

Selected current-use pesticides (CUPs) in coastal and offshore sediments of Bohai and Yellow seas

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Received: 21 November 2013 / Accepted: 10 February 2014 / Published online: 2 March 2014
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Abstract China is one of the largest producers, consumers, and traders for pesticides in the world. Currently, there are more than 600 pesticide-active substances registered in China, whereas few studies were conducted to improve our understanding of the occurrence and environmental impact of current-use pesticides (CUPs) in China's environment. In this work, 72 surface sediment samples were taken from the coastal and offshore of Bohai and Yellow seas and were analyzed for six CUPs (trifluralin, dacthal, quintozone, endosulfan, chlorpyrifos, and dicofol) and two metabolites (pentachloroanisole and endosulfan sulfate). Sediment samples were categorized as estuarine or near-shore sediments (Laizhou Bay, Taozi Bay, Sishili Bay, and Jiaozhou Bay) and offshore sediments. Trifluralin, α -endosulfan, endosulfan sulfate, chlorpyrifos, dicofol, and

pentachloroanisole were detected in more than 60 % of the samples. Dicofol was the predominant compound with concentrations mostly higher than 100 pg/g dry weight (dw) with the highest concentration of 18,000 pg/g dw. Concentrations of other compounds were mainly below 100 pg/g dw. CUP levels were much lower than the sediment screening benchmark calculated. The highest levels of α -endosulfan, endosulfan sulfate, trifluralin, and chlorpyrifos existed at Laizhou Bay, whereas pentachloroanisole and dicofol had highest mean concentrations at Jiaozhou Bay. Generally, no correlation between pesticide concentrations and total organic carbon was observed either for offshore samples or for near-shore samples.

Keywords Current-use pesticides · Bohai Sea · Yellow Sea · Sediment

Responsible editor: Ester Heath

Electronic supplementary material The online version of this article (doi:10.1007/s11356-014-2648-7) contains supplementary material, which is available to authorized users.

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Introduction

A large quantity of pesticides is used to control weeds, diseases, or insects and parts of these chemicals are entering into the environment and ecosystem inevitably. For example, it was reported that over two million tons of pesticides are used in agriculture worldwide every year (USEPA 2011). Some pesticides pose risk to both humans and sensitive ecosystems and are undergoing regional even global transport for their persistence in the environment and semivolatile property (Wania et al. 1998; Hoferkamp et al. 2010). Due to the properties of persistence, bioaccumulation, adverse effects including human and ecotoxicity, as well as potential for long-range transport (LRT), a dozen of pesticides are listed as persistent organic pollutants (POPs) under the Stockholm Convention and are banned for agricultural use worldwide (www.pops.int). However, some of the current-use pesticides possess parts of the POPs' properties and are still in use widely around the world and thus are of great concern.

After released into the environment, pesticides undergo a series of physicochemical processes and can transport to coastal and marine environment and even the polar region through riverine discharge and atmospheric transport (Hoferkamp et al. 2010). Through atmospheric transport, these chemicals reach seawater via dry deposition, wet deposition, and air-sea gas exchange (Bidleman and McConnell 1995; Bidleman 1999). Once they reached seawater, pesticides can undergo sedimentation processes by absorbing on particles and/or can be transported to the deep sea or ocean far away from their source regions (Dachs et al. 1996, 2002). Pesticides associated with sediment would be bioaccumulated by benthic invertebrates, which play a key role in the transfer of aquatic contaminants to higher trophic levels (Reynoldson 1987; DiPinto 1996). Re-emission of pesticides from sediment/surface seawater could happen since primary emission dramatically decreases or ceases (e.g., in the case of a global ban of use), making the ocean as secondary sources of pesticides (Lohmann et al. 2007; Breivik et al. 2004).

China is the largest producer and user of pesticide in the world. Until 2008, more than 600 pesticide active ingredients are produced in China with a production of approximately one million tons/year (He 2008). From January to November 2012, the total production of pesticides was 3.2 million tons in China, while the pesticide market demands for 2013 in China were estimated to be around 1 million tons (Shu and Zhao 2013). In the past 20 years, investigations on legacy organochlorine pesticides (OCPs) (such as dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs)) in China's coastal environment have been well documented, and the levels, distributions, and sources of legacy OCPs in sediment and biota samples and their risk assessments were widely reported (Zhang et al. 2002, 2009; Yang et al. 2005; Hu et al. 2009). However, there are few studies on the occurrence of CUPs (mainly focusing on organophosphorous and pyrethroid insecticides) in the terrestrial and coastal water samples and urban waterway sediment samples (Zhang et al. 2002; Mehler et al. 2011; Wang et al. 2012a). CUPs in coastal sediment samples were rarely reported, especially for the open sea region.

