



Occurrence of trace organic contaminants in Bohai Bay and its adjacent Nanpaiwu River, North China

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Abstract

Concentrations of hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), pentachlorobenzene (penta-CB), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), coplanar polychlorinated biphenyls (co-PCBs), 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDTs, including *p,p'*-DDT; *o,p'*-DDT; *p,p'*-DDD; *o,p'*-DDD; *p,p'*-DDE; *o,p'*-DDE; *p,p'*-DDMU), nonylphenol (NP), and nonylphenol polyethoxylates (NPEOs) were measured in sedimentary cores from Bohai Bay (one core) and its adjacent river, the Nanpaiwu River (two cores), North China. While α -, β -, and γ -HCHs were detected in similar abundance in the two cores from the Nanpaiwu River, only α -HCH was detected in the Bohai Bay core, suggesting that α -HCH might be more resistant to degradation than β - or γ -HCHs. The concentrations of HCHs and HCB in the core from Bohai Bay were in the range of 0.8–140 and 9.1–1300 ng/g dry wt, respectively, whereas in the cores from the Nanpaiwu River, the maximum concentrations of HCHs and HCB reached 84,200 and 141,400 ng/g dry wt, respectively. There was a similarity of sedimentary profiles between HCHs and HCB in the three cores. The concentration of PCDDs/DFs in Bohai Bay was 0.5–3.5 ng/g dry wt [1.6–6.4 toxic equivalents (TEQ) world health organization (WHO) pg/g], far lower than the concentrations in the core samples taken from the Nanpaiwu River (the maximum concentration: 9200 ng/g dry wt; 22,000 TEQ WHO pg/g). The congener profiles of PCDD/DFs and co-PCB in the cores were similar to those in PCP, and the concentration of co-PCBs was related to that of PCDDs/DFs. In addition, the concentrations of HCH, HCB, PCDD/Fs, and co-PCB all decreased linearly relative to total organic carbon content (TOC) in surface sediment from the river to Bohai Bay. The concentration of DDTs ranged from 1.6 to 12.3 ng/g dry wt in Bohai Bay, significantly different from the profiles from the Nanpaiwu River (29.3 ng/g dry wt). An abundance of the compounds *o,p'*-DDE and *o,p'*-DDD were detected in the cores. The sedimentary profiles of NP and NPEOs were similar, and two peak concentrations of NP/NPEOs were found at the subsurface and subbottom in the core from Bohai Bay, respectively. The concentration of NP and NPEOs in the cores from the Nanpaiwu

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River were about 15 times higher than those in the core from Bohai Bay, suggesting that the Nanpaiwu River was possibly one of the sources of NP and NPEOs in Bohai Bay.

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1. Introduction

Numerous papers have highlighted the potentially detrimental reproductive effects of certain anthropogenic compounds on wildlife and humans. Organic compounds reported to disrupt normal reproductive pathways in animals include pesticides, certain polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and alkylphenols (Miyamoto and Klein, 1998). With respect to the latter, 4-nonylphenol (4-NP) is of growing concern due to its estrogenic effects on aquatic organisms (Soto et al., 1991; Jobling and Sumpter, 1993; White et al., 1994) and its prevalence in the environment (Lye et al., 1999; Thiele et al., 1997). The residual 4-NP in the aqueous environment predominantly stems from the wide use of nonylphenol polyethoxylate (NPEOs) surfactants of various ethoxylate chain lengths. While much research has focused on NP monitoring in aquatic environments, there have been few studies on the occurrence of its precursor, NPEOs with an ethoxylate length of more than 2 (Shang et al., 1999; Jonkers et al., 2003).

Organochlorine pesticides such as hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethane (DDT) and its metabolite, and hexachlorobenzene (HCB) are of global concern due to their intensive use for agricultural and industrial purposes in developing countries in the past few decades. Although the application of organochlorine pesticides has been banned in developed countries, they are still ubiquitous in marine, freshwater, and estuarine food chains (Maruyama et al., 2000; Tanabe et al., 1994; Iwata et al., 1994; Bard, 1999; Glynn et al., 1995), and have been associated with abnormal development of the reproductive system of wild animals (Simonich and Hites, 1995; Connell et al., 2003; Weber and Goerke, 1996). Another category of compounds of global concern is dioxins including co-PCB. Surveys on the status of their pollution has been carried out in sediment cores (Czuczwa and Hites, 1984; Kjeller

and Rappe, 1995; Juttner et al., 1997; Vartiainen et al., 1997; Wu et al., 1997) and indicates that dioxin pollution is now in remediation in developed countries, although sediment cores from remote lakes in Germany and Finland showed increasing trends until recent years (Vartiainen et al., 1997). The above-mentioned compounds can enter into the sea through coastal processes (riverine discharges and run-off homeland), perhaps to be stored in sediments at the seabed or diluted and dispersed across the continental shelf and beyond to the global ocean.

Although the usage of DDT, industrial HCH and HCB were banned in China in 1983, DDT (Mao, 1995) is still produced as a raw material for manufacturing of the pesticide: Dicofol (outputs of dicofol: 2000 tons). Moreover, the stock of HCHs produced before the 1980s is still used as raw material for production of pentachlorophenolic sodium (PCP), and HCB is a byproduct of PCP production, in which the concentration of dioxins (including PCDD/DFs and co-PCBs) is about 7420 ng/g dry wt (360 ngWHO-TEQ/g) (Kim, 2002). The total output of PCP pesticide was about 25.6 ktons from 1962 to 1999 in China (China chemical plant statistical data, 2000); however, information about dioxins and HCB residue in China's aqueous environment is fragmentary compared with that of DDTs and HCHs. The environmental effects and fate of NPEOs have received little attention in China, although the annual output of NPEOs reached 50 ktons in 1997, about one-tenth of the total output worldwide (Nalor, 1996).

