Chemosphere 77 (2009) 663–672

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Occurrence and distribution of organochlorine pesticides (OCPs) in surface sediments of the Bohai Sea, China

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ARTICLE INFO

Article history:
Received 1 February 2009
Received in revised form 12 July 2009
Accepted 28 July 2009
Available online 25 August 2009

Keywords:
Organochlorine pesticides
Surface sediments
Principal component analysis
Biological risks
The Bohai Sea

ABSTRACT

Fifty-five surface sediment samples covering virtually the entire Bohai Sea (Bohai) were analyzed for organochlorine pesticides (OCPs), in order to provide the extensive information of recent occurrence levels, distribution, possible sources and potential biological risk of these compounds in this area. Concentrations of total dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) in Bohai ranged widely from 0.24 to 5.67 ng g^{-1} (mean 1.36 ± 0.93 ng g^{-1}) and 0.16 to 3.17 ng g^{-1} (mean 0.83 ± 0.57 ng g^{-1}), respectively. High concentrations of DDTs were observed in the coastal areas especially at the isolated sites neighboring the harbor or port regions. The recent DDT inputs could be mainly attributed to the agricultural activity (e.g. dicofol), wastewater of chemical plants and the usage of antifouling paint. The distribution pattern of HCHs was different from that of DDTs due to their different physical–chemical properties and amounts of production and usage in the past. (DDE + DDD)/DDT ratios indicated that the degradation of the parent DDT occurred significantly. The contributions of previous and current inputs of pesticides in the coastal areas were distinguished by means of principal component analysis, suggesting that the recent usage of DDT and technical chlordane could serve as important fresh input sources for OCPs. DDTs and chlordanes are the two-main species of OCPs with more ecotoxicological concern in Bohai.

1. Introduction

Organochlorine pesticides (OCPs), one of the persistent organic pollutants (POPs) groups, are ubiquitous in the environmental matrixes. OCPs were widely used in the world from the 1950s. There has been an extensive concern for OCPs due to their high toxicity, persistence, bioaccumulation and biomagnification in the environment (Zhang et al., 2002; Wan et al., 2005).

China is ever the world's second largest producer of such pesticides. Hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) were widely used in China between 1950s and 1980s due to their low cost and high insecticidal efficacy. HCHs and DDT were officially banned in 1983, however, over the past 25 years, the total production of HCHs and DDT in China was about 4.9 and 0.4 million tons, respectively, accounted for 33% and 20% of the total world production, respectively (Fu et al., 2003). Although the usage and production of these anthropogenic pollutants were prohibited and the residue level of OCPs in the aquatic environment has considerably declined in the past years (Wu et al., 1999), these organic pollutants could still be a problem in various environmental compartments, especially in the estuarine or marine sediments, which were usually regarded as an important sink of organic contaminants (Yang et al., 2005a). The sediments could also be a secondary contamination source to overlying water due to the resuspension (Wu et al., 1999; Liu et al., 2008).

The Bohai Sea (Bohai) in North China is a shallow marginal sea enclosed by Liaodong and Shandong Peninsulas, and is connected to the northern Yellow Sea by the Bohai Strait (Fig. 1). It has an area of 77,000 km^2, and the average water depth is 18 m (Sündermann and Feng, 2004). In recent years, the rapid industrialization and urbanization around the coastal regions has resulted in a severe environmental stress in Bohai. Furthermore, the surrounding areas of Bohai have been OCPs' production and application bases for several decades in China, especially for HCHs and DDTs. Several big manufactures of DDTs and HCHs such as the Dagu Chemical Company and Tianjin Chemical Company were located in the lower reaches of the Hai River, one of the largest river basins around

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doi:10.1016/j.chemosphere.2009.07.070