In the present study, surface sediments from the Bohai and Yellow seas were analyzed for six CUPs (trifluralin, dacthal, quintozone, endosulfan, chlorpyrifos, and dicofol) and two metabolites (pentachloroanisole and endosulfan sulfate). The physicochemical properties of these target compounds are given in Table 1. Surveys and long-term monitoring studies have demonstrated the presence of these CUPs in the Arctic environment (Hoferkamp et al. 2010; Zhong et al. 2012a), which suggests the potential

Table 1 Physicochemical properties of target compounds at 298 K

	Class	HLC (Pa m ³ /mol)	log K_{oa}	P_L (Pa)	S_L (mol/m ³)	log K_{ow}	log K_{oc}
α -Endosulfan	Insecticide	0.82 (Cetin et al. 2006)	8.5 (Staudinger and Roberts 2001)	0.0044 (Staudinger and Roberts 2001)	0.0063 (Staudinger and Roberts 2001)	4.9	4.1
β -Endosulfan	Insecticide	0.066 (Cetin et al. 2006)	8.6 (Staudinger and Roberts 2001)	0.0040 (Staudinger and Roberts 2001)	0.089 (Staudinger and Roberts 2001)	4.8	4.1
Chlorpyrifos	Insecticide	3.6 (Cetin et al. 2006)	8.9	0.0040	0.0010	5.0	3.7
Dacthal	Herbicide	0.22	8.3	0.0064	0.0015	4.3	3.7
Dicofol	Insecticide	0.0025	10	0.00018	0.78	5.0	3.7
Quintozone	Fungicide	4.4	7.4	0.0036	0.0015	4.6	4.0
Trifluralin	Herbicide	11 (Staudinger and Roberts 2001)	7.7	0.010	0.00060	5.3	4.2
Pentachloroanisole	Metabolite	2.9 (Nowell et al. 1999)	8.0	0.046	0.0013	5.7 (Nowell et al. 1999)	4.1
Endosulfan Sulfate	Metabolite	0.0033	8.5	0.0039	0.0011	3.7	3.1

Unless cited papers were given, all the Henry's law constants (HLC), log K_{oa} , vapor pressure (P_L), water solubility (S_L), log K_{ow} , and log K_{oc} values are collected from the database EPI Suite™ (USEPA 2012), which is owned by the US Environmental Protection Agency

for long-range transport. Trifluralin, dacthal, endosulfan, chlorpyrifos, and dicofol also have been detected in marine air and seawater of East Asia (Zhong et al. 2012a). The Bohai and Yellow seas border on important agricultural regions (Liaoning, Hebei, Shandong, and Jiangsu provinces and Tianjin Municipality) of China, and these regions account for 6 % of the total land area of China but 23.5 % of the total pesticide consumption of the country (www.stats.gov.cn). Jiangsu and Shandong provinces were the first and second largest pesticide producers of China in 2011, of which they account for 29 and 20 % of the total production, respectively (www.chinapesticide.gov.cn). Several important rivers with huge amounts of runoff and sediment load are emptying into the Bohai and Yellow seas, including Liaohe River (drainage area 2.2×10^5 km²), Haihe River (drainage area 2.7×10^5 km²), Yellow River (drainage area 7.5×10^5 km²), and Yangtze River (drainage area 1.8×10^6 km²). Concentrations, distributions, and potential ecological risk of these CUPs in Bohai and Yellow sea sediments are discussed in this paper. These results will facilitate further research on the environmental impact and fate of CUPs in these regions.

Materials and methods

Sample collection

Seventy-two surface sediment samples were collected from the Bohai and Yellow seas with a stainless steel grab sampler in September 2009 for Laizhou Bay at the south of Bohai Sea (top 10 cm sediment collected) and with a stainless steel box corer in April 2010 for other sampling areas (top 5 cm sediment collected). The sediment samples were stored at -20°C prior to freeze-drying. Sampling sites are shown in Fig. 1.

