai Sea (Y4) was as high as one-third of the $\sum$TEQ. PCDD/F-TEQ has the contributions of 68.9–95.0%. The main contributions from PCDD/Fs also showed different patterns. The first two dominant congeners were 1,2,3,7,8-PeCDD (21–37%) and 2,3,4,7,8-PeCDF (14–17%) for the Yellow Sea (Q1 and R4), 2,3,7,8-TCDF (9%) and 2,3,4,7,8-PeDCF (9%) for the Bohai Sea (Y5), 1,2,3,7,8-TCDD (20%) and 2,3,4,7,8-PeCDF (19%) for Nanyang Lake, and 2,3,4,7,8-PeCDF (28%) and 2,3,7,8-TCDF (16%) for Weishan Lake, respectively.

4. Conclusions

PCDD/Fs and dioxin-like PCBs were detected in all of the 5 sampling sites, showing their ubiquity in lake and coastal sea sediments in the Shandong Peninsula. The total PCB concentrations were in the order of the Nansi Lakes > Yantai > Qingdao > Rizhao. Compared with PCB levels reported in other areas of the Bohai Sea and Yellow Sea, the PCB concentrations found in the sediments from the Nansi Lakes as well as the coastal sea areas in Shandong Peninsula were from background to low polluted levels. The PCBs in the coastal sea sediments were dominated by lower chlorinated PCBs, while in the Nansi Lakes the homologue groups were at similar levels. Total PCDD/Fs found in the sediments from Nansi Lakes and the coastal sea areas were all at low polluted levels, with the order of the Nansi Lakes > Rizhao > Yantai > Qingdao.

Contrary to the case of PCBs, homogeneity on 2,3,7,8-PCDD/Fs pattern in all sampling sites indicates same sources affecting all sampling sites. The congener profiles of 2,3,7,8-substituted PCDD/Fs for the sediments are generally similar which were characterized by predominant OCDD followed by much less 1,2,3,4,6,7,8-HpCDF and OCDF, resembling the pattern of PCDD/F congener profiles of PCP and Na-PCP products in China, suggesting that PCP and Na-PCP might be a possible source for our sampling sites.

The lowest and highest $\sum$TEQ were found to be in the sediments from the Bohai Sea coastal water and Weishan Lake, respectively. In sediments from the Nansi Lakes and the Yellow Sea coastal sites, contributions of dioxin-like PCBs to $\sum$TEQ were similar. In contrast, the dioxin-like PCBs contribution to $\sum$TEQ from the Bohai Sea sampling site was as high as one-third, suggesting a larger contamination of dioxin-like PCBs in the Bohai Sea.