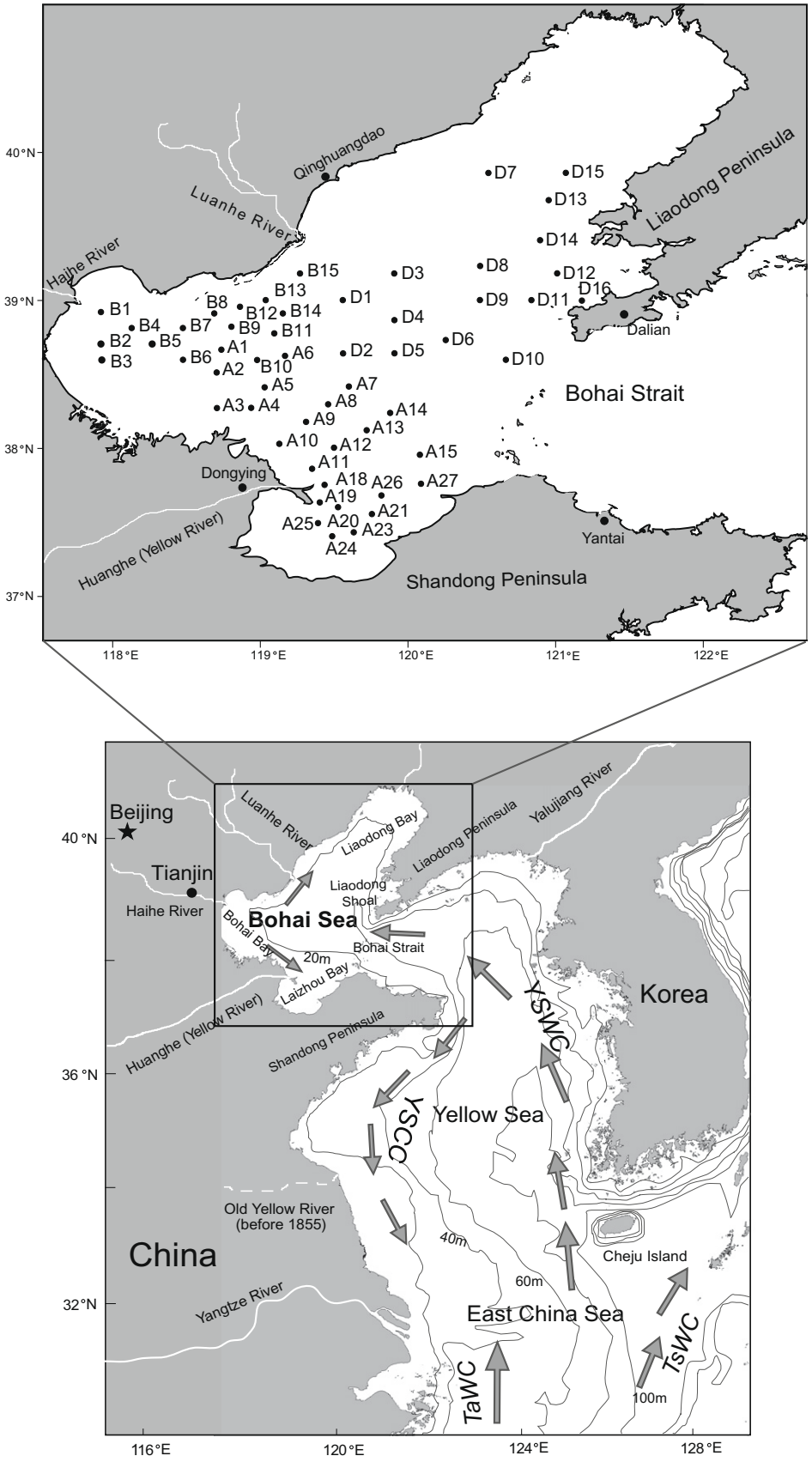

Fig. 1. The study area and locations of sampling sites in Bohai. Current circulation system (from Hu and Yang, 2001): TaWC: Taiwan Warm Current; TsWC: Tsushima Warm Current; YSCC: Yellow Sea Coastal Current; YSWC: Yellow Sea Warm Current.

Bohai. It was reported recently that the average level of DDTs in the sediments of the Hai River system was 340 ± 930 ng g^{-1} (based on dry weight) (Tao et al., 2007), and the average level of DDTs in the soils of ambient areas of Tianjin was 56 ± 134 ng g^{-1} with a maximum value of 970 ng g^{-1} (Gong et al., 2004).

There are several studies on the different environmental matrixes of OCPs in Bohai as well as its adjacent areas including air (Wu et al., 2005), rivers (Tao et al., 2007), soils (Gong et al., 2004), seawater (Xu et al., 2007), sediments (Liu et al., 2006) and biota (Liu et al., 2007). The occurrence of DDTs in surface sediments of Bohai was ever reported (Ma et al., 2001; Liu et al., 2006), however, most samples in those studies were mainly collected from the coastline area within 5 m bathymetric water depth, and only few samples were located in the open Bohai. Therefore, the previous studies mainly reflected the status of DDTs in the coastal areas of Bohai. In addition, samples in these previous studies were collected in 1991 (Ma et al., 2001) and 1998 (Liu et al., 2006), respectively, while the marine environment especially in the Huanghe (Yellow River) Estuary has changed since 1990s (especially after 1998), owing to the stepwise decreases of sediment loads into Bohai by river discharge (Wang et al., 2007). This could influence the distribution and fate of these organic pollutants in Bohai. More importantly, the distribution and assessment of HCHs in surface sediments in Bohai remains scarcely documented. In this work, 55 surface sediment samples collected in 2006, covering virtually the entire Bohai, were measured for OCPs (including both HCHs and DDTs) to provide a better understanding of recent distribution, possible sources as well as potential biological risk of these compounds in this area.

2. Materials and methods

2.1. Sampling

The sampling sites are shown in Fig. 1. Two cruises were conducted in August and October, 2006, respectively. Surface sediment samples of A1–A27 were collected using a stainless steel box corer deployed from R/V Dong Fang Hong 2 of the Ocean University of China (OUC) in October 2006, and the remaining samples were obtained using a stainless steel grab sampler from R/V Ke Yan 59 in August 2006. All sediment samples (0–3 cm) were wrapped in aluminum foil and stored at −20 °C until analysis.

2.2. Analysis of OCPs and quality assurance/quality control (QA/QC)

A 100 ng mL^{-1} standard solution of OCPs, including HCHs (α-HCH, β-HCH, γ-HCH, δ-HCH), DDTs (*p, p′*-DDT; *o, p′*-DDT; *p, p′*-DDD and *p, p′*-DDE), chlordanes (*trans*-chlordane and *cis*-chlordane), hexachlorobenzene (HCB), endosulfans (α-endosulfan and β-endosulfan), heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin and endosulfan sulfate, was purchased from AccuStandard, Inc. (USA) and diluted to the desired concentrations. All solvents were of analytical grade and redistilled to remove impurities prior to use.

OCPs were measured at the State Key Laboratory of Organic Geochemistry (SKLOG), and the procedures for the OCPs' extraction, fractionation and instrumental analysis were described in detail elsewhere (Zhang et al., 2002). Briefly, 15 g of homogenized and freeze-dried sample was spiked with surrogate standards of 2, 4, 5, 6-tetrachloro-*m*-xylene (TC*m*X) and decachlorobiphenyl (PCB209) and was extracted with dichloromethane in a Soxhlet extractor for 48 h. Activated copper was added for desulphurization. The extract was concentrated and solvent-exchanged to hexane, and then subjected to a 1:2 alumina/silica gel glass column for clean-up and fractionation. The column was eluted with dichloromethane/hexane (1:1) to yield the organochlorine pesticide fraction. The fraction was concentrated to 0.5 mL under a gentle nitrogen stream. A known quantity of pentachloronitrobenzene (PCNB) was added as an internal standard prior to gas chromatography–electron capture detector (GC–ECD) analysis.

OCPs were determined using a HP-5890 Series II GC equipped with a Ni electron capture detector and HP-5 capillary column (60 m × 0.32 mm × 0.17 μm). Split/splitless injection of 1 μL sample was performed with 1 min solvent delay time. Nitrogen was used as carrier gas at 2.5 mL min^{-1}. The oven temperature began at 100 °C and increased to 290 °C (10 min hold time) at a rate of 4 °C min^{-1}. Injector and detector temperatures were maintained at 250 and 300 °C, respectively. The inlet degradation of DDT was checked daily and controlled within 15% before field samples were injected and analyzed. Identification of the compounds was based on the retention time with corresponding standards and confirmed on an Agilent-5975 GC–MSD system.