Extraction, clean-up, and analysis

Freeze-dried and homogenized sediments (10 g) were Soxhlet-extracted with dichloromethane (DCM) for 16 h, and activated granulated copper was used for desulfurization; 500 pg of d^{14} -Trifluralin was added as surrogate before extraction. The extracts were concentrated to 2 mL using a rotary evaporator and further cleaned on a 2.5-g 10 % water-deactivated silica gel (mesh size 70 to 140) column topped with 3 g anhydrous granulated sodium sulfate. The column was eluted with 20 mL hexane (fraction 1), followed by

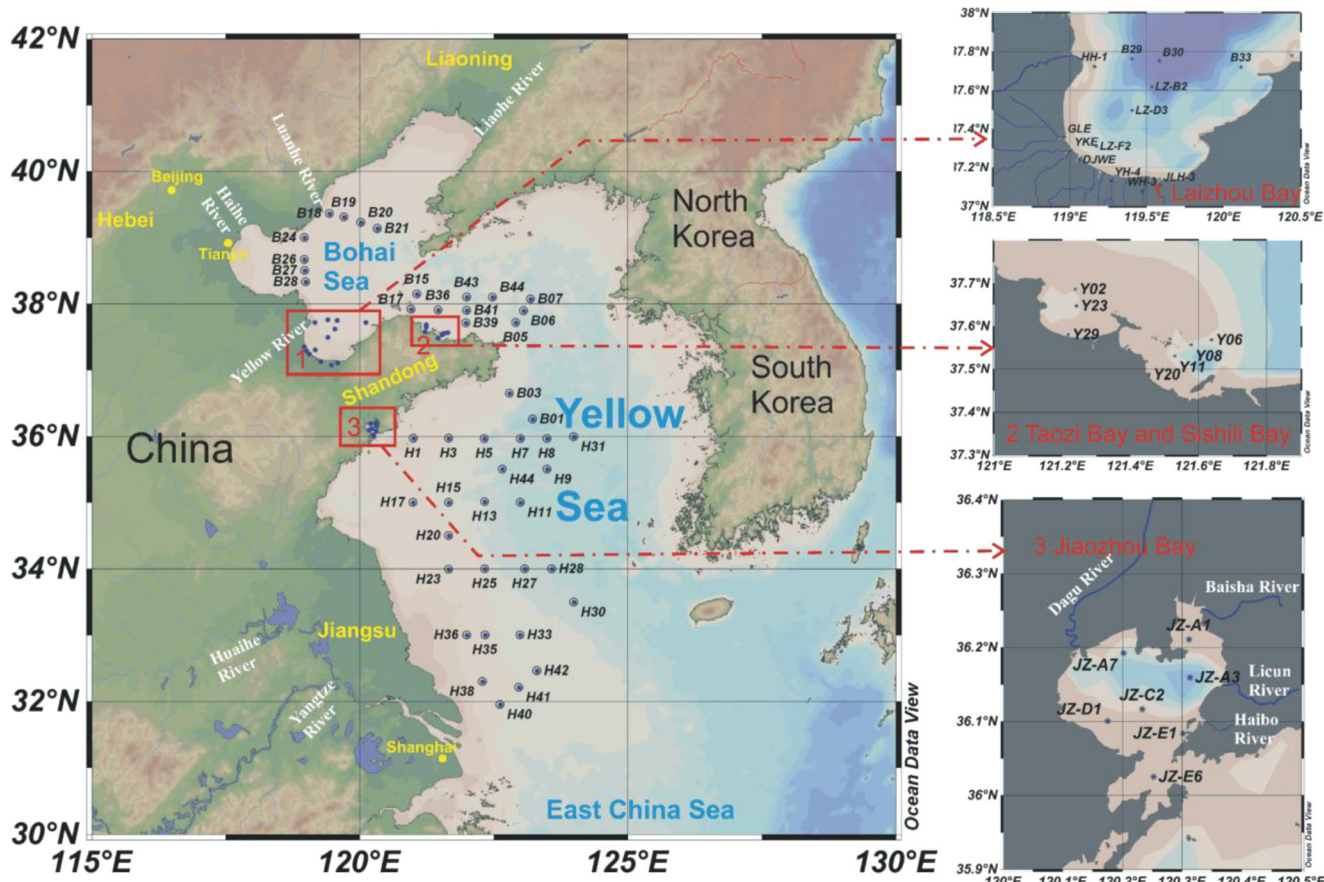


Fig. 1 Location of sampling sites at the Bohai and Yellow seas

30 mL dichloromethane/acetone (1:1) (fraction 2). Each fraction was evaporated to a final volume of ~30 μ L. The solvent of fraction 2 was changed to hexane during evaporation; 500 pg of ^{13}C -PCB 141 was added to both fractions as an internal standard.