Bohai Bay is a large, semienclosed shallow water basin located along the western region of the Bohai Sea in the northeastern part of China. Input of continental wastewater to Bohai Bay is largely from the Nanpaiwu River. This river receives industrial and municipal wastewaters from Tianjin City which has many chemical factories, including the largest DDT and PCP producer in the country. A systematic survey on inputs of the above chemical pollutants from Tianjin City to Bohai Bay has never been conducted

despite the fact that the Bohai Sea is an important fishery area in China. In this study, we report concentrations of HCHs, HCB, PCDDs, PCDFs and co-PCBs, DDTs, NP and NPEOs in three sedimentary cores, one from Bohai Bay and two from the adjacent Nanpaiwu River, to provide information on the potential source of these chemicals in Bohai Bay.

2. Materials and methods

2.1. Sampling location

Fig. 1 shows the sampling locations. The area of estuary coast around Bohai Bay is about 170,000 km², and the population is about 70 million. Approximately 87% of pollutants in Bohai Bay are discharged from land, and 95% of pollutants generated in the area are transported by rivers into Bohai Bay (Liu et al., 2003). With an area about 80,000 km² and the average water depth about 18 m, Bohai Bay is a typical inner sea located in the northeast region of China. The

Nanpaiwu River is a major source of wastewater to Bohai Bay. It receives industrial and domestic wastewater from the cities of Tianjin and Beijing, and is the most heavily polluted river in the Haihe basin. A sediment core was collected from Bohai Bay (Station C-3; N38°57', E117°44'), and two from the Nanpaiwu River (Station C-1 and C-2; N38°59', E117°39' and N38°58', E117°41', respectively) using a 2-m-long, 10-cm diameter box corer in November 2002. The cores were sliced into 5-cm-thick disks immediately after collection using a stainless steel slicer. Each section was stored at -20 °C until analysis.

2.2. Reagents

α -, β -, γ -HCH; *o,p*-DDD; *p,p*-DDD; *o,p*-DDT; *p,p*-DDT; *o,p*-DDE; and *p,p*-DDE were all purchased from Chemservice (Chester, England) and *p,p*-DDMU was from Sigma. HCB and penta-CB were purchased from Accu Standard (CT, USA). Nonylphenol mono-ethoxylate (NP₁EO), nonylphenol di-ethoxylate (NP₂EO), nonylphenol tri-ethoxy-

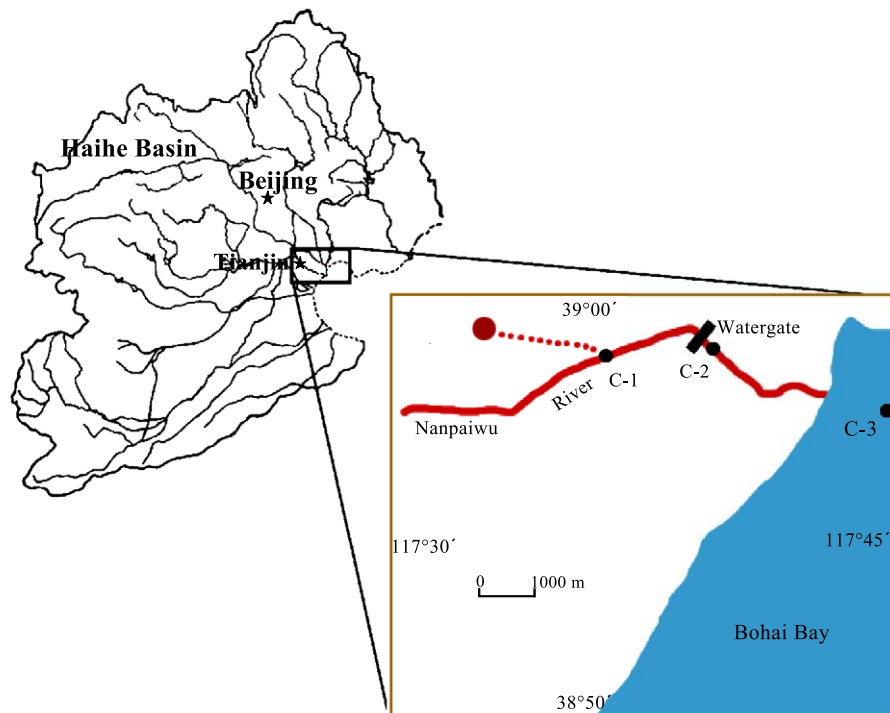


Fig. 1. Map of sampling locations. C-1: from the Nanpaiwu River, N38°59'E117°39'; C-2: from the Nanpaiwu River, N38°58'E117°41'; C-3: from Bohai Bay, N38°58'E117°44'. ●: Industrial zone;: drainage pipe.

late (NP₃EO), nonylphenol tetra-ethoxylate (NP₄EO), nonylphenol penta-ethoxylate (NP₅EO), nonylphenol hexa-ethoxylate (NP₆EO), and a mixture of NPEOs with an average of 15 EO units were obtained from Hayashi Pure Chemicals (Tokyo, Japan). PCDDs/PCDFs, co-PCBs and their internal standards were from Wellington Laboratories (Ontario, Canada).

2.3. Chemical analysis

2.3.1. HCHs, HCB, penta-CB, DDTs, NP, and NPEOs

Sediments were air-dried and 10 g dry samples (mixed with 20 g Na₂SO₄) spiked with recovery surrogate (PCB 30; IUPAC) were Soxhlet extracted for 24 h using 200 ml dichloromethane/methanol (7:3 v/v) mixture solution. Extracts were passed through 12 g 5% H₂O deactivated neutral Al₂O₃ (200 mesh size, Shanghai Ludu Chemicals, China) packed in a glass column (10 mm i.d.) for cleanup and fractionation. The first fraction eluted with 30 ml high-purity hexane, 30 ml hexane/dichloromethane (3:1 v/v) contained HCHs, DDTs, penta-HCB, and HCB. NP and NPEOs were eluted in the second fraction with 30 ml hexane/dichloromethane (50:50 v/v), 40 ml dichloromethane, and 30 ml dichloromethane/methanol (85:15 v/v), and 30 ml dichloromethane/methanol (50:50 v/v). HCHs, HCB, DDTs, and NP were determined by gas chromatography-mass spectrometers (GC-MS). And NPEOs were analyzed using an electrospray ionization-liquid chromatography-mass spectrometers (ESI-LC-MS) method (Shao et al., 2002).

