

# HCH and DDT in Sediments from Marine and Adjacent Riverine Areas of North Bohai Sea, China

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**Abstract** Residues of organochlorine pesticides (OCPs), hexachlorocyclohexanes (HCHs), and dichlorodiphenyltrichloroethanes (DDTs) and their environmental risks in surface sediments collected from marine and adjacent riverine/estuarine areas in the northern Bohai Sea, China, were investigated. Concentrations of  $\Sigma$ HCH and  $\Sigma$ DDT in sediments ranged from below detection (<LOD) to 1964.97 ng g<sup>-1</sup> dry wt (dw; mean, 92.51 ng g<sup>-1</sup> dw) and <LOD to 86.46 ng g<sup>-1</sup> dw (mean, 9.23 ng g<sup>-1</sup> dw), respectively. Concentrations of HCH and DDT were generally higher in marine than riverine sediments. Concentrations of HCH and DDT residues found in the present study were higher than those reported in marine and river/estuary sediments from other areas of the world. The source of HCH in sediments could be explained by the

large amount of historical use, while DDT seemed to be a combination of erosion of the weathered soils and long-range atmospheric transport. Concentrations of HCH in sediments from the study areas did not exceed sediment quality guidelines (SQGs), with the exception of  $\gamma$ -HCH. However, risks posed by concentrations of DDT observed in sediments were found to be moderate to high compared with those posed by consensus-based SQGs. Although the mean sedimentary concentrations of HCH and DDT found in the area of the northern Bohai Sea, China were lower than suggested SQGs in general, their concentrations in some locations were close to or above the SQGs for adverse effects in benthic organisms and, thus, remain a cause for concern.

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Synthetic organochlorine pesticides (OCPs) such as hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) are resistant to degradation by biological, photochemical, or chemical processes. These compounds can enter aquatic environments through effluent release, atmospheric deposition, runoff, etc., and can be transferred into food chains and, finally, accumulated in aquatic organisms (Zhou et al. 2008). As is well known, DDT was listed by the Stockholm Convention as 1 of 12 persistent organic pollutants (POPs) in 2004 (Zhu et al. 2005), and more recently,  $\alpha$ -HCH,  $\beta$ -HCH, and  $\gamma$ -HCH (lindane) were added to the list in 2009. Since HCH and DDT have an affinity for particulate matter and one of their major sinks is thought to be marine and riverine sediments (Bakan and Ariman 2004), rivers/estuaries can serve as important sources of organic contaminants to coastal marine environments and, also, act as sinks for fine-grain sediment and associated particle-reactive contaminants (Feng et al. 1998). There is growing concern over the

environmental conditions of riverine/estuarine and coastal areas, and it has been recognized that polluted sediments can cause adverse biological effects even when water criteria are not exceeded (Liu et al. 2003). Thus, they remain a cause for concern in aquatic ecosystems.

Technical HCH and DDT were widely used in China from the 1950s until their production was officially banned in 1983 (Gong et al. 2007), however, measurable concentrations of HCH and DDT still exist in environmental media in China (Liu et al. 2007; Wang et al. 2007a; He et al. 2008; Zhou et al. 2008; Hu et al. 2009). From a developing-country perspective, the lack of data and information about the sources, releases, and environmental levels of persistent organic pollutants (POPs) hampers effective assessment and risk evaluation of specific compounds and indicates a great need for research (Bouwman 2004). Therefore, investigation of the concentrations of historical residues and the risks they pose in sediments from coastal regions of the northern Bohai Sea would provide a valuable record of target contaminants in aquatic environments for these areas.

The Bohai Sea, together with nearby coast and rivers/estuaries, is a major commercial artery and has been a region of significant urbanization and industrialization (Liu et al. 2003). Its proximity to Beijing, the capitol of China, makes it one of the busiest seaways in the world. The Yellow, Liaohe, Haihe, Luanhe, and Dalinhe rivers are the major freshwater sources discharging directly into the Bohai Sea. Agriculture in these watersheds is intensive and highly productive, thus agrochemicals were used intensively to improve crop yields in these areas in the past, but their ultimate input into the coastal environment by these rivers has not been well characterized. The environmental quality in the estuarine and nearby coastal area has been severely affected by agricultural runoff and other anthropogenic inputs. Rapid social and economic development has caused this area to be contaminated with POPs (Liu et al. 2006). Because the Bohai Sea is semienclosed, water exchange with the Pacific Ocean is relatively slow, and in turn, pollutants tend to accumulate and concentrate for a long time. Hence the Bohai Sea is considered one of the most polluted marine environments in China (Zhang et al. 2009). Accordingly, the removal rate of OCPs from this semienclosed sea is slow, placing marine organisms at risk (Wu et al. 1999). Studies of contaminants in seawater, marine sediment, and biota have been conducted in the coastal areas of the Bohai Sea (Liu et al. 2007), but few studies have reported the residue levels and environmental risk of HCH and DDT from both marine and riverine/estuarine sediments. Therefore, supplementary data on sediments are urgently needed for a more comprehensive understanding of the environmental quality in different environmental media of the entire region.