Both fractions were analyzed with a GC/MS system (6890 GC/5973 MSD) in electron capture negative chemical ionization mode (ECNCI) equipped with an HP-5MS column (30 m \times 0.25 mm i.d. \times 0.25 μ m film thickness, J&W Scientific). Methane was used as the ionization gas. The injector was operated in pulsed-splitless mode (injection pulse 20 psi for 2 min) with an inlet temperature program as follows: 60 $^{\circ}\text{C}$ for 0.1 min and 500 $^{\circ}\text{C}/\text{min}$ until 280 $^{\circ}\text{C}$ and held for a final 20 min. The GC oven program was as follows: initial 60 $^{\circ}\text{C}$ for 2 min, 30 $^{\circ}\text{C}/\text{min}$ until 150 $^{\circ}\text{C}$, 2 $^{\circ}\text{C}/\text{min}$ until 240 $^{\circ}\text{C}$, and 20 $^{\circ}\text{C}/\text{min}$ until 300 $^{\circ}\text{C}$ and held for 5 min. The temperature of the MS transfer line was held at 280 $^{\circ}\text{C}$. The ion source and quadrupole temperature was 150 $^{\circ}\text{C}$. Total amounts of individual compounds in the samples are the sum of fractions 1 and 2.

Quality assurance and quality control

One method blank was run for each batch of samples extracted (12 samples per batch) and six method blanks were obtained in total for the 72 samples extracted. Mean absolute blank values of CUPs ranged from 0.27 to 14 pg. Method detection limits (MDLs) were derived from mean field blank values plus three times the standard deviation (σ) (for compounds not present in the field blanks), then instrumental detection limits at a signal-to-noise ratio of three were used instead. Using a mean sediment sample mass of 10 g, the MDLs ranged from 0.067 to 2.6 pg/g. Concentrations calculated from GC/MS signals which were below the MDLs were defined as not detected in this work. The spike test recoveries for α -endosulfan, β -endosulfan, endosulfan sulfate, trifluralin, pentachloroanisole, quintozone, dicofol, chlorpyrifos, and dacthal were 66 ± 4 , 96 ± 7 , 65 ± 67 , 58 ± 8 , 49 ± 3 , 58 ± 4 , 123 ± 27 , 51 ± 28 , and 109 ± 9 %, respectively. Surrogate recoveries in this study were 52 ± 19 %. Therefore, the analysis of CUPs in this study was semiquantitative. The concentrations were corrected with surrogate recoveries. Namely, the concentrations calculated from GC/MS signals are divided by the surrogate (d^{14} -Trifluralin) recovery to get the reported concentrations in this paper. Details of MDLs, spike test recoveries, and surrogate recoveries are provided in Tables S1 and S2 in the Supplementary material.

Total organic carbon (TOC) analysis

Total organic carbon of freeze-dried powdered sediments was determined by a LECO[®] RC612 multiphase carbon and hydrogen/moisture analyzer. Total organic carbon is analyzed

by placing approximately 0.20 g of dried, ground, and homogenized sediment sample into a clean, carbon-free combustion boat. The sample is placed into an oven set at 60 $^{\circ}\text{C}$ and then combusted at 550 $^{\circ}\text{C}$ until no more CO_2 is created (~15 min). CO_2 from the combustion is quantified by infrared detection and used to estimate TOC. TOCs for sediments in this study range from 0.035 to 1.3 % (average 0.54 ± 0.33 %). TOCs of individual sampling sites were provided in Table S2 in the Supplementary material. Pearson correlation between TOC and pesticide concentrations was performed using the program SPSS 16.0 for Windows (SPSS Inc., Chicago, IL).

Results and discussion

Concentrations

Concentrations (dry weight, dw) for individual sampling sites were listed in detail in Table S2. The sampling sites were classified into two groups (Table S2), namely near-shore samples along the coast of Shandong Peninsula (Laizhou Bay, Taozi Bay, Sishili Bay, and Jiaozhou Bay) and the offshore samples.

α -Endosulfan, endosulfan sulfate, trifluralin, chlorpyrifos, dicofol, and pentachloroanisole were the most frequently detected compounds with 60 % of the samples detected. β -Endosulfan, dacthal, and quintozone were detected in 36, 17, and 7 % of the samples, respectively. Dicofol was the predominant compound with ~90 % of the concentration values larger than 100 pg/g, followed by chlorpyrifos, with a maximum level of 140 pg/g dw. Other compounds had maximum concentrations around 10 pg/g dw. The levels of the target compounds (excluding dicofol) in surface sediments (ranging from 0.0050 to 140 pg/g) were lower than previously reported levels of legacy OCPs, i.e., HCHs and DDTs (160–5,700 pg/g), while these two pesticides accounted for about 78 % of the total pesticide production and usage in China during the 1960s to 1983 (Hu et al. 2009).