GC-MS analysis was performed with a Hewlett-Packard 5890 gas chromatograph connected to a Hewlett-Packard 5971 mass spectrometer. The mass spectrometer was operated in the electron impact ionization mode with an ionizing energy of 70 eV. The injector temperature was maintained at 250 °C, and the source temperature was kept at 280 °C. An HP-5MS capillary column (30 m×0.25 mm i.d. with a film thickness of 0.25 µm) used for HCHs, HCB, DDTs analysis was programmed to increase from 50 °C (2 min) to 186 °C at 10 °C/min (keeping this temperature for 2 min), and to 235 °C at 5 °C/min, which was held for 2 min. The same capillary column for NP analysis was programmed from 50 °C (2 min) to 200 °C at 20 °C/min (keeping this temperature for 2 min), and to

260 °C at 5 °C/min. The injection volume was 2 µl, and splitless mode was used.

LC-MS was performed on an Alliance 2690 HPLC (Waters, USA) equipped with a quaternary gradient pump, an autosampler with 100 ml injection loop, a C₁₈ precolumn (2.1 mm in ID×50 mm in length, 3 mm Capcell Pak, Shiseido, Japan) and a silica analytical column (2.1 mm in ID×150 mm, 3 mm Spherisorb SW3, Waters). The flow was kept at 0.1 ml/min for 1 min with 100% acetonitrile, then increased linearly to 0.35 ml/min over 34 min. The solvent composition was changed linearly to 75% acetonitrile/25% water over 35 min, then linearly to 100% acetonitrile over 5 min, while the flow was kept at 0.35 ml/min for 10 min. Flow was then held at 0.1 ml/min for 40 min to equilibrate the columns before the next injection. A platform ZMD single-quadrupole mass spectrometry (Micromass, Manchester, UK) was used with a Z-Spray ion-source fitted with a pneumatically assisted electrospray probe. In the positive mode, typical ion source parameters were used as follows: ESI capillary voltage at 3.5 kV; extractor voltage at 5 V; source block temperature at 120 °C; desolvation temperature at 1800 °C; ion energy at 0.8 V; multiplier voltage at 650 V. Nitrogen was used as the desolvation gas with a flow rate between 270 and 350 l/h and cone gas with a rate of 70–100 l/h; the cone voltage was ramped from 25 to 70 V with the full scan mass ranging from 280 to 1500 dalton with a scan time of 1.2 s.

Dichloromethane, methanol, and hexane were HPLC grade or pesticide grade from Fisher Scientific (NJ, USA). The procedure described above was validated for recoveries (ranging from 89% to 120% for HCHs, 99% to 113% for DDTs, 92% to 105% for NPEOs, 80% for NP, and 101% for penta-CB and HCB). Percent recovery of surrogate determined in sediment was 76.3±9.7%, and concentrations reported here have not been corrected for recovery. Precision is estimated at better than 20% based on analysis of three replicate samples collected in Nanpaiwu River.

2.3.2. PCDDs, PCDFs, and co-PCBs

Sediments were air-dried and 20 g dry samples were Soxhlet extracted with toluene for 24 h. After the addition of 17 ¹³C-labeled PCDD/F and 14 ¹³C-labeled Co-PCB internal standards, the extracts were

first treated with concentrated sulfuric acid. The extract was then passed through 1 g silica gel (Wako Pure Chemical Industries, Japan) and 2 g 44% H₂SO₄ silica gel (Wako Pure Chemical Industries) packed in a glass funnel by eluting with 50 ml hexane. After being treated with activated copper, concentrated extracts were passed through 10% AgNO₃ silica gel (Wako Pure Chemical Industries) and activated carbon-impregnated silica gel (Kanto Chemical, Japan) columns. The silica gel column was packed with 2 g 10% AgNO₃ silica gel heated at 130 °C for 3.5 h, and 200 ml hexane was utilized for elution. The activated carbon-impregnated silica gel column was packed with 1 g activated carbon dispersed silica gel. This column was first eluted with 40 ml hexane and then 250 ml toluene. The last fraction was concentrated and spiked with two ¹³C-labeled PCDD/F and four ¹³C-labeled Co-PCB internal standards for high-resolution GC (Hewlett-Packard HP 6890)/high-resolution MS (JMS-700 MS Spectrometer, JEOL, Japan) analysis. CP-Si1188 (length, 60 m; inner diameter, 0.32 mm; film thickness, 0.13 μm; Chrompack) was used to separate TCDD/Fs, PCDD/Fs, and some HCDD/Fs. The column oven temperature was programmed to increase from 100 °C (1 min) to 180 °C at a rate of 20 °C/min, and then to 260 °C at a rate of 3 °C/min, which was maintained for 20 min. The congeners of HpCDD/Fs, OCDD/Fs, and some of HCDD/Fs were separated on a DB-17 capillary column coated at 0.25 μm (length, 30 m; inner diameter, 0.25 mm; J & W Scientific). The column oven temperature was: 120 °C for 2 min, 20 °C/min to 180 °C, and 4 °C/min to 300 °C, maintained for 3 min. DB-5 (length, 60 m; inner diameter, 0.25 mm; film thickness, 0.25 μm; J&W Scientific) was used to separate Co-PCBs with the same temperature program of DB-17. The mass spectrometer was operated at a resolution of more than 10,000 and in a selected ion-monitoring (SIM) mode. Both the injector and the ion source were kept at 260 °C. The electron-impact ionization energy was 38 eV and the ion current was at 500 μA. The PCDD/PCDF congeners were monitored by SIM mode at the two most intensive ions at the molecular ion cluster. Recoveries of ¹³C-labelled PCDD and PCDF congeners through the analytical procedure ranged from 70% to 110%.