Method blanks (solvent), duplicate samples and spiked blanks (standards spiked into solvent) were analyzed. The average surrogate recoveries were 94 ± 9% and 97 ± 15% for TC*m*X and PCB209, respectively. Method detection limit (MDL) ranged from 0.01 to 0.05 ng g^{-1} for most OCPs. Actual detection limits were adjusted based on the sample size used.

2.3. Analysis of total organic carbon

Dried samples were treated with 4 M hydrochloric acid to remove carbonate and dried overnight at 60 °C. The carbonate-free samples were then analyzed for total organic carbon (TOC) with a Vario EL-III Elemental Analyzer and average values were reported. Replicate analysis of one sample ($n = 6$) gave a precision of ±0.02 wt.% for TOC.

2.4. Principle component analysis (PCA)

PCA, a multivariate analytical tool, was used to explore the relationship of the measured parameters and facilitate the assessment of potential input sources. Prior to analysis, the non-detectable values were first replaced with concentration values of one half the method detection limits (Zaghden et al., 2007). Then the raw data matrix was Z-scoring standardized and mid-range normalized in order to eliminate the influence of different units and make each determined variable have equal weighting in the PCA (Yunker et al., 1995). PCA with varimax rotation was performed using the program *SPSS 13.0* for Windows (SPSS Inc., Chicago, Illinois).

3. Results and discussion

3.1. Occurrence levels of OCPs in surface sediments

OCP compounds occurred frequently in our samples in Bohai were DDTs, HCHs, HCB, heptachlor, chlordanes (*trans*-chlordane and *cis*-chlordane), α-endosulfan, β-endosulfan and endosulfan sulfate. Particularly, the detection frequencies for DDT and HCH compounds, chlordanes and HCB in our samples ($n = 55$) were up to 100%, indicating a wide occurrence of these compounds in different regions of Bohai (Table S1). These low detection frequency OCP species including aldrin, dieldrin, endrin and heptachlor epoxide were only from synthetic experiment carried out in China and there was no industrial production (MEP, 2007).Therefore, these four OCP species were not discussed in this work.

Concentrations of OCP compounds and the TOC content were shown in Table 1. The minimum, maximum, media, and the 25th, 50th and 75th percentiles of the concentration levels of these individual OCPs in surface sediment samples are shown in Fig. 2.

Table 1
Concentrations (ng g^{-1}, dry wt.) of OCPs, contents of TOC and ratios of DDTs' degradation products in surface sediments of Bohai.

Sampling sites	DDTs	HCHs	Chlordanes	HCB	Heptachlor	α-Endosulfan	β-Endosulfan	End-sulfate	TOC (%)	*p*, *p*′-DDE/*p*, *p*′-DDD	(*p*, *p*′-DDE + *p*, *p*′-DDD)/*p*, *p*′-DDT
A1	0.95	0.93	0.61	0.41	0.06	0.04	0.04	n.d.	0.48	0.75	10.29
A2	1.51	1.16	0.46	1.00	0.43	0.05	0.06	0.07	0.46	0.75	8.94
A3	0.96	0.66	0.30	0.38	0.16	0.04	n.d.	n.d.	0.20	0.55	8.93
A4	1.29	0.68	0.50	0.49	0.10	n.d.	0.05	0.07	0.42	0.56	3.11
A5	1.19	0.74	0.39	0.60	0.07	n.d.	0.03	0.04	0.50	0.70	2.71
A6	1.02	0.91	0.62	0.45	0.15	0.04	n.d.	0.04	0.59	0.94	6.75
A7	2.18	1.30	0.93	0.35	0.65	0.08	0.12	0.07	0.47	1.35	8.05
A8	0.90	0.95	0.79	0.31	0.08	0.04	n.d.	n.d.	0.50	1.39	5.25
A9	1.16	0.87	0.62	0.62	0.36	0.04	0.04	0.03	0.64	0.57	6.04
A10	1.09	0.56	0.22	0.20	n.d.	n.d.	n.d.	n.d.	0.22	0.39	11.45
A11	1.39	0.33	0.49	0.21	0.43	n.d.	n.d.	n.d.	0.54	1.12	20.13
A12	1.09	0.86	0.50	0.57	0.45	0.05	0.04	0.08	0.48	1.11	5.97
A13	0.93	0.67	0.35	0.25	n.d.	0.07	n.d.	n.d.	0.41	1.45	8.04
A14	0.70	0.38	0.24	0.10	0.11	n.d.	n.d.	0.06	0.28	0.89	3.92
A15	1.09	0.70	0.90	0.23	0.64	0.05	0.06	0.06	0.29	1.29	7.94
A18	1.14	0.72	0.65	0.41	0.76	0.03	0.04	n.d.	0.42	1.76	4.43
A19	0.85	0.56	0.40	0.27	0.26	0.03	n.d.	0.04	0.27	1.64	6.68
A20	1.00	0.50	0.34	0.28	0.54	n.d.	0.04	0.04	0.20	1.72	5.75
A21	5.67	0.20	0.31	0.07	0.10	0.03	0.11	n.d.	0.08	0.12	5.27
A23	0.66	0.29	0.23	0.13	0.38	n.d.	0.05	n.d.	0.11	0.68	9.38
A24	0.55	0.16	0.14	0.18	0.04	n.d.	n.d.	n.d.	0.15	1.79	18.00
A25	1.06	0.62	0.27	0.27	0.05	n.d.	n.d.	n.d.	0.36	1.39	10.42
A26	1.28	0.68	0.76	0.37	0.17	0.06	0.05	n.d.	0.37	0.88	5.27
A27	0.97	0.60	0.37	0.18	0.09	n.d.	0.04	n.d.	0.30	1.08	5.94
B1	2.17	3.17	0.75	0.94	0.22	0.09	0.09	0.46	0.45	0.64	3.92
B2	1.78	0.96	0.47	0.81	0.40	0.04	0.05	0.05	0.45	0.97	8.92
B3	1.29	0.88	0.55	1.11	0.12	0.08	0.09	0.36	0.31	0.98	9.32
B4	1.28	0.56	0.38	0.57	n.d.	0.03	0.04	0.08	0.40	0.59	4.85
B5	1.21	2.71	0.55	0.68	0.10	0.04	0.04	0.04	0.40	0.92	4.98
B6	1.11	2.69	0.49	0.67	0.17	0.04	n.d.	n.d.	0.45	0.98	7.43
B7	1.06	0.64	0.44	0.80	0.16	0.03	0.03	0.04	0.55	0.82	6.45
B8	0.84	0.70	0.39	0.15	0.18	0.04	n.d.	0.11	0.14	0.89	4.63
B9	1.25	0.63	0.46	0.26	0.40	0.03	0.08	0.13	0.37	0.63	2.51
B10	1.61	1.19	1.01	0.56	0.84	0.05	0.09	0.05	0.51	0.85	2.70
B11	4.57	1.11	0.42	0.42	0.10	0.14	0.27	0.32	0.55	0.41	1.31
B12	0.70	0.48	0.45	0.16	0.16	n.d.	0.06	0.09	0.17	1.14	4.69
B13	0.60	0.45	0.22	0.18	0.15	n.d.	n.d.	0.29	0.14	1.41	5.38
B14	0.98	0.48	0.61	0.25	0.08	0.07	0.08	0.07	0.26	0.95	4.47
B15	1.47	0.98	0.49	0.34	0.07	0.13	0.19	0.23	0.29	0.88	2.98
D1	1.25	1.17	0.55	0.51	0.10	0.04	0.04	0.05	0.69	1.36	7.46
D2	1.59	0.91	0.74	0.19	0.41	0.05	0.09	0.07	0.68	1.73	4.10
D3	2.77	1.22	1.05	0.30	n.d.	0.73	0.40	0.13	0.56	0.82	5.98
D4	0.61	0.45	0.25	0.13	0.06	n.d.	n.d.	n.d.	0.25	1.54	7.24
D5	0.97	0.86	0.41	0.25	0.24	n.d.	0.04	0.07	0.34	1.20	5.14
D6	0.93	0.63	0.31	0.17	0.37	n.d.	n.d.	0.29	0.13	1.28	4.91
D7	1.33	1.06	0.38	0.25	0.17	0.04	n.d.	0.06	0.59	1.32	6.62
D8	2.27	0.97	0.35	0.21	0.37	n.d.	0.05	0.07	0.33	1.19	5.53
D9	0.83	0.50	0.20	0.11	0.18	n.d.	0.15	n.d.	0.17	1.22	4.47
D10	0.60	0.29	0.21	0.07	0.13	n.d.	n.d.	n.d.	0.23	1.84	2.07
D11	2.30	1.12	0.56	0.40	0.65	0.04	0.07	0.07	0.66	1.22	3.72
D12	0.99	0.60	0.42	0.16	0.68	n.d.	0.04	0.15	0.46	1.17	4.18
D13	1.36	0.66	0.27	0.17	0.13	0.08	0.05	0.03	0.24	1.95	4.63
D14	0.24	0.30	0.13	0.08	0.08	n.d.	n.d.	0.13	0.04	1.70	3.77
D15	0.74	0.39	0.25	0.12	0.69	0.21	n.d.	0.18	0.20	1.70	4.86
D16	3.27	0.84	0.63	0.38	0.36	n.d.	0.08	0.56	0.42	1.87	2.46