Results presented here were collected as part of a larger systematic investigation of concentrations and environmental risks of HCH and DDT in sediments from marine and adjacent riverine/estuarine areas of the northern Bohai Sea. The purposes of this study were (1) to determine concentrations of HCH and DDT in sediments from coastal regions of the northern Bohai Sea and compare these concentrations to those in sediments from other areas, (2) to elucidate the relative proportions and possible sources of HCH and DDT in the sediments, and (3) to identify the potential environmental risk of HCH and DDT in sediments. This study of historical contamination and sources of HCH and DDT in sediments from coastal areas of northern Bohai Sea is significant for assessing contamination potential and, also, for improving management strategies.

## Materials and Methods

### Study Area and Sample Collection

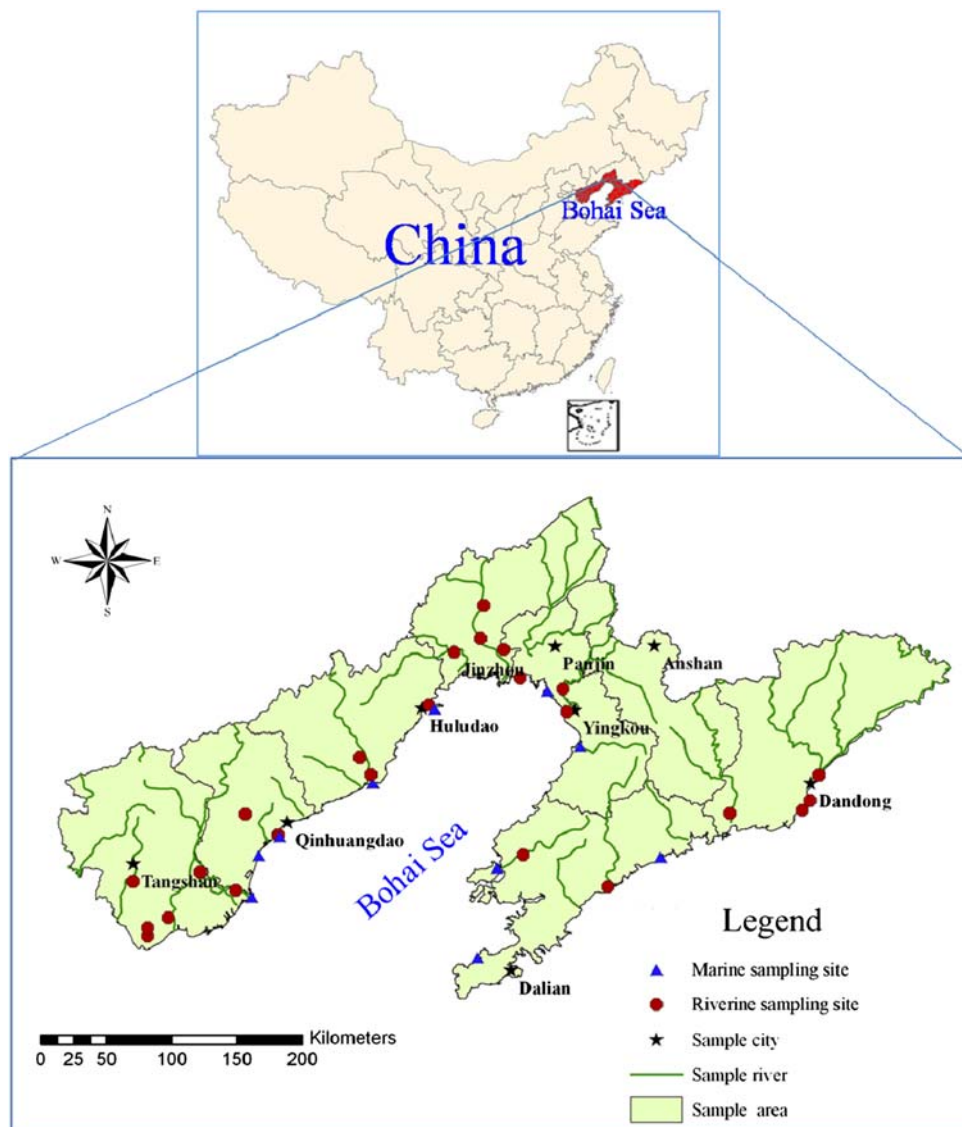
This study focused on the coastal and riverine/estuarine areas of the northern Bohai Sea, in northerneast China, including the following eight cities: Tangshan, Qinhuangdao, Huludao, Jinzhou, Panjin, Yinkou, Dalian, and Dandong. The Bohai Sea is a semienclosed coastal water body of the northwestern Pacific Ocean with a surface area of  $\sim 7.8 \times 10^4$  km<sup>2</sup>. Benefiting from rich resources and convenient transportation, the economic contribution of the Bohai Sea amounts to one-tenth of the gross domestic product of China. Economists call the zone around the Bohai Sea “the golden necklace” of northern China.