2.4. Total organic carbon analysis

Dry sediment (about 5 mg) was put into small precombusted (600 °C, 4 h) quartz sample boats. Phosphoric acid (44%) was added to remove inorganic carbon in the sample. Finally, the sample was analyzed using a Total Organic Carbon (TOC) Analyzer (Apollo 9000, Tekmar-Dohrmann, USA).

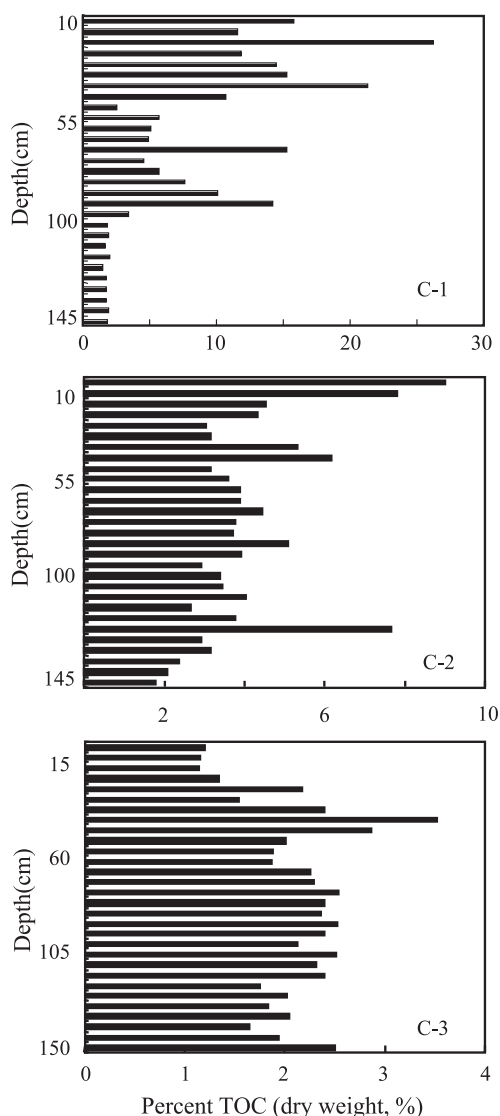


Fig. 2. Vertical profiles of TOC content (% dry wt) in sedimentary cores from Bohai Bay and its adjacent Nanpaiwu River. C-1, C-2: sedimentary cores from the Nanpaiwu River; C-3: sedimentary core from Bohai Bay.

3. Results and discussion

3.1. HCHs, HCB, and penta-CB

Fig. 2 shows the vertical profiles of TOC in the three sediment cores and Fig. 3 shows the vertical profiles of total HCHs, HCB, and penta-CB. The concentrations of HCH, HCB in three cores are much higher than those reported by Khim et al. (1999) in Masan Bay, Korea. This may be due to a direct

discharge of wastewater from PCP manufacturing plant where HCH is the raw material and HCB is an intermediate into Bohai Bay through Nanpaiwu River, while there is little farming activity around Masan Bay and OC pesticide use was banned in Korea in the 1970s. Of three HCHs (α -, β -, and γ -HCH), only α -HCH was detected in all sections of core C-3 from Bohai Bay. In this core, the highest concentration was 140 ng/g dry wt at a depth of 65 to 70 cm followed by 83.0 ng/g dry wt at the bottom of