n.d., not detected.

Concentrations of OCPs (sum of DDTs, HCHs, HCB, heptachlor, chlordanes, α-endosulfan, β-endosulfan and endosulfan sulfate) in surface sediments from Bohai ranged from 0.95 to 7.88 ng g^{-1}, with a mean value of 3.45 ± 1.57 ng g^{-1} (based on dry weight). The highest value was found at site B1 close to the Hai River Estuary in the Bohai Bay. The lowest value of OCPs occurred at site D14 located in the outer part of the Liaodong Bay, corresponding to the lowest content of TOC (0.04%). It was found that TOC distribution was correlated well with the grain size of sediments in this area, suggesting the effect of hydrodynamics on the accumulation of sedimentary organic matter (Hu et al., 2009). There was a correlation between the OCPs and TOC as shown in Table S3 ($r = 0.6$, $p < 0.01$), suggesting a potential influence of TOC on the distribution of OCPs in surface sediments.

The status of OCPs contamination in this work was compared with those in other riverine/estuarine and coastal regions (Table 2). DDTs (sum of *p*, *p*′-DDT; *o*, *p*′-DDT; *p*, *p*′-DDD and *p*, *p*′-DDE) and HCHs (sum of α-, β-, γ-, δ-isomers) could be the most two important contaminants in this area due to their relatively higher fractions in the total OCPs (average in 38% for DDTs and 24% for HCHs). Concentrations of DDTs in Bohai ranged from 0.24 to 5.67 ng g^{-1} (mean 1.36 ± 0.93 ng g^{-1}), which were comparable to the data reported for several coastal sediments in China (e.g. Pearl River Estuary, East China Sea, Danshui River Estuary) and some other regions over the world such as Osaka Bay, Japan, Kyeonggi Bay, Korea, coastal areas of Singapore and northern part of the Baltic Sea. Concentrations of HCHs in this study varied from 0.16 to 3.17 ng g^{-1} (mean 0.83 ± 0.57 ng g^{-1}) and were compared to those found in many other