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References

[1] P. Mocarelli, P. Brambilla, P.M. Gerthoux, D.G. Patterson, L.L. Needham, Change in sex ratio with exposure to dioxin, Lancet 348 (1996) 409.
[2] World Health Organization, European Centre for Environment and Health, International Programme on Chemical Safety, Assessment of the Health Risk of Dioxins: Re-evaluation of the Tolerable Daily Intake (TDI), WHO Consultation, Geneva, Switzerland, 1998.
[3] S. Safe, Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and related compounds: environmental and mechanistic considerations which support the development of toxic equivalent factors (TEFs), Crit. Rev. Toxicol. 21 (1990) 51–80.
[4] World Health Organization, Dioxins and their effects on human health, 1999 (Fact sheet no. 225).
[5] M. Berg, L. Birnbaum, A.T.C. Bosveld, B. Brunstrom, P. Cook, M. Feeley, J.P. Giesy, A. Hanberg, R. Hasegawa, S.W. Kennedy, T. Kubiak, J.C. Larsen, F.X.R. Leeuwen, A.K.D. Liem, C. Nolt, R.E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Waern, T. Zacharewski, Toxic equivalent factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife, Environ. Health Perspect. 106 (1998) 775–792.
[6] P. Jonsson, Sediment burial of PCBs in the offshore Baltic Sea, Ambio 29 (2000) 260–267.
[7] A.J. Niimi, PCBs, PCDDs and PCDFs, in: P. Carlow (Ed.), Handbook of Ecotoxicology, vol. 2, Blackwell Scientific, Oxford, 1994, pp. 35–37.
[8] H. Iwata, S. Tanabe, N. Sakai, A. Nishimura, R. Tatsukawa, Geographical distribution of persistent organochlorines in air, water, and sediments from Asia and Oceania, and their implications for global redistribution from lower latitudes, Environ. Pollut. 85 (1994) 15–33.
[9] Q.H. Zhang, G.B. Jiang, Polychlorinated dibenzo-p-dioxins/furans and polychlorinated biphenyls in sediments and aquatic organisms from the Taihu Lake, China, Chemosphere 61 (2005) 314–322.
[10] L.R. Gao, M.H. Zheng, B. Zhang, W.B. Liu, X.R. Zhao, Q.H. Zhang, Declining polychlorinated dibenzo-p-dioxins and dibenzofurans levels in the sediments from Dongting Lake in China, Chemosphere 73 (2008) S176–S179.
[11] J. Pan, Y.L. Yang, D.Z. Chen, Q. Xu, H. Tang, Y. Li, L.M. Nie, K. Jiang, D.L. Xi, Distribution characteristics and source analysis of dioxins in sediments and mussels from Qingdao coastal sea, Chemosphere 70 (2008) 1699–1706.
[12] M. Zheng, B. Zhang, Z.C. Bao, H. Yang, Analysis of PCDD/Fs from sediments of Dongting Lake in China, Organohal. Compd. 62 (2003) 190–192.
[13] M.H. Zheng, Z.C. Bao, K.O. Wang, H. Yang, X.B. Xu, Polychlorinated dibenzo-p-dioxins and dibenzofurans in lake sediments from Chinese schistosomiasis areas, Bull. Environ. Contam. Toxicol. 59 (1997) 653–656.
[14] A. Hassanin, K. Breivik, S.N. Meijer, E. Steinnes, G.O. Thomas, K.C. Jones, PBDEs in European background soils: levels and factors controlling their distribution, Environ. Sci. Technol. 38 (2004) 738–745.
[15] Z.F. Yang, Z.Y. Shen, F. Gao, Z.W. Tang, J.F. Niu, Y. He, Polychlorinated biphenyls in urban lake sediments from Wuhan, Central China: occurrence, composition, and sedimentary record, J. Environ. Qual. 38 (2009) 1441–1448.
[16] T.L. Metcalfe, C.D. Metcalfe, The trophodynamics of PCBs, including mono- and non-*ortho* congeners, in the food web of central Lake Ontario, Sci. Total Environ. 201 (1997) 245–272.
[17] H.A. Morrison, D.M. Whittle, C.D. Metcalfe, A.J. Niimi, Application of a food web bioaccumulation model for the prediction of polychlorinated biphenyl, dioxin, and furan congener concentrations in Lake Ontario aquatic biota, Can. J. Fish. Aquat. Sci. 56 (1999) 1389–1400.
[18] J. Pan, Y.L. Yang, Q. Xu, D.Z. Chen, D.L. Xi, PCBs, PCNs and PBDEs in sediments and mussels from Qingdao coastal sea in the frame of current circulations and influence of sewage sludge, Chemosphere 66 (2007) 1971–1982.

[19] P. Zhang, J.M. Song, Z.G. Liu, G.X. Zheng, N.X. Zhang, Z.P. He, PCBs and its coupling with eco-environments in Southern Yellow Sea surface sediments, Mar. Pollut. Bull. 54 (2007) 1105–1115.
[20] T. Wang, J. Huang, G. Yu, Distribution of polychlorina ted biphenyls and organochlorine pesticides in sediments of the Haihe River and Bohai Bay, J. Tsinghua Univer. (Sci. Technol.) 48 (2008) 1462–1471.
[21] J. Hu, Y. Wang, B. Shao, X. Jin, W. An, F. Jin, M. Yang, X. Wang, M. Sugisaki, Occurrence of trace organic contaminants in Bohai Bay and its adjacent Nanpaiwu River, North China, Mar. Chem. 95 (2005) 1–13.
[22] Y.M. Hui, M.H. Zheng, Z.G. Liu, L.R. Gao, PCDD/Fs and dioxin-like PCBs in sediments from yellow estuary and Yangtze estuary, China, Bull. Environ. Contam. Toxicol. 83 (4) (2009) 614–619.
[23] Z.C. Bao, K.O. Wang, J.X. Kang, L.W. Zhao, Analysis of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in pentachlorophenol and sodium pentachlorophenate, Environ. Chem. 14 (1995) 317–321 (in Chinese).
[24] H.X. Liu, Q.H. Zhang, Y.W. Wang, Z.W. Cai, G.B. Jiang, Occurrence of polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls pollution in sediments from the Haihe River and Dagu Drainage River in Tianjin City, China, Chemosphere 68 (2007) 1772–1778.
[25] E. Eljarrat, J. Caixach, J. Rivera, Effects of sewage sludges contaminated with polychlorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls on agricultural soils, Environ. Sci. Technol. 31 (1997) 2765–2771.
[26] E. Eljarrat, A. De La Cal, D. Larrazabal, B. Fabrellas, A.R. Fernandez-Alba, F. Borrull, R.M. Marce, D. Barcelo, Occurrence of polybrominated diphenylethers, polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls in coastal sediments from Spain, Environ. Pollut. 136 (2005) 493–501.