For this survey, 10 marine sediments and 25 lake sediments were collected along the marine and adjacent riverine/estuarine areas of the northern Bohai Sea, China, in May 2008 (Fig. 1). Drainage areas of these rivers are important agricultural and chemical production areas (Wang et al. 2007a). Throughout the survey, a global positioning system (GPS) was used to locate and map all of the sampling sites. Surface sediments (top 10-cm layer) were collected using a trowel from the sedimentation basin of the bed close to the bank. Representative samples were prepared by mixing five subsamples from an area of about 5 m<sup>2</sup>. Wet samples ( $\sim 1$  kg) were wrapped in polyethylene boxes and transported to the laboratory, where they were homogenized, freeze-dried, ground with a mortar and pestle, sieved using a 2-mm sieve, and stored at 4°C in precleaned glass jars until analysis.

### Extraction, Cleanup, and Quantification

HCH and DDT were quantified by solid–liquid extraction followed by quantification by gas chromatography (GC)

**Fig. 1** Study area and sampling locations along the coast of the northern Bohai Sea, China



equipped with electron capture detection (Hu et al. 2009). Residues were extracted from soil with *n*-hexane and dichloromethane (J. T. Baker, HPLC grade). Anhydrous sodium sulfate (analytical grade) and silica gel (60 mesh, for column chromatography) were activated at 180°C for 24 h. Solid-phase extraction (SPE; 6 ml; Supelco, Bellefonte, PA, USA) cartridges containing 1 g of fluorisil were washed with 10 ml of *n*-hexane before use. Each sediment sample (5.0 g dry weight) was mixed with 1 g anhydrous sodium sulfate. One milliliter of 2,4,5,6-tetrachloro-*m*-xylene (TCMX) at the concentration of 0.08 µg ml<sup>-1</sup> was added. The mixture was extracted twice with 35 ml of hexane/dichloromethane (1/1, v/v) by ultrasonication for 60 min and then centrifuged. The supernatant was transferred to a K-D flask, concentrated down to about 2 ml by rotary evaporation, and further purified with SPE cartridges loaded with 1 g silica gel and 1 g anhydrous sodium

sulfate. Analytes were eluted with 20 ml of hexane/dichloromethane (7/3, v/v). Eluent was concentrated to a final volume of 1 ml for GC analysis. Reagent blanks were analyzed simultaneously with experimental samples.

A mixed standard solution containing  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -HCH isomers, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT at 1 mg g<sup>-1</sup> per compound was obtained from the National Research Center for Certified Reference Materials of China. The mass of analytes in extracts was quantified by use of an internal standard (TCMX; Supelco, Bellefonte, PA, USA). An Agilent 6890 gas chromatograph (GC) equipped with <sup>63</sup>Ni electron capture detector ( $\mu$ ECD) (Agilent Technologies, Wilmington, DE, USA) was used for identification and quantification of HCH and DDT isomers. The column used was a HP-5 silica capillary column, 30 m  $\times$  0.32-mm i.d  $\times$  0.25- $\mu$ m film thickness. The GC- $\mu$ ECD was operated in splitless injection mode

with ultrapure nitrogen as the carrier gas and the makeup gas. The injector and detector temperatures were 220 and 300°C, respectively. The oven temperature was initially set at 100°C with a 2-min hold, ramped at 10°C min<sup>-1</sup> to 160°C with a 2-min hold, 4°C min<sup>-1</sup> to 230°C with a 5-min hold, and 10°C min<sup>-1</sup> to 270°C with a 2-min hold. Four HCH isomers ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ ) and four DDT homologues (*p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT) were identified by retention time matched to standards and were quantified based on peak area. Concentrations of  $\sum$ HCH and  $\sum$ DDT were calculated by summing the four HCH isomers and four DDT metabolites, respectively, and are reported on a dry weight (dw) basis.