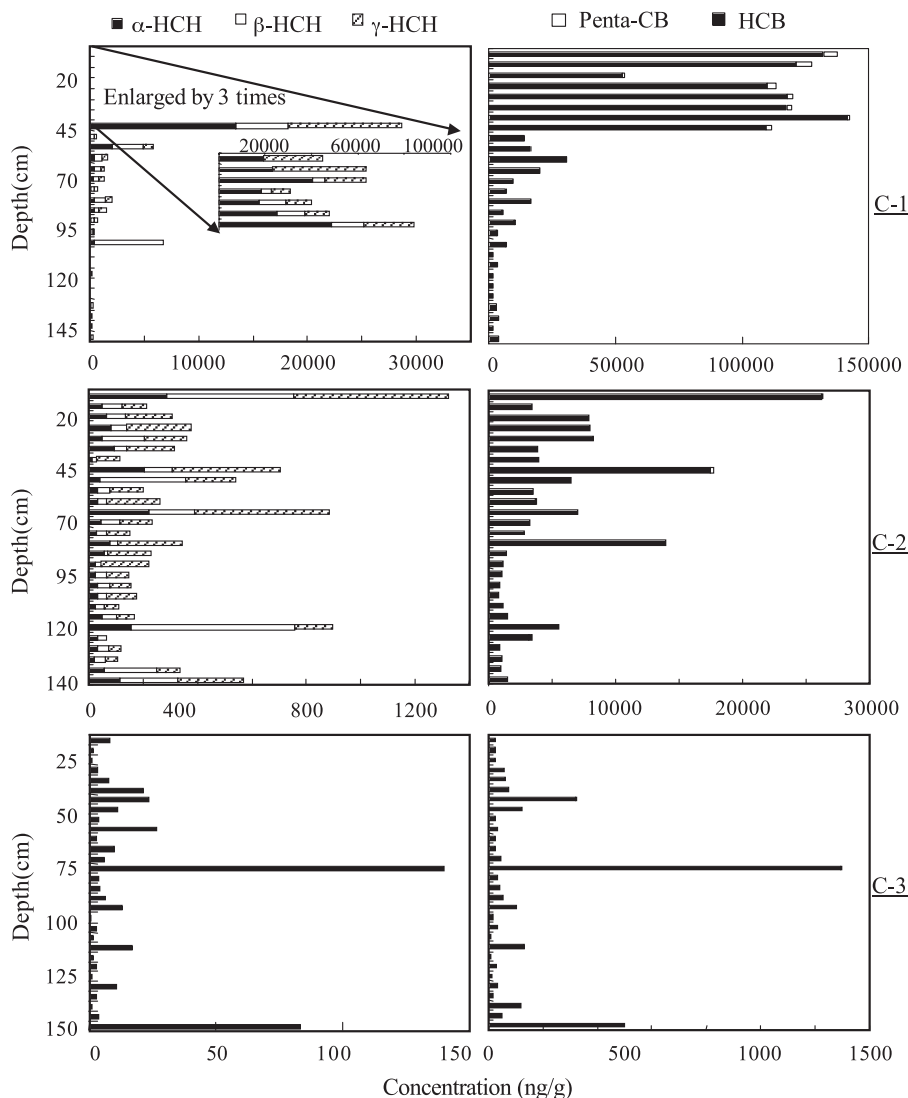


Fig. 3. Vertical profiles of HCH, HCB and penta-CB concentrations in sedimentary cores from Bohai Bay and its adjacent Nanpaiwu River. C-1, C-2: sedimentary cores from the Nanpaiwu River; C-3: sedimentary core from Bohai Bay.

the core. At the other depths, the concentration of α -HCH was in a range from 0.8 to 27.0 ng/g dry wt. Similarly, the profile of HCB was also characterized by two concentration maxima at depths coincident with those of α -HCH (i.e., a maximum concentration of 1300 ng/g dry wt followed by 501 ng/g dry wt). In the other sections, HCB concentrations ranged from 14.8 to 319 ng/g dry wt. The similar profiles of HCH and HCB imply that they might originate from a common source. The total organic carbon content (TOC) in the sediment intervals of C-3 were between 1.1% and 3.5% and the variation was small (Fig. 2). From the vertical profile, no relationship was found between TOC and the concentration of HCHs and HCB.

In contrast with C-3, the vertical profiles of HCH isomers and HCB in core C-2 and C-1 demonstrate that all of the HCH isomers existed in the Nanpaiwu River. In both of C-2 and C-1, the profile of total HCHs is similar to that of HCB, suggesting that HCHs and HCB might be discharged from the same sources. The maximum concentration of total HCHs in C-2 was 1300 ng/g dry wt at the surface, 20 times higher than the lowest concentration (65.5 ng/g dry wt; 120–125 cm). The maximum concentration of HCB (26,200 ng/g dry wt) was also observed at the surface, 30 times higher than the lowest concentration (799 ng/g dry wt). In addition, penta-CB was also detected in a range from 4.5 to 261 ng/g dry wt. For core C-1, the highest concentrations of total HCHs and HCB were 84,200 and 141,400 ng/g dry wt, which were 194 and 100 times higher than the lowest concentration of 106 and 1400 ng/g dry wt, respectively. In addition, penta-CB was also detected to be in a range from 5400 (surface) to 2200 ng/g dry wt (40 cm). Both HCHs and HCB showed the same increasing trend with the decrease of core depth in C-2 and C-1, indicating a recent increase in pollutant discharge. Such a trend was also found in the vertical profiles of TOC in C-1 and C-2 (Fig. 2).

From the above results, it is clear that estuarine HCHs in Nanpaiwu River sediments (C-1 and C-2) were significantly higher than those in the sediment from Bohai Bay. Fig. 4 shows the relationship between concentration of HCHs and HCB and TOC in surface intervals from C-1, C-2, and C-3. It was found that the spatial distribution in C-1, C-2, and C-3 was related with TOC in sediment, indicating that the

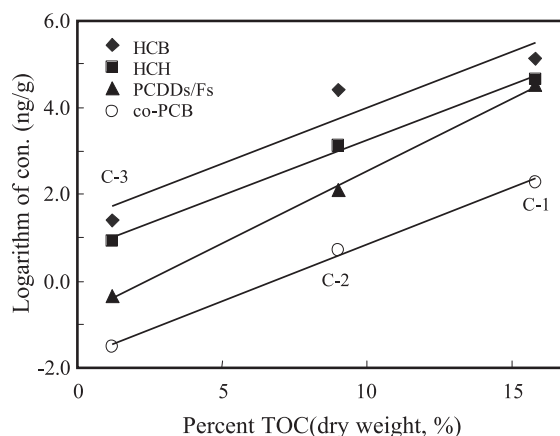


Fig. 4. Relationship between concentrations of PCDD/Fs, co-PCB, HCH, HCB and TOC in surface section from C-1, C-2 and C-3. HCH, HCB, and co-PCB: slope=0.26, PCDDs/Fs: slope=0.33.

riverine discharge was the likely source of contamination in Bohai Bay.

It is interesting to note that while α -HCH concentration reached 139 ng/g dry wt, β -HCH and γ -HCH were not detected in Bohai Bay (C-3) samples, although the latter were detected at a relatively high ratio to α -HCH in estuarine sediment from the Nanpaiwu River (C-1 and C-2). One explanation for this is that α -HCH might be the most persistent HCH in the coastal sedimentary environment, although β -HCH was reported to be the most persistent with respect to microbial degradation (Willett et al., 1998). Further studies are required to verify the above speculation.