The levels of dicofol in the Bohai and Yellow sea sediments spanned a wide range from 0.30 to 18,000 pg/g dw with an average of $1,300\pm2,500$ pg/g dw. Dicofol is a broad spectrum insecticide with excellent efficacy. It is widely used for mites control on a wide variety of fruits and crops. Dicofol has been produced in China since 1976 and its production in China was estimated to be 3,500 tons per year in recent years (Project Document for China Dicofol Project 2008). Dicofol contains DDT as an impurity, since it is mainly synthesized from DDT. It is widely accepted that dicofol usage is an important current source of DDT in China (Qiu et al. 2005; Yang et al. 2008), while only a few studies focus on dicofol itself. Xue et al. analyzed dicofol in water and sediment of the Beijing Guanting Reservoir and reported a mean concentration of 49 ± 15 pg/g dw (Xue et al. 2005). The relatively high

concentrations of dicofol in the present study indicate that the occurrence of dicofol in China's coastal environment deserve more attention.

The predominance of dicofol in the Bohai and Yellow seas could be attributed to its high consumption volume and physicochemical properties. The $\log K_{oc}$ values can be used to estimate the sorption of hydrophobic pollutants on natural sediments. Among target compounds, dicofol has a relatively low $\log K_{oc}$ value (Table 1), suggesting its weak partitioning in sediment. However, it has the lowest Henry's law constant or the largest water solubility (Table 1), which could lead to relatively high dicofol concentrations in seawater due to stronger net deposition during air-seawater gas exchange or greater input of dicofol via riverine transport. Thus, the relatively high concentrations of dicofol in sediment samples resulted from its low Henry's law constant or high water solubility rather than its $\log K_{oc}$. This explanation is supported by the results from our recent study on CUPs in the air and seawater of the Bohai and Yellow seas. Dicofol was found to have low concentrations in the air but relative enrichment in seawater compared with other CUPs with higher Henry's law constant or lower water solubility (Zhong et al. 2014).

Endosulfan has been agriculturally used in China since 1994. It has been listed in Annex A of the Stockholm Convention in May 2011 (UNEP 2013), and new registrations of endosulfan-based products in China are prohibited since July 2011 (MOA 2011). The total usage of endosulfan on cotton, wheat, tea, tobacco, and apples in China was estimated to be 25,700 tons between 1994 and 2004 within the regions of Hebei, Shandong, and Jiangsu provinces, and the coasts of Bohai and Yellow seas were the regions of most intensive endosulfan usage (Jia et al. 2009). Technical grade endosulfan contains two isomers, known as α -endosulfan and β -endosulfan. The α -/ β -endosulfan isomer ratio ranges from

2.0 to 2.3 depending on the technical mixture (Herrmann 2002). Endosulfan is subject to degradation in aquatic systems and the main metabolite in sediments is endosulfan sulfate (Weber et al. 2010). In this study, endosulfan sulfate accounted for 60 ± 22 % of total endosulfans (sum of α -endosulfan, β -endosulfan, and endosulfan sulfate) (Table S2), indicating a significant degradation of endosulfan in the sediments of Bohai and Yellow seas.

α -Endosulfan, β -endosulfan, and endosulfan sulfate in our study had maximum levels of around 20 pg/g dw (Table S2), which were lower than the reported levels of these compounds in the surface sediments collected in 2006 in the Bohai Sea (30 to 700 pg/g dw) (Hu et al. 2009). Lin et al. (2012) analyzed endosulfan in surface sediments from the coast of East China Sea in 2007 and found that both endosulfan isomers were detected only in few sediment samples (Lin et al. 2012). Comparison of endosulfan concentrations in coastal sediment samples from different areas in the world is given in Table 2. Endosulfan concentrations in our study are at similar levels as those for the Persian Gulf, Gulf of Oman, and coast of Campeche, Mexico (de Mora et al. 2005; Carvalho et al. 2009a), but lower than those observed in sediments from the Portuguese coast, three estuaries of the Cantabrian Coast, Spain (Carvalho et al. 2009b; Gomez et al. 2011), as well as the Daliao River Estuary, and Yangtze River Estuary, China (Tan et al. 2009; Liu et al. 2003).

In this study, concentration ranges for both endosulfan isomers were comparable (Table 2), but the ratios of α -/ β -endosulfan spanned wide ranging from 0.0086 to 23 with 60 % of the values lower than the ratios for technical mixtures (2.0–2.3). Previously reported α -/ β -isomer ratios (0.3 to 1.8) for Bohai Sea surface sediments in 2006 were also lower than those for technical mixtures, but the ratios were within a smaller range (Hu et al. 2009). Estimated K_{oc} values of the

Table 2 The range of endosulfans' concentrations (in pg/g dw) in marine sediments of different areas in the world