For quality assurance and control, procedural blanks and matrixes spiked with the standard solution were analyzed. None of the target compounds were detected in the procedural blanks. All solvents used were distilled in glass (PR grade) and were checked for interferences or contamination prior to use. Recoveries of four HCH isomers ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ ) and four DDT homologues (*p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT) spiked to sediment were 73.3%, 90.3%, 75.8%, and 85.6% and 80.0%, 93.8%, 95.4%, and 96.2%, respectively. Extraction efficiency, as indicated by recovery of the surrogate standards (TCMX), was 75 ± 10%. Limits of detection (LOD) were defined as three times the signal-to-noise ratio (S/N). The detection limit ranged from 0.05 to 0.20 ng g<sup>-1</sup> dw. GC analysis was repeated twice for each replicate sample and the relative standard deviation (RSD) of replicate analyses was <10%.

## Data Analysis

ArcGis (ESRI, US) was used for mapping the sampling sites. T-test was used to identify the differences in HCH and DDT concentrations between marine and riverine sediments using SPSS 11.5 for Windows.

## Results and Discussion

### Concentrations of HCH and DDT in Sediments

Mean concentrations of  $\sum$ HCH and  $\sum$ DDT were 92.51 and 9.23 ng g<sup>-1</sup> dw, ranging from <LOD to 1964.97 ng g<sup>-1</sup> dw and <LOD to 86.46 ng g<sup>-1</sup> dw, respectively (Table 1). Concentrations of  $\sum$ HCH were higher than those of  $\sum$ DDT, which accounted for 91% of the total HCH and DDT concentrations. This could be a result of the historical production and use of HCH in this region, as China was the world's largest HCH user. Documents about the production and pesticide application history are not available, however, based on the official application history of HCH and DDT in China and the statements of local farmers, it is likely that the

**Table 1** Concentrations (ng g<sup>-1</sup> dw)<sup>a</sup> of HCH and DDT isomers in sediments

	Mean	SD	Min	Max	Median	Detection rate (%)
$\alpha$ -HCH	0.61	1.66	<LOD	8.92	0.00	34.29
$\beta$ -HCH	7.27	11.87	<LOD	51.67	1.69	77.14
$\gamma$ -HCH	0.91	2.16	<LOD	9.24	0.00	31.43
$\delta$ -HCH	83.71	324.64	<LOD	1920.9	0.30	82.86
$\sum$ HCH <sup>b</sup>	92.51	330.44	<LOD	1964.97	9.07	97.14
<i>p,p'</i> -DDE	1.75	2.3	<LOD	10.25	0.65	85.71
<i>p,p'</i> -DDD	1.24	2.46	<LOD	11.59	0.45	54.29
<i>o,p'</i> -DDT	0.79	2.37	<LD	13.16	0.00	22.86
<i>p,p'</i> -DDT	5.45	10.89	<LOD	59.49	2.22	88.57
$\sum$ DDT <sup>c</sup>	9.23	15.83	<LOD	86.46	5.21	97.14

<sup>a</sup> Concentration mean, standard deviation (SD), minimum, maximum, and median were calculated assuming less than LOD (limits of detection) to be equal to zero for statistical purpose

<sup>b</sup>  $\sum$ HCH:  $\alpha$ -HCH +  $\beta$ -HCH +  $\gamma$ -HCH +  $\delta$ -HCH

<sup>c</sup>  $\sum$ DDT: *p,p'*-DDE + *p,p'*-DDD + *o,p'*-DDT + *p,p'*-DDT

historical application amount of HCH in this region was relatively greater than that of DDT. HCH isomers have been identified as a worldwide contaminant (Doong et al. 2002). The properties of higher water solubility, vapor pressure, and biodegradability, and lower lipophilicity and particle affinity, of HCH relative to DDT (Yang et al. 2005a) could account for the higher concentrations of HCH in sediments. These results were inconsistent with previous observations on OCP residues in freshwater sediments in China due to the difference in physicochemical and biochemical characteristics (Tang et al. 2007). Detection rates of both  $\sum$ HCH and  $\sum$ DDT in sediments were nearly 100%. The great frequency of HCH detection in sediments also indicated that the contamination was widespread in this study area.