3.2. PCDDs, PCDFs, and co-PCB

The concentration of total PCDDs/DFs in Bohai Bay (C-3) ranged from 430 to 3100 pg/g dry wt (Table 1), which is lower than that reported in Tokyo Bay, where the PCDDs/DFs originated from several independent sources: use of PCP and chloronitrofen (CNP), emission from municipal solid waste incineration (MSWI), municipal sewage sludge, etc (Yamashita et al., 2000). The concentration of PCDDs was over 10 times higher than that of PCDFs. The maximum concentrations of PCDDs and PCDFs were observed at depths 50–100 cm. On the other hand, the maximum concentrations of PCDD/DF in the C-2 and C-1 cores were 151.1 and 8714.5 ng/g dry wt, respectively, about 50 times and 3000 times higher than that in core (C-3) from Bohai Bay. The congener

Table 1
Concentrations (pg/g dry wt) of PCDDs and PCDFs in the sediment from the Nanapaiwu River and Bohai Bay, North China

Depth (cm)	C-1				C-2				C-3						
	0–5	25–30	85–90	135–140	0–5	50–55	95–100	135–140	0–5	45–50	65–70	85–90	105–110	125–130	145–150
2378- TeCDD	0.0	500	11.0	2.2	28.0	31.0	14.0	3.8	0.3	0.2	0.4	0.1	0.1	0.07	0.2
12378- PeCDD	2000	800	26.0	3.8	61.0	62.0	16.0	8.1	0.1	0.6	0.9	0.8	0.3	0.31	0.5
123478- HxCDD	19,000	21,000	280	50.0	680	610	240	84	1.6	4.9	12.0	6.6	6.0	1.5	3.7
123678- HxCDD	44,000	29,000	160	63.0	890	270	200	130	3.8	2.2	6.1	2.6	2.6	0.9	1.6
123789- HxCDD	20,000	12,000	77.0	32.0	390	140	110	58.0	2.1	1.9	2.8	2.5	2.0	0.8	1.1
1234678- HpCDD	560,000	660,000	15,000	1700	13,000	3900	6100	1600	40.0	72.0	160	100	79.0	43	33.0
OCDD	2,400,000	7,100,000	1,000,000	61,000	98,000	34,000	140,000	13,000	370	1500	2700	1700	1600	1200	690
Total PCDDs	3,045,000	7,823,300	1,015,600	62,900	113,000	39,000	146,700	14,900	400	1600	2900	1800	1700	1200	730
2378- TeCDF	0.0	0.0	81.0	1.5	4.0	32.0	8.0	2.2	1.2	1.3	1.3	1.9	1.0	1.4	1.1
12378- PeCDF	6500	6300	390	28.0	160	550	68.0	22.0	1.1	4.6	3.2	5.1	4.2	2.1	6.3
23478- PeCDF	1900	2000	41.0	4.7	35.0	100	16.0	5.6	0.2	1.0	0.9	0.8	0.9	0.15	0.6
123478- HxCDF	25,000	39,000	45.0	140	730	1500	350	130	4.5	20.0	19.0	22.0	20.0	2.2	8.1
123678- HxCDF	5000	4800	5.0	16.0	98.0	68.0	31.0	16.0	0.8	3.6	3.6	5.9	3.7	1.7	1.4
123789- HxCDF	4000	400	10.0	1.1	9.0	2.7	9.0	1.7	0.1	0.3	0.2	0.2	0.4	0.15	0.1
234678- HxCDF	2300	1700	4.0	3.4	37.0	55.0	22.0	3.1	0.2	2.0	1.1	2.3	2.7	0.38	1.3
1234678- HpCDF	21,000	65,000	900	120	750	500	580	100	3.8	23.0	21.0	28.0	24.0	4.8	9.6
1234789- HpCDF	8900	22,000	90.0	27.0	230	86.0	150	34.0	1.0	2.9	5.0	4.2	3.2	0.4	1.1
OCDF	170,000	750,000	2700	720	6200	2300	3200	850	17.0	62.0	120	85.0	73.0	12	32.0
Total PCDFs	244,600	891,200	4300	1100	8300	5200	4400	1200	30	121	175	155	133	25	61.5
Total PCDDs/ DFs	3,289,600	8,714,500	1,019,900	64,000	121,300	44,200	151,100	16,100	430	1721	3100	2000	1800	1200	791.6
ΣTEQ (PCDD/Fs)	22,000	22,000	400	65	550	490	220	77	2.5	6.3	8.6	7.4	6.2	2.1	3.6

profiles at various depths were similar, and the inventory profiles are dominated by OCDD (56–91%), H7CDD (1–17%), and OCDF (1–9%). This corresponds well with the impurities in PCP (OCDD: 76%; H7CDD: 10.4%; OCDF: 10%) used in China (Bao et al., 1995), suggesting that the contamination of PCDD/DFs in the Nanapaiwu River and Bohai Bay

might stem from the use or production of PCP pesticide. Complete identification of sources will, however, require further investigation.

Co-PCBs were also detected and the concentrations are shown in Table 2. PCB77, PCB118, and PCB105 were found to be dominant and the inventory profiles are very similar with those of co-PCB in PCP pes-

Table 2
Concentrations (pg/g dry wt) of co-PCB in the sediment from the Nanpaiwu River and Bohai Bay, North China

Depth (cm)	C-1				C-2				C-3						
	0–5	25–30	85–90	135–140	0–5	50–55	95–100	135–140	0–5	45–50	65–70	85–90	105–110	125–130	145–150
PCB77	64,000	37,000	220	75.0	1200	1100	340	200	4.4	15.0	15.0	530	13.0	6.5	7.0
PCB81	0.0	1900	22.0	1.9	50.0	8.2	0.0	6.8	0.2	0.0	0.1	0.2	0.6	0	0.1
PCB126	8300	8100	58.0	15.0	140	220	54.0	27.0	0.9	1.5	1.9	13.0	1.1	0.23	1.0
PCB105	26,000	52,000	100	81.0	510	590	130	160	4.8	14.0	17.0	7.1	14.0	5.2	10.0
PCB114	1800	20,000	7.0	2.4	20.0	140.0	9.0	43.0	0.2	0.8	0.9	0.3	0.6	0.18	0.4
PCB118	49,000	85,000	310	160	1700	3900	1000	310	12.0	47.0	47.0	51.0	50.0	28	39.0
PCB123	0.0	1900	42.0	10.0	110	220	23.0	27.0	0.7	2.1	1.9	0.8	1.9	0.9	1.3
PCB169	0.0	1400	6.0	0.8	14.0	22.0	4.0	2.2	0.1	0.2	0.4	0.6	0.3	0.15	0.2
PCB156	19,000	38,000	50.0	53.0	410	490	110	73.0	2.7	8.2	10.0	6.4	8.1	9.6	8.9
PCB157	8000	22,000	78.0	36.0	270	160	33.0	57.0	1.8	3.0	5.9	2.3	3.1	1.6	2.0
PCB167	12,000	26,000	100	38.0	300	390	54.0	64.0	2.4	5.1	8.0	3.5	5.0	5.2	3.9
PCB189	4600	22,000	87.0	25.0	220	110	29.0	32.0	1.0	3.4	5.2	4.0	3.5	3.7	3.3
Total	500	1100	315,300	192,700	5000	7400	1800	1000	31.1	100	113	620	101	61.3	77.1
Co-PCBs															
ΣTEQ (Co-PCBs)	2.0	6.0	880	860	15.0	23.0	5.7	2.9	0.1	0.2	0.2	1.4	0.1	0.0	0.1