Sampling areas	Sampling year	α -Endosulfan	β -Endosulfan	Endosulfan sulfate	Reference
Bohai and Yellow Seas	2010	<0.0082 to 22	<0.0066 to 17	0.0081 to 18	This study
Bohai Sea	2006	<30 to 730	<30 to 400	<30 to 560	Hu et al. (2009)
East China Sea	2007	Detected in few samples ^a	Detected in few samples ^a	No data	Lin et al. (2012)
Coast of Persian Gulf and Gulf of Oman	2000 and 2001	<0.2 to 16	<0.95 to 29	<1.3 to 11	de Mora et al. (2005)
Coast of Campeche, Mexico	2000	<0.55	<0.65 to 7.2	No data	Carvalho et al. (2009a)
Coast of Portugal	2007 and 2008	680 to 5,900	No data	No data	Carvalho et al. (2009b)
Three estuaries in the Cantabrian Coast, Spain	2006	200 to 600	<210 to 400	<170	Gomez et al. (2011)
Daliao River Estuary, Bohai Sea	2007	10 to 200	10 to 800	No data	Tan et al. (2009)
Yangtze Estuary and nearby coastal areas, China	2001	<30 to 1,230	<100 to 160	No data	Liu et al. (2003)

In this table, samples in which endosulfans were not detectable are excluded when we summarize the range of concentrations

^a Details are not given in this paper

α - and β -isomer are the same (Table 1). However, α -endosulfan has greater tendency of volatility from both solid and aqueous surfaces than the β -isomer (Antonious et al. 1998). Moreover, isomeric conversion from β -endosulfan to α -endosulfan has been demonstrated to occur in the environment (Schmidt et al. 1997; Walse et al. 2002). These are the possible reasons that high ratios of α -/ β -endosulfan were observed. However, remobilization experiments showed that α -endosulfan desorbed more readily from sediments than the β -isomer (Peterson and Batley 1993) and the α -isomer is converted more readily to endosulfan sulfate than the β -isomer (Leonard et al. 2001; Walse et al. 2003). A combined influence of the factors mentioned above may explain the wide range of α -/ β -endosulfan ratios.

Pentachloroanisole is a metabolite of quintozone and pentachlorophenol (PCP) (China Pesticide Information 2012). In our study, detection frequency and concentrations of pentachloroanisole were higher than those of quintozone. Much higher concentrations of pentachloroanisole than those of quintozone were also observed in the air and seawater samples of the German Bight (North Sea) in our previous work (Zhong et al. 2012b). Domestic consumption of quintozone is estimated to be 32 tons per year (Wang et al. 2012b). Annual production of PCP together with pentachlorophenol-Na (Na-PCP) ranged from 1,000 to 10,000 tons during 1983 to 2003, but PCP production was discontinued in 1995 and Na-PCP was produced until 2003 (Wang et al. 2010). The much higher concentrations of pentachloroanisole compared with quintozone possibly resulted from the significant degradation of quintozone and additional pentachloroanisole contribution from the degradation of PCP.

Chlorpyrifos had the second highest concentrations in the sediments of Bohai and Yellow seas and this is possibly attributed to its relatively high consumption volume in recent years. The domestic market demand of chlorpyrifos was 18,000 tons in 2008 (<http://www.ccpia.com.cn/>, China Crop Protection Industry Association). Trifluralin is expected to be prone to accumulation in sediments, since it has a relatively high $\log K_{oc}$ value of 4.2. However, high Henry's law constant (Table 1) might result in its low partitioning in seawater during air-water gas exchange, thereby going against its enrichment in sediment. Dacthal had low detection frequency in sediments of Bohai and Yellow seas, whereas it was one of the most abundant CUPs in the air of the Centre Region (France) and North America (Kuang et al. 2003; Peck and Hornbuckle 2005; Brun et al. 2008; Yusa et al. 2010). This result is consistent with the fact that dacthal has not been registered in China (China Pesticide Information 2012).

Spatial distributions

Spatial distributions of compounds with high detection frequencies (>60 %), namely dicofol, α -endosulfan, trifluralin,

chlorpyrifos, pentachloroanisole, and endosulfan sulfate, are discussed below. Generally, the highest mean concentrations appeared at near-shore sampling sites (Table S2). For instance, the highest mean concentrations of α -endosulfan, endosulfan sulfate, trifluralin, and chlorpyrifos were found in Laizhou Bay, whereas pentachloroanisole and dicofol had the highest mean concentrations in Jiaozhou Bay. Sampling sites with high concentrations were generally at/close to estuaries. Relatively high-contaminated near-shore sites of Laizhou Bay were DJWE where high levels of chlorpyrifos, dicofol, α -endosulfan, trifluralin, and pentachloroanisole were detected and YKE where high levels of trifluralin, chlorpyrifos, and dicofol were detected (Fig. 2). Similarly, the highest chlorpyrifos levels occurred close to the Baisha River and Haibo River estuaries (JZ-A1 and JZ-E1) and the highest dicofol levels were found close to Licun River and Haibo River estuaries (JZ-A3 and JZ-E1) in Jiaozhou Bay (Fig. 2). For the offshore sampling sites, mean concentrations of most compounds at the Bohai Sea were higher than those at the Yellow Sea.