Concentrations and patterns of OCPs distribution could be influenced by the chemical-physical properties of residue compounds and the environmental conditions. Topography, redox potential, and hydrodynamic condition as well as other factors all play important roles in controlling the distribution and fate of OCPs (Su et al. 2006). Looking for the site-specific distribution of the target compounds, concentrations of HCH and DDT in marine and riverine sediments were compared (Table 2). In marine sediments, mean concentrations of  $\sum$ HCH and  $\sum$ DDT were found to be 214.87 and 18.55 ng g<sup>-1</sup> dw, respectively. In riverine sediments, the  $\sum$ HCH and  $\sum$ DDT were detected as mean of 43.56 and 5.51 ng g<sup>-1</sup> dw, respectively. Concentrations of  $\gamma$ -HCH,  $\delta$ -HCH,  $\sum$ HCH, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, and  $\sum$ DDT in marine sediments were significantly ( $p < 0.05$ ) higher than those of riverine sediments. After the ban on the production and application of HCH and DDT was enforced, the input

**Table 2** Mean (ng g<sup>-1</sup> dw) and *t*-test of HCH and DDT between marine and riverine sediments

	$\alpha$ -HCH	$\beta$ -HCH	$\gamma$ -HCH	$\delta$ -HCH	$\sum$ HCH	<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	$\sum$ DDT
Marine ( <i>n</i> = 10)	0.94	5.1	1.68	207.16	214.87	2.11	3.04	2.35	11.04	18.55
Riverine ( <i>n</i> = 25)	0.48	8.14	0.61	34.33	43.56	1.61	0.52	0.16	3.22	5.51
<i>t</i>	0.74	-0.68	1.34	1.45	1.41	0.58	3.06	2.68	2.00	2.34
<i>p</i> -value	0.06	0.69	0.04*	0.00**	0.00**	0.25	0.00**	0.00**	0.02*	0.01**

Note: Difference is significant \* at the 0.05 level and \*\* at the 0.01 level

through industrial discharge and soil erosion from agriculture soils with higher HCH and DDT concentrations to lake/river sediments was decreased, while the input from lake/river flow to estuary and marine environments may have served as a continuing source of the higher concentrations of HCH and DDT in marine sediments. The predominance of HCH and DDT residues in marine sediments indicated that marine sediments were more contaminated than were riverine sediments. Greater water discharge and/or sediment loads and biogeochemical processes such as biodegradation and volatilization may be responsible for the low concentrations detected in riverine sediments (Wu et al. 1999). The observed variation in concentrations of  $\sum$ HCH and  $\sum$ DDT in marine and riverine sediments is likely caused by high rates of contaminant influx into estuaries through the rivers and drainage of contaminated water from the surrounding agricultural fields. Also contributing to this is the abiotic degradation of pesticides influenced by various physicochemical characteristics of

the sediments, as well as microbial growth (Bakan and Ariman 2004).

#### Comparison of HCH and DDT in Sediments from Other Areas

In general, concentrations of HCH and DDT in sediments along the coast of the northern Bohai Sea, China, were higher than those in sediments reported from other areas (Table 3). Among the Chinese marine and riverine sediments, concentrations of  $\sum$ HCH in sediments from this study were the highest, with only those from Dagu Drainage River and Liaodong Bay being comparable (Yang et al. 2005b; Lu et al. 2008). Compared with other regions of the world, the mean concentration of  $\sum$ HCH in sediment was significantly higher than those in sediments from other areas (Table 3). The mean  $\sum$ DDT concentrations observed in this study were lower than the reported