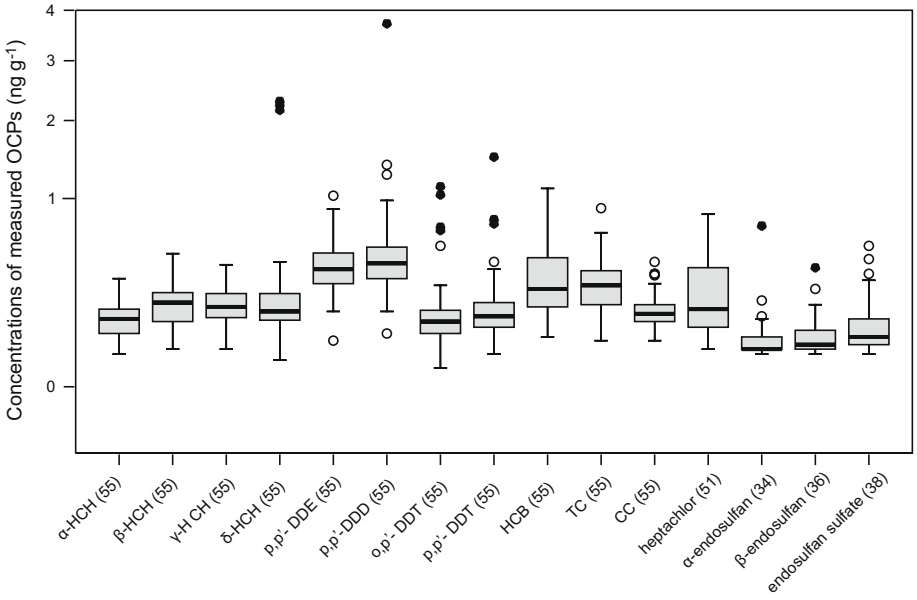

Fig. 2. Concentrations of OCPs in surface sediments of Bohai. In the box plots, the results are presented as medians, 25th, 50th and 75th percentile values, respectively. The number of detectable sites for each compound is presented in parentheses.

Table 2
Comparison of HCHs and DDTs concentrations in surface sediments of Bohai and other riverine/coastal areas in the world (ng g^{-1}, dry wt.).

Locations	Sampling year	HCHs	DDTs	Reference
Bohai Sea, China	2006	0.2–3.6 (0.8)	0.24–5.7 (1.4)	This study
Yangtze Estuary, China	2002	0.5–17.5 (6.0)	0.9–33.1 (8.2)	Liu et al. (2008)
Pearl River Estuary, China	2002	0.08–1.38 (0.36)	0.04–2.48 (0.87)	Chen et al. (2006)
East China Sea	2002	<0.05–1.45 (0.76)	<0.06–6.04 (3.05)	Yang et al. (2005a)
Haihe River, China	2003	1.88–18.76 (7.33)	0.32–80.18 (15.94)	Yang et al. (2005b)
Danshui River Estuary, Taiwan	2004	0.28–0.69 (0.46)	0.25–4.63 (1.61)	Hung et al. (2007)
Osaka Bay, Japan	1989–1991	4.5–6.2	2.5–11.9	Iwata et al. (1994)
Mandovi River Estuary, India	1989	3.8	73	Iwata et al. (1994)
Coastal areas of Vietnam	2003–2004	n.d.-1.00	0.31–274	Hong et al. (2008)
Coastal areas of Singapore	2003	3.4–46.1	2.2–11.9	Wurl and Obbard (2005)
Kyeonggi Bay, Korea	1995	0.15–1.2 (0.44)	0.046–4.2 (0.70)	Lee et al. (2001)
Casco Bay, USA	1991	<0.25–0.48	<0.25–20	Lee et al. (2001)
Northern part of the Baltic Sea	1991–1992	5–7	1.9–6.9	Strandberg et al. (1998)

coastal areas, except for some more polluted regions such as the Yangtze River Estuary and Hai River in China and some other regions in the world (Table 2). Liu et al. (2006) reported that the concentrations of DDTs in surface sediment samples collected mainly from the coastal Bohai in 1998 were in the range of 0.26–12.14 ng g^{-1}. Generally, levels of DDTs in this work were relatively lower than those reported for the similar areas of Bohai in previous studies.

3.2. Spatial distribution of DDTs and HCHs

As shown in Fig. 3a, concentrations of DDTs were relatively higher in the coastal areas of the Bohai Bay (sites B1, B11), Laizhou Bay (site A21), and Liaodong Bay (site D16). The surrounding areas of the Bohai Bay were ever the important production bases for the pesticides in China in the past decades. The contamination of DDTs in soils and surface sediments of Hai River Plain adjacent to the Bohai Bay was very serious due to the long-term and large usage in agriculture (Yang et al., 2005b; Tao et al., 2008). Most samples in the central area of Bohai had relatively low DDTs values (<2 ng g^{-1}) compared to the coastal sites. Concentrations of DDTs were much lower (<1 ng g^{-1}) in the eastern Bohai (Liaodong shoal), where the sediments were mainly composed of coarse sand induced by the strong rectilinear tidal environments (Zhu and Chang, 2001).

A different spatial distribution pattern was found for HCHs (Fig. 3b). The residual HCH levels in the Hai River Estuary and its adjacent Bohai Bay were much higher than those in other regions of Bohai. HCH isomers have the less lipophilic and higher volatility and water solubility nature relative to the DDTs (Lee et al., 2001), thus, it could be more easily transferred from the land into the sea by the riverine discharge. This could be partially responsible for the spatial variation between these two OCP species in this area, in addition to their different amount of usage and production in the past decades (Fu et al., 2003).

There were several chemical manufactures of HCH and DDT in the lower reaches of Hai River, such as the Tianjin Chemical Company and Dagu Chemical Company which were the most important producers of technical HCH in China in the past decades. Although the production of HCHs and DDT was officially banned in China in 1983, the actual application and production of technical HCH and lindane in Dagu Chemical Company was not terminated until 2000 (Tao et al., 2008). The contamination level of HCHs in surface sediments of the Hai River system (Yang et al., 2005b), and in soils in the Hai River Plain (Tao et al., 2008) was very serious due to the long-term and large usage of HCHs in agriculture (Yang et al., 2005b). Thus, according to these reported results and the composition profile of HCH isomers in this study (see below), the higher