ticides made in China (Kim, 2002). Additionally, the concentration of co-PCBs varies almost linearly relative to that of PCDDs/DFs ($r^2=0.803$, $n=15$). Finally, relationships between concentrations of PCDD/Fs/co-PCB and TOC in surface section from C-1, C-2, and C-3 were also found (Fig. 4). A seaward decreasing trend

in PCDDs/Fs, co-PCB was observed from estuary to the Bohai Bay, which was similar with those of HCHs and HCB. The above results suggests that the four groups of contaminants might have common sources, and PCDD/Fs and co-PCB contamination in Bohai Bay might be mainly due to the riverine discharge.

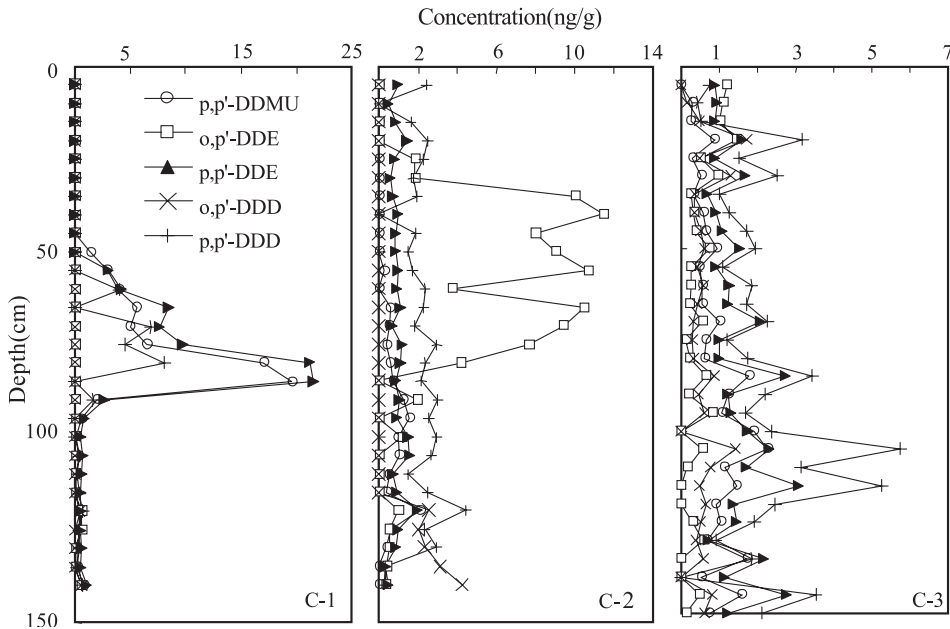


Fig. 5. Vertical profiles of DDT concentrations in sedimentary cores. C-1, C-2: sedimentary cores from the Nanpaiwu River; C-3: from Bohai Bay.

3.3. DDTs

Fig. 5 shows the vertical profiles of DDTs in the three sedimentary cores from the Nanpaiwu River and Bohai Bay. The total DDT concentrations are much lower than the levels detected in the San Francisco Bay (Venkatesan et al., 1999) and the Palos Verdes Shelf, CA (Eganhouse et al., 2000). For C-1, DDTs were only detected in depths from 50 to 95 cm (maximum concentration: 46.2 ng/g) suggesting that no DDTs had recently been discharged into the

Nanpaiwu River above C-1. For C-2, markedly different profiles were found: a high total concentration was observed at depths from 30 to 90 cm, where *o,p'*-DDE accounted for more than 60% of total DDTs. The sedimentary profiles of *p,p'*-DDE and *p,p'*-DDD were relatively uniform, while *p,p'*-DDMU; *o,p'*-DDE; and *o,p'*-DDD were not detected in the surface layers. In contrast, all of the five DDTs were detected in core C-3. The total concentration of DDTs ranged from 1.6 to 12.3 ng/g dry wt, and the sedimentary profile was relatively uniform. While *p,p'*-DDD was