**Table 3** Comparison of HCH and DDT in sediments from other coastal and river/estuary regions (ng g<sup>-1</sup> dw)

Location	No.	Year	$\sum$ HCH	$\sum$ DDT	Reference
Lake Dongting, China	8	2004	0.21–9.59	ND–10.15	Qian et al. (2006)
Catchment of Yangtze River, China	13	2005	0.10–21.10 (4.03)	0.79–35.61 (6.93)	Tang et al. (2007)
Liaodong Bay, China	3	2006	20.1–103.0 (68.6)	7.7–76.9 (42.8)	Lu et al. (2008)
Daliaohe River, China	12	2005	1.86–21.48	0.5–2.81	Wang et al. (2007b)
Haihe River, China	40	2003	1.88–18.76 (7.33)	0.32–80.18 (15.94)	Yang et al. (2005a)
Dagu Drainage River, China	9	2003	33.24–141.03 (87.74)	3.60–83.49 (35.52)	Yang et al. (2005a)
Yangtze estuary, China	10	2004	0.5–17.5 (6.0)	0.9–33.1 (8.2)	Liu et al. (2008)
Pearl River estuary, China	20	1998	0.28–1.23 (0.68)	1.36–8.99 (2.84)	Hong et al. 1999)
Songhuajiang River, China	10	2007	2.42–7.95	0.14–5.12	He et al. (2008)
Daya Bay, China	13	2003	1.79–4.64 (2.72)	8.69–34.34 (19.05)	Wang et al. (2008)
Victoria Harbour, Hong Kong	10	1994	ND–2.3 (0.5)	1.38–30.3 (9.10)	Hong et al. 1995)
Wu-Shi River estuary, Taiwan	19	1998	0.99–14.5 (3.79)	0.53–11.4 (2.51)	Doong et al. (2002)
Ulsan Bay, Korea	32	2000	0.02–4.55 (0.64)	0.02–41.9 (3.34)	Khim et al. (2001)
Andes Mountain lakes	17	1999	<0.005–0.23	0.019–4.1	Borghini et al. (2005)
James Ross Island, Antarctica	25	2005	0.14–0.76	0.19–1.15	Klanova et al. (2008)
Black Sea coast of Samsun, Turkey	14	2000	5–16	18–55	Bakan and Ariman (2004)
Coast of Bohai Sea, China	35	2008	<LOD–1964.97 (92.51)	<LOD–86.46 (9.23)	This study

ND under detectable limit, LOD limit of detection

mean  $\sum$ DDT concentrations in sediments from Liaodong Bay, Haihe River, Dagu Drainage River, and Daya Bay. However, the mean  $\sum$ DDT concentration was higher than in the other areas in China (Table 3). The mean  $\sum$ DDT concentration observed in this study was also higher than those reported for Ulsan Bay Korea, Mountain Andean Lakes, James Ross Island, Antarctica, and the Black Sea coast of Samsun, Turkey (Table 3). The relatively higher concentrations of HCH and DDT in sediments along the coast of the northern Bohai Sea than in sediments from other areas is most likely due to higher historical applications of HCH and DDT in this region. According to our investigation, agriculture in this region is intensive and highly productive, thus agrochemicals were used intensively to improve crop yields in this area in the past.

#### Relative Proportions of HCH and DDT Components and Possible Sources

HCH is one of the most widely used and most readily detected OCPs in environmental samples. It was used either as the technical HCH mixture (a formulation dominated by the  $\alpha$ -isomer) or as lindane (a formulation containing almost 100% of the  $\gamma$ -isomer) (Chrysikou et al. 2008). The typical technical HCH generally contains 55–80%  $\alpha$ -HCH, 5–14%  $\beta$ -HCH, 8–15%  $\gamma$ -HCH, and 2–16%  $\delta$ -HCH (Yang et al. 2005b). The physicochemical properties of these HCH isomers are different, which leads to differential partitioning in the environment. Among the HCH isomers,  $\alpha$ -HCH is more likely to partition to the air and transport over long distances, while  $\beta$ -HCH is more resistant to hydrolysis and environmental degradation and is the dominant isomer in soils, animal tissue, and fluids (Willett et al. 1998). After long-term migration and transformation,  $\beta$ -HCH is generally the dominant isomer in sediments of rivers or estuaries (Yang et al. 2005b). In this study, the relative proportions of  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -HCH were 1%, 8%, 1%, and 90%, respectively, with a greater proportion of  $\delta$ -HCH observed. This pattern is different from the relative proportions of typical technical HCH.  $\delta$ -HCH has the longest half-life of HCH isomers (Satpathy et al. 1997). Thus, it was the most heavily polluted isomer, although its original level was not higher.  $\beta$ -HCH is the least water-soluble isomer of HCH, has a higher vapor pressure and octanol/water partitioning coefficient, and is relatively resistant to microbial degradation, which makes it the most stable isomer (Willett et al. 1998; Yang et al. 2005b). After a long period of weathering,  $\alpha$ - and  $\gamma$ -HCH can be transformed into  $\beta$ -HCH (Yang et al. 2005a). The observation of a greater relative proportion of  $\beta$ -HCH (8% of  $\sum$ HCH) than  $\alpha$ - and  $\gamma$ -HCH indicated that the HCH was mainly due to historical use (Toan et al. 2007) and that

technical HCH has not recently been used in this region. The relatively small proportion of  $\gamma$ -HCH further supports the conclusion that there are few new inputs of HCH.