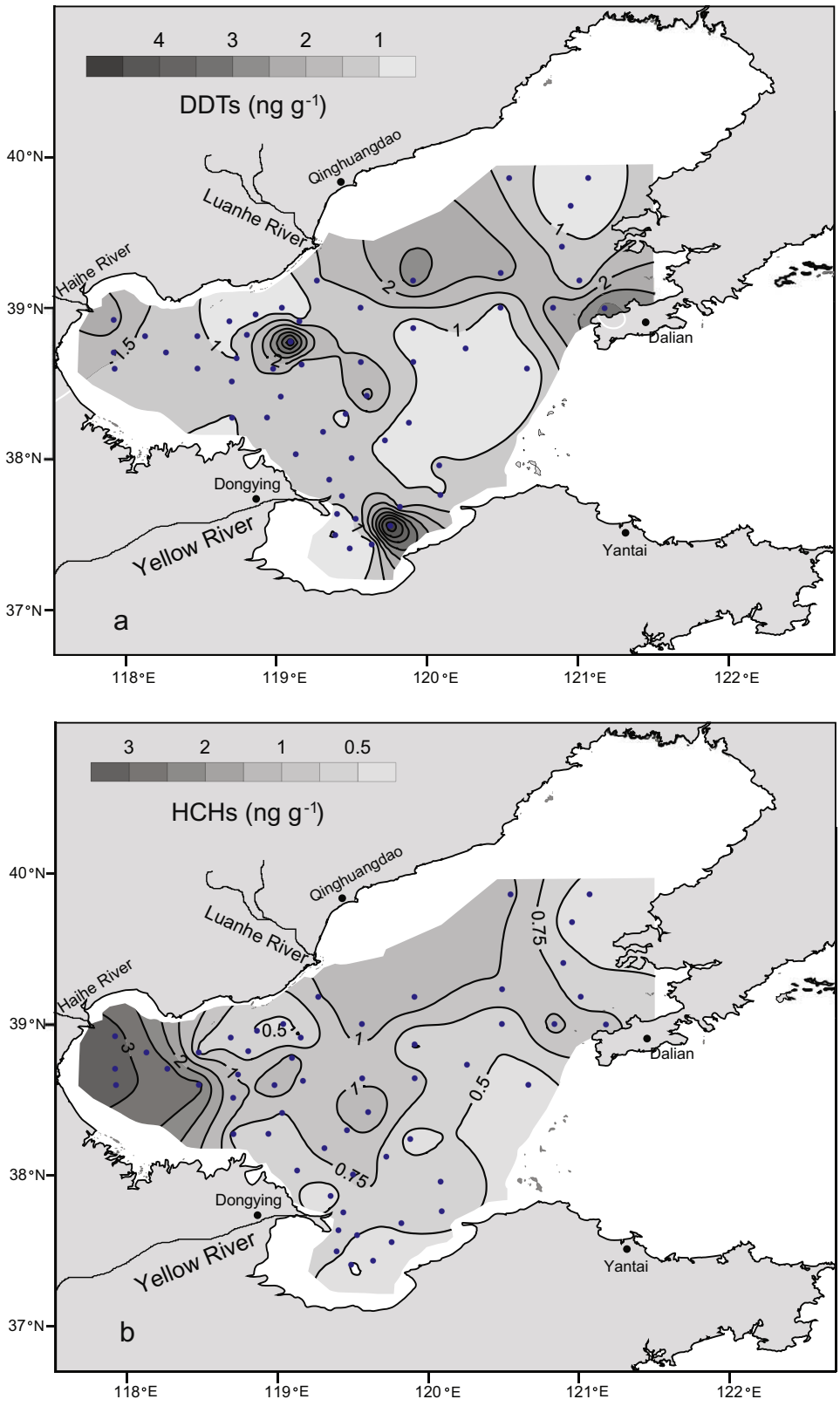

Fig. 3. Spatial distribution of DDTs (a) and HCHs (b) in surface sediments in Bohai.

HCH level in our samples located in the Hai River Estuary could be mainly associated with the soil runoffs and inflows from surrounding agricultural areas with a high HCH residual levels. Furthermore, regarding the composition difference of HCH isomers in sediments of the Hai River (Yang et al., 2005b) and the large chemical producers surrounding The Bohai Bay, the contribution of wastewater from chemical plants could not be negligible.

Interestingly, the levels of HCHs in the Huanghe Estuary in the Laizhou Bay were much lower compared with the Hai River Estuary in the Bohai Bay. Actually, the lower reaches of Huanghe are

characterized by the "aboveground river", meaning that its riverbed is higher than the ground elevation outside banks. Contaminants driven by soil runoffs cannot be easily transferred from the ambient farmlands and cities into the Huanghe. Therefore, the fluvial input of pollutants into Bohai carried by the Huanghe discharge could be relatively small. Furthermore, as the Huanghe was ever the second largest river in the world in terms of its sediment load, the large flux of terrigenous sediments mainly derived from the low-polluted upper and middle reaches could lead to a dilution effect at the river mouth for the concentration levels of these contaminants.

3.3. Compositions of HCHs and DDTs

The isomers α-, β-, γ-, and δ-HCH measured in this work accounted for about 18.5%, 26.5%, 26.1%, and 29.0% of total HCHs, respectively. The typical technical HCH mixtures which have been widely used as a broad-spectrum pesticide generally contain 55–80% of α-HCH, 5–14% of β-HCH, 8–15% of γ-HCH and 2–16% of δ-HCH, respectively (Lee et al., 2001). In the present work, compared with its original components, the percentage of HCH isomers changed obviously, which could be attributed to their different physical–chemical properties. The higher percentage of β-HCH in sediments can be explained by its low vapor pressure and less degradable property compared to other HCHs (Willett et al., 1998). α- and γ-HCH are more volatile due to their relatively high vapor pressures and are readily lost in sediments. It should be noted that the α- and γ-HCH can also be transformed to β-HCH in the aged environmental samples (Walker et al., 1999). The high δ-HCH fraction in sediment samples was also reported in some other studies, such as in surface sediments of the Yangtze Estuary (9.0–89.4%, except for no detection) (Liu et al., 2008) and in agricultural soils of central Germany (Manz et al., 2001). δ-HCH was observed to have the longest half-life in HCH isomers (Satpathy et al., 1997).