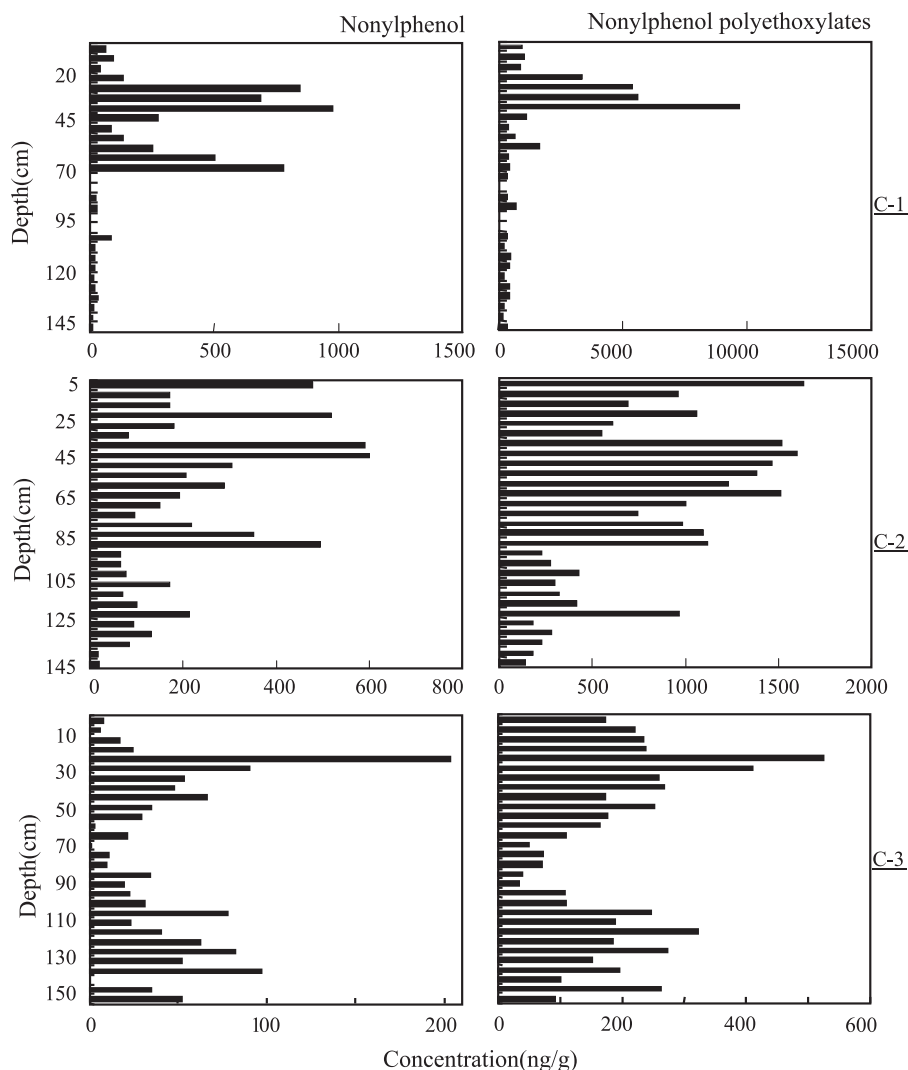


Fig. 6. Vertical profiles of nonylphenol (NP) and nonylphenol polyethoxylates (NPEOs) concentrations in sedimentary cores: C-1, C-2: sedimentary cores from the Nanpaiwu River; C-3: sedimentary core from Bohai Bay.

the most abundant at depths below 20 cm, *o,p'*-DDE was the most abundant congener close to the sediment surface.

From the above distinctive congener and vertical profiles in the three cores, it can be inferred that the contribution of DDTs to Bohai Bay from the Nanpaiwu River was relatively minor. Moreover, since environmental levels of *o,p'*-DDD and *o,p'*-DDE are often lower than that of *p,p'*-DDD and *p,p'*-DDE, we attribute the relatively high levels of *o,p'*-DDE, *o,p'*-DDD to the production or utilization of dicofol pesticide. The composition of dicofol is about 3.54–10.78% DDT, with *o,p'*-DDT as the major DDT compound, followed by *o,p'*-DDE and *p,p'*-DDE (Mao, 1995). Thus, only *p,p'*-DDT in industrial DDT is transferred to dicofol in a dicofol-manufacturing process, and *o,p'*-DDT remains in the pesticide as an impurity, and is biodegraded into *o,p'*-DDE/*o,p'*-DDD in the environment following the use or production of dicofol pesticide.

3.4. NP and NPEOs

Fig. 6 shows variations of NP and NPEOs in the three cores. For all three cores, the vertical profiles of NP are quite similar to those of NPEOs, indicating that the occurrence of NP is related to NPEOs. From C-1 and C-2 to C-3, the concentrations of NP and NPEOs follow a decreasing trend. However, depth variations of NP and NPEOs in each core are different. For C-1, a high concentration zone appears above 70 cm, and maximum concentrations of NP and NPEOs (970 and 9700 ng/g dry wt, respectively) occurred at 35 cm. The mean ratio of NPEOs to NP was estimated to be 7.7. For C-2, NP and NPEOs increased gradually with the decrease of depth, indicating increasing discharge of the pollutants in the upper stream. The highest concentration (NP: 589 ng/g dry wt, NPEO: 1600 ng/g dry wt) was about 10 times higher than the lowest concentration (NP: 17.8 ng/g dry wt, NPEO: 143 ng/g dry wt). The concentration profiles of NP and NPEOs in C-3 showed a bimodal distribution. This profile of NP is largely different from that in Tokyo Bay which shows subsurface maximum of NP concentration (Isobe et al., 2001). The highest concentrations of NP and NPEOs were 203 and 524 ng/g dry wt, respectively. While the concentration of NP in the Nanpaiwu River

was similar with that in Sumidagawa River in Japan, the concentration of NP in Bohai Bay was much lower than the concentration in the core from Tokyo Bay. There is no correlation between NP or NPEOs and TOC in sediment. Because the total concentrations of NP and NPEOs in the cores from the Nanpaiwu River were about 15 times higher than those in the core from Bohai Bay, the Nanpaiwu River was potentially a source of NP and NPEOs to Bohai Bay sediments. The mean ratio of NPEOs to NP was 4.9 for site C-2 which is lower than that in C-1. From this result, there is a need to investigate whether the biodegradation from NPEOs into NP occurred during the riverine discharge.

4. Conclusions

The occurrence of trace organic contaminants (HCHs, HCB, penta-CB, PCDD/Fs, co-PCBs, DDTs, NP, and NPEOs) in sediments from Bohai Bay and its adjacent Nanpaiwu River, North China was examined. Comparison of the vertical profiles among these compounds is effective to discuss the possible sources of the target contaminants. While HCHs, HCB, PCDD/Fs, and co-PCB in Bohai Bay appear to share a common source, i.e., the riverine discharge from Nanpaiwu River, the pollution of DDTs in Bohai Bay was from different sources. Input from the Nanpaiwu River is responsible for the majority of NP and NPEOs in Bohai Bay. Determination of the pollution history of these organic contaminants in this region will require further geochemical characterization and development of sediment chronologies.

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