Because the use of DDT in China was banned in the early 1980s, the presence of DDT in the sediment was thought to be predominantly from historical usage. DDT undergoes slow degradation to DDD and DDE in the natural environment by chemical and biological processes (Yuan et al. 2001). The ratios of various degradation products may, therefore, reflect some of the effects of environmental conditions on the degradation process (Yuan et al. 2001). The ranking of relative concentrations of DDT metabolites were found to be in the order  $p,p'$ -DDT (59%),  $p,p'$ -DDE (19%),  $p,p'$ -DDD (13%),  $o,p'$ -DDT (9%). The relatively high concentration of DDT relative to DDD and DDE in these samples indicated either that there was minimal degradation of DDT in this region or that there has been more recent input of technical DDT at some sampling locations (Yuan et al. 2001). One possibility is that, after the ban on the use of DDT in agricultural production, the input of agricultural application was cut, while weathered agricultural soils and atmospheric deposition might have served as continuing input sources (Villa et al. 2003; Gioia et al. 2005). It has been reported that washout of DDT from soils was a process which possibly caused increasing concentrations of DDT in recent years (Santschi et al. 2001). Coastal cities around the Bohai Sea experienced rapid economic development and large-scale land reclamation in the early 1990s, which has led to serious soil erosion along the Liaohe and Luanhe rivers. Therefore, DDT residues in agricultural soil transported by enhanced surface runoff to the sediments may be the major reason for the increase in DDT concentrations in riverine and marine sediments. As a whole, results obtained in this study indicate that DDT in sediments may be derived from aged and weathered agricultural soils and transported by surface runoff and atmospheric deposition to the marine and riverine sediments. The predominance of DDE over DDD in these sediments indicates reductive dechlorination of DDT to DDE under anaerobic conditions. Differences in the relative concentrations of DDD and DDE in the sediment samples indicated different environmental conditions under which DDT was degraded. In addition, the Bohai Sea is an open system with active hydrodynamic processes. The aerobic conditions in marine and riverine environment may favor the microbial metabolization of DDT to DDE, which would result in the greater proportions of DDE and lesser proportions of DDD (Yuan et al. 2001).

#### Environmental Risk Assessment of HCH and DDT in Sediments

The status and trends of HCH and DDT and potential sources are significant factors in the management and

long-term conservation of marine ecosystems (Szlinger-Richert et al. 2008). The ecological effects of pesticides are varied and often complex. Effects at the organism or ecosystem level are usually considered to be an early warning indicator of potential human health impacts (Qian et al. 2006). Due to the complex nature of sediments, it is difficult to determine the potential effects of pollutants including HCH and DDT in sediments. Despite the fact that many studies have been conducted, there is no uniform standard available for sediments (McCauley et al. 2000). In China, no environmental standards have been established for HCH or DDT in marine or riverine sediments. Therefore, in this study, the environmental risks of HCH and DDT in sediments were compared to published numerical sediment quality guidelines (SQGs) including threshold-effect concentrations (TECs) and probable-effect concentrations (PECs) (MacDonald et al. 2000; Tang et al. 2007). It is understood that these published values are not accurate representations of the probability of actual effects and may overestimate the potential risks. However, in the absence of other criteria, they can be used as a reference point to indicate the relative potential for effects at this time.

Concentrations of HCH and DDT in marine, riverine, and all sediments were compared to SQGs (Table 4). Overall, concentrations of HCH and DDT in marine sediments posed relatively greater environmental risks compared to riverine sediments. Concentrations of  $\alpha$ -HCH in most sediments were found to be lower than the lowest effect level (LEL). Although SQGs for  $\gamma$ -HCH varied depending on the guidelines, mean concentrations of  $\gamma$ -HCH (1.68 ng g<sup>-1</sup> dw) in marine sediment exceed some TEC (0.94 ng g<sup>-1</sup> dw TEL) and PEC (1.38 ng g<sup>-1</sup> dw PEL) values, indicating that there is the potential for adverse effects on some species inhabiting sediments (Sarkar et al. 2008). In general, the concentrations of  $\alpha$ - and  $\gamma$ -HCH in most sediments from the riverine and