The composition difference of DDT and its metabolites have been used to identify the possible sources of DDT as well as their fate in the aquatic environment (Lee et al., 2001; Tao et al., 2007). DDT can be degraded into DDD under anaerobic conditions and into DDE in aerobic environments. A higher amount of DDE than DDT and DDD in sediments and waters was observed in developed countries, where DDT has been banned for a long time, showing a (DDE + DDD)/DDT ratio above 10 (Hitch and Day, 1992; Zhang et al., 2002). The (DDE + DDD)/DDT ratio has been used to indicate the possibility of the continuous illegal use of DDT in some lake areas of China (Peng et al., 2005). In this work, the (DDE + DDD)/DDT ratios were higher than 1 (Table 1), implying that degradation of the parent DDT occurred significantly in the study area. Nevertheless, the usage of DDT in agricultural activities was not terminated until the end of 2000 despite of the official ban in 1983 (Tao et al., 2007), while dicofol with high impurity of DDT compounds is still allowed and widely used in agricultural practice such as cotton cultivation and becomes an important source for current DDT pollution in China (Liu et al., 2008). Wan et al. (2005) reported that the production and application of dicofol could be the main source for DDT pollution in the Hai River Basin; and for the Bohai Bay, the main source for recent DDT pollution could be from the production in these chemical plants and the usage of DDT in the area. In our work, the recent DDT inputs in the coastal areas of the Bohai Bay mainly from the agricultural

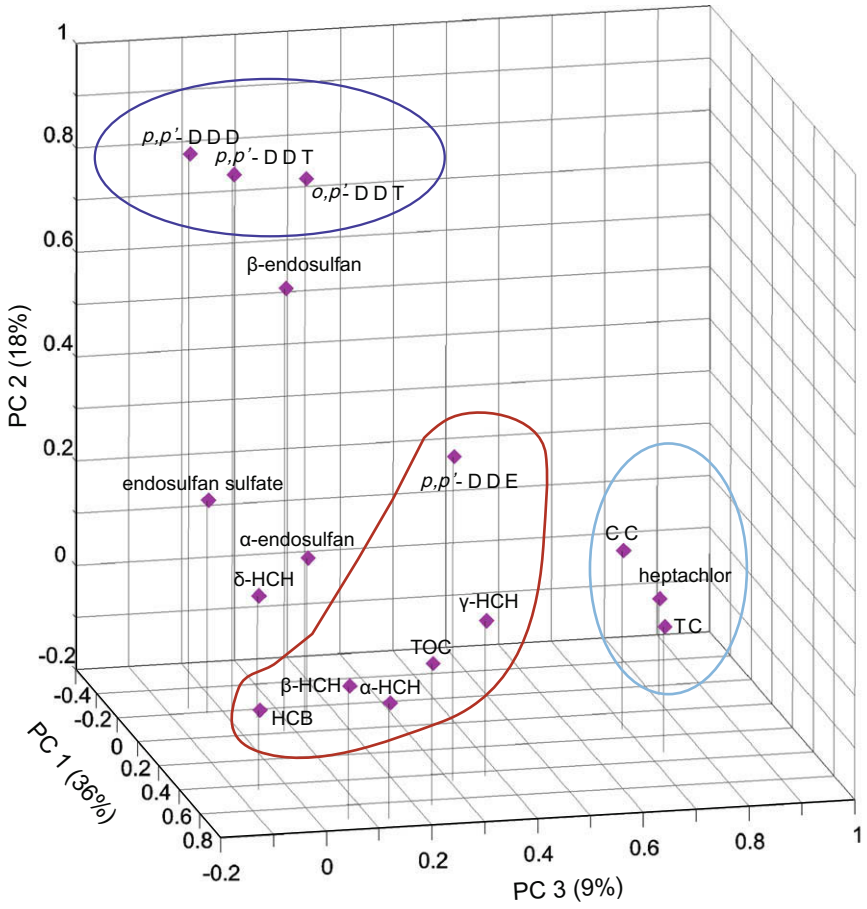

Fig. 4. Principal component analysis for OCPs.

activity (e.g. dicofol) and chemical plants could be inevitable, although the parent DDT in most sites of Bohai has gone through a long-term degradation. High levels of DDTs at several isolated sites neighboring the harbor or port regions (e.g. site A21 close to the Laizhou Harbor, and site D16 adjacent to the fishing port of Lüshun) could be partially linked to the historical/current usage of antifouling paint for the ships since DDT is still used as an active ingredient for antifouling paint in China (Hong et al., 2008).

The DDE/DDD ratio could be an indicator for the aerobic/anaerobic conditions in the sediment environment (Liu et al., 2008). As shown in Table 1, DDE/DDD ratios in the eastern Bohai (Liaodong shoal and Bohai Strait, e.g. sites D10, D11) and most of the sites in the Huanghe Estuary were more than 1, indicating relatively aerobic conditions in these sedimentary environments. This is consistent with the distribution patterns of the surface sediments and hydrodynamic conditions in these areas. Surface sediments in the eastern Bohai were mainly composed of fine sand induced by the strong tidal currents (Zhu and Chang, 2001). As for the Huanghe Estuary, given the high current/wave energy and turbidity at the river mouth, as well as high $CaCO_3$ content sediments in the coastal areas, the sedimentary environment could also be aerobic there (Bigot et al., 1989).

3.4. PCA

After performing PCA on the datasets containing these individual OCP compounds and TOC, the scree plot of eigenvalues indicated that 77% of the data variance could be explained by the first five components (Fig. S1 and Table S2). The remaining 23% of data variance could not be clearly explained possibly due to the large diversity and blocks among the large datasets of the original variables (Gonçalves et al., 2006). The scree plot also becomes flat, meaning that additional components contribute less to the overall data variance. In this work, we mainly considered the extracted first three principal components (PCs) accounted for 63% of the total variance.

The PC1 accounting for 36% of the total variance was distinguished by the high positive loadings of *p, p′*-DDE, HCB; α-HCH, β-HCH, γ-HCH and TOC (Fig. 4). HCB has been found as an impurity in some pesticides such as lindane due to its formation as a by-product during production process (Barber et al., 2005). The occurrence of HCB and HCH isomers in the same group of PC1 could suggest the same origin of these pesticides. Historically, HCB was produced only in Dagu Chemical Company in China since 1983 and the total production was 79, 278 tons from 1988 until now. *p, p′*-DDE and β-HCH were relatively more persistent than other homologues or isomers, and γ-HCH can be degraded and transformed into α-HCH by microbes more easily (Liu et al., 2008). Furthermore, as shown in Fig. 4, TOC gave a high positive loading on the PC1, and there was a correlation between these organic compounds and TOC (e.g. for *p, p′*-DDE; $r = 0.7$; $p < 0.01$) (Table S3). This indicated that the distribution of these relatively "old" accumulated pesticides could also be influenced by the distribution of organic matter due to the post-depositional sorption besides the input sources (Hung et al., 2007; Hong et al., 2008).