Spatial distributions of hydrophobic pollutants in sediments can significantly correlate with the distributions of TOC due to the post-depositional sorption or co-emission (Hung et al. 2006). Good correlations between hydrophobic pollutants and TOC are supposed to be observed in offshore areas and continental shelf, since these relatively homogeneous environmental conditions provide a TOC-dependent post-depositional sorption environment (Lee et al. 2001; Zhang et al. 2007).

In this work, a correlation between concentrations and TOC was basically not observed for offshore samples (Table S3). This result may be due to the fresh input of these compounds. Previous studies showed good correlations between TOC and legacy organochlorines for the sediments of Bohai and Yellow seas (Zhang et al. 2007; Hu et al. 2009). The restriction of use of organochlorines (for examples, DDTs, HCHs, hexachlorobenzene, and polychlorinated biphenyls) would favor a post-depositional sorption-dominated distribution of these chemicals in offshore sediments because of a lack of fresh inputs, which could give rise to the possibility of a concentration distribution inconsistent with the TOC distribution.

A correlation between concentrations and TOC was generally not found for near-shore sampling sites too, except that pentachloroanisole and dicofol concentrations significantly correlated with TOC at Jiaozhou Bay ($r=0.957$, $p=0.003$ for pentachloroanisole and $r=0.883$, $p=0.009$ for dicofol). This result suggests spatially limited or defined sources near the coast. For instance, Zhong et al. (2011) reported good correlations between legacy OCPs and TOC for offshore sediments of Laizhou Bay but not for adjacent estuarine and riverine sediments, some of which especially high OCP concentrations were detected (Zhong et al. 2011). A lack of correlation between legacy OCPs and TOC was also observed for coastal