coastal areas of the northern Bohai Sea were lower than the suggested guidelines, thus the current concentrations of these isomers present little risk to marine benthic organisms.  $\delta$ - and  $\beta$ -HCH were the predominant isomers, representing 90% and 8% of the  $\Sigma$ HCH, respectively, observed in this study, but there are no criteria established for these isomers in sediments. While the exact potential risks of  $\delta$ - and  $\beta$ -HCH are unknown, they must still be considered to represent a potential concern when assessing sediments. Meanwhile, the potential risk caused by the measured concentrations of DDT was found to be relatively high compared to that of HCH isomers. For example, concentrations of DDT for over 80% and 60% of marine sediment samples exceeded the ERL (effect range low; adverse effects in 10% of tests in the Biological Effects Database) and ERM (effect range median; adverse effects in 50% of tests), respectively. As is well known, the ERL values indicated possible adverse biological effects on aquatic organisms and the ERM values suggested a good possibility of the posing of detrimental biological effects on aquatic organisms (Long and Morgan 1991; Tang et al. 2007). The potential for effects of DDT in these sediments was considered to be moderate to high at this time. Concentrations of  $\Sigma$ DDT also exceeded the ERM in some riverine sediments of the Liaohe, Luanhe, and Yalu rivers. In general, the observed concentrations of DDT pollution were sufficient to potentially cause adverse effects on benthic invertebrates in both marine and riverine sediments, especially at locations where the highest concentrations of DDT were observed. Continuing research effort is necessary to establish the most appropriate indicators to be used in describing coastal conditions and also to provide the appropriate weighting factors to be combined for an overall assessment of OCPs including HCH and DDT in marine and riverine areas in China (EPA 2001).

**Table 4** Comparison between HCH and DDT levels in this study and sediment concentrations as guideline values (ng g<sup>-1</sup> dw)

OCP	TEC				PEC				OCPs in sediments: range (mean)		
	TEL	LEL	ERL	CB-TEC	PEL	SEL	ERM	CB-PEC	Marine ( <i>n</i> = 10)	Riverine ( <i>n</i> = 25)	All samples ( <i>n</i> = 35)
$\alpha$ -HCH	NA	6	NA	NA	NA	NA	NA	NA	ND–8.92 (0.94)	0.26–3.42 (0.48)	ND–8.92 (0.61)
$\gamma$ -HCH	0.94	3	NA	2.37	1.38	10	NA	4.99	ND–9.24 (1.68)	ND–7.56 (0.61)	ND–9.24 (0.91)
DDE	1.42	5	2	3.16	6.75	190	15	31.3	ND–10.25 (2.11)	ND–6.27 (1.61)	ND–10.25 (1.75)
DDD	3.54	8	2	4.88	8.51	60	20	28.0	ND–11.59 (3.04)	ND–2.60 (0.52)	ND–11.59 (1.24)
DDT	NA	8	1	4.16	NA	710	7	62.9	ND–72.65 (13.09)	ND–33.26 (3.50)	ND–72.65 (6.24)
$\Sigma$ DDT	7	7	3	5.28	4450	120	350	572	0.97–86.46 (18.55)	ND–42.13 (5.51)	ND–86.46 (9.23)

TEC threshold-effect concentration, PEC probable-effect concentration, TEL threshold-effect level, PEL probable-effect level, LEL lowest-effect level, SEL severe-effect level, ERL effect range low, ERM effects range median, CB-TEC consensus-based TEC, CB-PEC consensus-based PEC (MacDonald et al. 2000; Tang et al. 2007), NA not available, ND under detection limit. ERL: the concentration of a contaminant that will result in adverse effects in ~10% of tests in the Biological Effects Database. ERM: the concentration of a contaminant that will result in adverse effects in ~50% of tests. ERL and ERM values are from Long and Morgan (1991) and Long et al. (1995)

## Conclusions

Concentrations of HCH and DDT were higher in marine than in river sediments. Concentrations of HCH and DDT in sediments of the northern Bohai Sea were higher than in other coastal regions. The origin of HCH in sediments was primarily historical use, while DDT enters the sea from a combination of erosion of weathered soils and long-range atmospheric transport. Concentrations of  $\alpha$ - and  $\gamma$ -HCH in the study area did not exceed benchmark values and are thus of little concern, while the potential risk of  $\delta$ - and  $\beta$ -HCH is still of concern. Risks posed by the concentrations of DDT observed in sediments were deemed to be moderate to high, warranting a continuing research effort.

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