PC2 accounting for 18% of the total variability was mainly related with *p, p′*-DDT; *o, p′*-DDT; *p, p′*-DDD. The presence of *p, p′*-DDD and DDT residues in the same group of PC2 could suggest the occurrence status of these pesticides in the coastal areas. As discussed above, the recent DDT inputs in the coastal areas could be mainly from the agricultural activity (e.g. dicofol), wastewater of chemical plant and antifouling paint (especially in the areas neighboring the harbor and port regions). The sedimentary condition in these coastal areas is anoxic due to the semi-closed setting. The historical/fresh inputs of DDT in these areas could be more easily degraded into DDD under an anoxic condition, inducing a common appearance of DDT and DDD in PC2. Wan et al. (2005) reported that the concentrations of DDD were higher than those of DDE in coastal sediment samples of the Bohai Bay. Thus, PC2 could mostly reflect the presence of these historical/current inputs of DDT and its degradation products in the coastal areas.

As for PC3, which explained 9% of the data variance, the loadings of *trans*-chlordane (TC), *cis*-chlordane (CC) and heptachlor were significant, indicating the same origin of these chlordane species. Chlordane, as a broad-spectrum pesticide, is still being extensively used in China for the control of termites in buildings, with an estimated amount of over 200 tons per year recently (Xu et al., 2004). Most abundant components in the mixture of technical chlordane are TC (13%), CC (11%), heptachlor (5%) and *trans*-nonachlor (5%) (Bidleman et al., 2002). Relatively higher levels of CC, TC, and heptachlor in air and soils were also observed by other recent studies in China (Xu et al., 2004; Li et al., 2006, 2008). PC3 could mostly represent the contamination of these chlordane-related compounds in the study area.

3.5. Potential biological effects of OCPs

As shown in Table 3, two widely used sediment quality guidelines, i.e. the effects range-low value (ERL) and effects range-median value (ERM) guidelines (Long et al., 1998; Long and MacDonald, 1995), as well as the threshold effects level (TEL) and probable effects level (PEL) guidelines (CCME, 2002) were applied to evaluate the possible ecotoxicological risks of OCPs in the study area. Concentration levels of DDT (*o, p′*- and *p, p′*-DDT) and *p, p′*-DDD were higher than ERL values at 4 sites (A21, B11, D8, and D16) and 1 site (A21), respectively. Meanwhile, these compounds also exceeded the TEL value at the same sites, but were significantly lower than the PEL and ERM values. The level of lindane was over the TEL value at 6 sites mostly located in the Bohai Bay and coastal regions of Bohai, whereas they were below the PEL value. This suggested that

Table 3
Assessments of potential biological risks of selected OCPs in surface sediments of Bohai using two sediment quality guidelines (SQG).

Chemical	Range (ng g^{-1})	ER-L[a]	Above ER-L (%)[e]	ER-M[b]	Above ER-M (%)[e]	TEL[c]	Above TEL (%)[e]	PEL[d]	Above PEL (%)[e]
o, p′- and *p, p′*-DDT	0.08–2.62	1	7	7	0	1.19	7	4.77	0
p, p′-DDE	0.06–1.03	2.2	0	27	0	2.07	0	374	0
p, p′-DDD	0.08–3.72	2	2	20	0	1.22	5	7.81	0
DDTs	0.24–5.67	1.58	20	46.1	0	3.89	4	51.7	0
γ–HCH	0.04–0.42	–	–	–	–	0.32	11	0.99	0
Chlordanes[f]	0.13–1.05	0.5	36	6	0	2.26	0	4.79	0

[a] Effect range-low value.
[b] Effect range-median value.
[c] Threshold effect level.
[d] Probable effect level.
[e] Percentage of samples above the corresponding levels.
[f] Sum of *cis*- and *trans*-chlordane.

the concentration levels of DDT (*o, p′*- and *p, p′*-DDT), *p, p′*-DDD and lindane at most sites were lower than the values that may cause adverse biological risk. For chlordanes and DDTs, although not exceed than ERM and PEL values, 20% and 36% of total sites in the study area (mostly observed in the Bohai Bay and coastal regions of Bohai) were higher than ERL values (Table 3), respectively, suggesting that the exposure of chlordanes and DDTs may cause ecological risk on the neighboring benthic organisms. Therefore, DDTs and chlordanes could be the two-main species of OCPs with more ecotoxicological concern in Bohai, especially in the Bohai Bay and coastal regions of the study area, while other OCPs in surface sediments would be less possible to cause adverse biological effect.

4. Conclusions

DDTs and HCHs could be the most important contaminants of OCPs in Bohai due to their relatively higher fractions in the total measured OCPs. Levels of DDTs and HCHs in this study were comparable to other riverine/estuarine and coastal regions in the world. The level of DDTs in the similar areas of Bohai was relatively lower than those reported in the previous studies. Compositional analysis of DDTs indicated that parent DDT was degraded significantly in our samples although there were some recent DDT inputs in the coastal areas mainly from the agricultural activity (e.g. dicofol), wastewater of chemical plants and antifouling paint. PCA results suggested that the distribution of these relatively "old" accumulated pesticides could be influenced by the distribution of organic matter due to the post-depositional sorption in addition to the input sources. Based on the sediment quality guidelines, DDTs and chlordanes would be more concerned for the ecotoxicological risk in Bohai.

Acknowledgements

This work was supported by the National Basic Research Program of China (973) (Nos. 2007CB407306 and 2005CB422304), the Natural Science Foundation of China (NSFC) (No: 40776062), and in part by Chinese Academy of Sciences (KZCX1-YW-06) and Shandong Province (2007GG2QT06018). We wish to thank the crew of R/V of Dong Fang Hong 2 of OUC and R/V of Ke Yan 59 for collecting samples. The anonymous reviewers should be sincerely appreciated for their constructive comments that greatly improved this study.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2009.07.070.

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