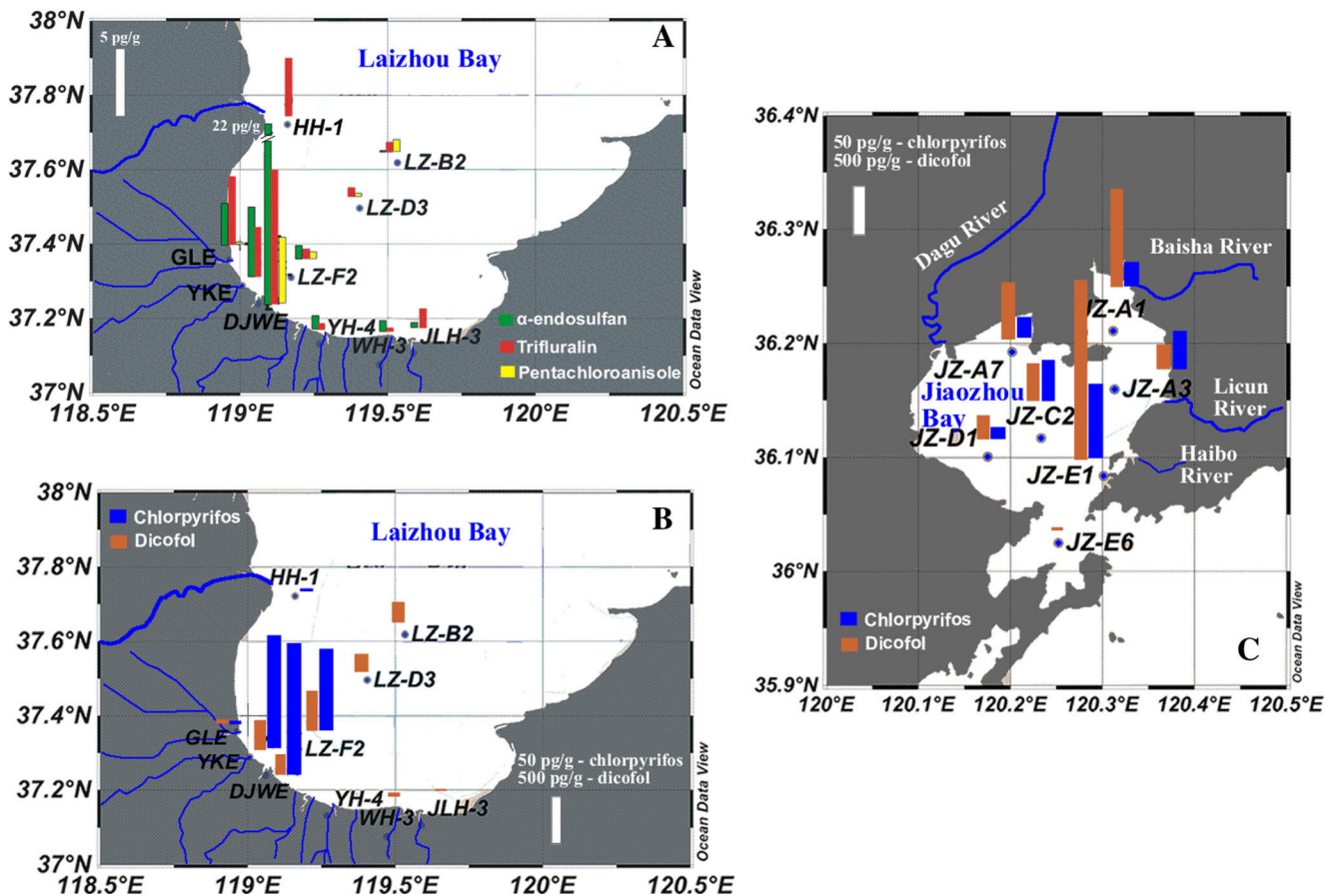


Fig. 2 Distributions of α -endosulfan, trifluralin, and pentachloroanisole in Laizhou Bay (a) and distributions of dicofol and chlorpyrifos in Laizhou Bay (b) and Jiaozhou Bay (c)

East China Sea sediments, and high HCH and DDT concentrations, respectively, existed at the estuaries and in the near-shore area with a significant decrease gradient seaward owing to nonpoint sources of the coast (Lin et al. 2012).

Evaluation of ecological effects

Ecological effects of CUPs in sediment can be preliminarily evaluated by comparing CUP concentrations in the present study with sediment screening benchmarks. However, sediment screening benchmarks of the six frequently detected CUPs are unavailable. Sediment screening benchmarks can be estimated from water screening benchmarks using the equilibrium partitioning approach by Di Toro et al. (1991):

$$SSB = WSB \times K_{oc} \times f_{oc}/100 \quad (1)$$

where SSB is the sediment screening benchmark ($\mu\text{g/g}$), WSB is the water screening benchmarks ($\mu\text{g/L}$), and f_{oc} is the TOC content of the sediment samples (%). Marine water screening benchmarks for chlorpyrifos, α -endosulfan, and endosulfan sulfate are 0.0056, 0.0010, and 0.009 $\mu\text{g/L}$, respectively (EPA

Region 3 Ecological Risk Assessment, www.epa.gov). Marine water screening benchmarks are unavailable for dicofol, trifluralin, and pentachloroanisole, so freshwater screening benchmarks were used instead, i.e., 19.8 $\mu\text{g/L}$ for dicofol (Texas Surface Water Quality Standards, www.tceq.state.tx.us), 0.2 $\mu\text{g/L}$ for trifluralin (EPA Region 3 Ecological Risk Assessment, www.epa.gov), and unavailable for pentachloroanisole. CUP concentrations in our study are much lower than the resulting sediment screening benchmarks for chlorpyrifos, α -endosulfan, endosulfan sulfate, dicofol, and trifluralin, which are at the microgram per gram level (0.0044–1,300 $\mu\text{g/g}$).

Conclusion

Six current-use pesticides and two of their metabolites were detected in the coastal and offshore sediments of Bohai and Yellow seas, and lower concentrations of CUPs (except dicofol) than legacy OCPs previously reported were found. Dicofol had relatively high concentrations compared with the other compounds and especially high levels were observed at Jiaozhou Bay. The high levels of dicofol in sediments can be

attributed to its high consumption amount recently, together with its low Henry's law constant and high solubility in water. The occurrence and fate of dicofol in the aquatic environment deserves further research. Concentrations of endosulfan sulfate were higher than its parent compounds (i.e., α -endosulfan and β -endosulfan). This case is expected to be continued, since endosulfan has been listed in the Stockholm Convention and its primary emissions are expected to decrease. High concentrations of the compounds generally occurred at near-shore sampling sites especially at sampling sites at/close to estuaries. It can be explained by the riverine input nearby, since a correlation between concentrations and TOC was not found, except for pentachloroanisole and dicofol at Jiaozhou Bay.

Acknowledgment This study was financially supported by the Chinese Academy of Sciences (KZCX2-EW-QN210, KZZD-EW-14, and YZ201161) and the National Natural Science Foundation of China (40933048 and 41073064). We are grateful for the field assistance from the crew of Research Vessel Dongfanghong 2 of the Ocean University of China.

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