1 **Sources, concentrations and risk factors of organochlorine pesticides**
2
3 **in soil, water and sediment in the Yellow River estuary**
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Abstract

The environmental occurrence, sources and risk factors of organochlorine pesticides (HCHs and DDTs) and their isomers or metabolites were studied using comprehensive surveys (including soil, surface water, groundwater and sediment sampling) conducted in the Yellow River Delta (YRD). HCHs and DDTs were all detected in multi environmental media. Compared with reported organochlorine pesticide values in China and abroad and with related environmental quality standards, the concentrations of HCHs and DDTs were generally at low levels in the YRD. Composition of OCPs (DDT metabolites and HCH isomers) showed that DDTs in the multiple environments of the YRD not only came from residues of dicofol but also from atmospheric deposition, while HCH pollution results from the historical usage of a mixture of technical HCH and lindane. Furthermore, the sum of Excess Lifetime Cancer Risk ($\sum$ ELCR) exposure to HCHs exceeded the generally acceptable risk level of 1.0E-06 recommended by the USEPA for carcinogenic chemicals.

Keyword

Residue characteristics; Comprehensive surveys; Multiple environments; Yellow River Delta (YRD); Excess Lifetime Cancer Risk ($\sum$ ELCR).

Due to their bioaccumulation potential, persistence, toxicity and long-range environmental transport ability, organochlorine pesticides (OCPs) are of concern to scientists, environmental quality managers and policy makers (MEP, 2007), and measurement of their concentrations and evaluation of ecological risk in a large-scale region is of great importance (Feng *et al.*, 2011; Sudaryanto *et al.*, 2011). A large amount of work has been carried out. The United Nations Environment Programme (UNEP) (UNEP, 2003), International Programme on Chemical Safety (IPCS) (IPCS, 2000), Intergovernmental Forum on Chemical Safety (IFCS) (Peterson *et al.*, 2010), Inter-Organization Programme for the Sound Management of Chemicals (IOMC) (Keita-Ouane *et al.*, 2001) and other international organizations are actively involved in the study of OCP characteristics, hazards, and so on.

OCPs were widely used as well as produced in China, especially from 1960 to 1980. About 192,000 tons of HCH and DDT were used in China in 1970, accounting for 80.1% of all pesticide use (Wang *et al.*, 2005). OCP application in China from 1950-1990 is presented in Table 1.

[Table 1 here]

Between 1950 and 1980, pesticide consumption in China increased considerably. From 1960 to 1980, the use of HCH increased by 3.5 times, the use of DDT increased by 2 times, and the total production of pesticides increased by 4.3 times (Wang *et al.*, 2005). Even after the ban of technical HCH and DDT in 1983, 3200 t of lindane (almost pure γ -HCH) was still in use between 1991 and 2000, and DDT production continues due to export demand and dicofol production (Figure 1) (Zhou *et al.*, 2006). OCP pollution of multiple environments was universal in China (Wang *et al.*, 2005).

[Fig. 1 here]

The Yellow River is the second longest river in China and the world's second largest river in terms of sediment discharge to the sea (Wang *et al.*, 2010). Over the course of human history, the river valley has had great influence on civilization and the origin of Chinese culture, such that the Yellow River is referred to as the Mother River of China. The Yellow River Delta (YRD), which is a typical ecotone of the Yellow River and Bohai Bay (Chen *et al.*, 2007), is experiencing enormous environmental deterioration from industrialization. Extremely high sediment loads (>1000 million tons per year, Mt/yr) have been discharged to the sea over thousands of years as a result of poor agricultural practices in the loess region. The accumulation of sediment in the

1 estuary formed the Modern YRD. With an area of 2200 km², the YRD is the widest and youngest
2 wetland in the warm temperate zone of China, and is also the youngest land in the world (Li *et al.*,
3 2001). The high sediment loading from the river and transport by hypopycnal flows into the
4 estuary have made a considerable contribution to the deltaic depositional system (Wang *et al.*,
5 2010). During the transport process, organic pollutants such as OCPs, polycyclic aromatic
6 hydrocarbon (PAHs), polychlorinated biphenyls (PCBs) and so on are adsorbed (Chen *et al.*,
7 2012).

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9 In the last decades, with the rapid economic development in Asian countries, environmental
10 pollution caused by OCPs has been identified in several delta areas, e.g., the Mekong Delta
11 (Sudaryanto *et al.*, 2011), the Pearl River Delta (Li *et al.*, 2006), and the Yangtze River Delta
12 (Tang *et al.*, 2008). Most investigations of pollutants in the YRD have focused on hydrocarbon,
13 nitrate, PCB, and trace metal pollutants (Li *et al.*, 2001; Chen *et al.*, 2007; Wang *et al.*, 2009b);
14 few reports of OCP concentrations in the YRD are available. Although the application of OCPs
15 has been forbidden for a considerable period in China, OCPs pollution of multiple environments
16 was universal (Cai *et al.*, 2008; Zhou *et al.*, 2006). About 80% of the pesticides are used in
17 agriculture in China (Wang *et al.*, 2005) and moved in the environment by means of volatilization,
18 runoff, infiltration, etc. The residues continue to induce a significant impact on the environment
19 and its ecosystems (Feng *et al.*, 2011). A comprehensive investigation of the distribution of OCPs
20 in the YRD can be used to determine the sources, associated ecological risks and strategies for
21 remediation of OCP pollutants.

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23 The Yellow River is a sediment-filled river that flows from the Bayan Har Mountains to the
24 Bohai Sea, where it builds and rebuilds the YRD. The YRD is the youngest wetland in the world
25 and is one of the three most economically important deltas in China, developing quite fast in
26 recent years. Study sites were selected in the YRD between 37° 26' to 38° 10' N and 118° 21' to
27 119° 20' E. In the modern era, a shift in the Yellow River has created a new alluvial fan over an
28 area of approximately 2200 km² (Gao *et al.*, 1989). Mean annual precipitation in the study area is
29 590 mm, mostly occurring from July to September, and mean annual air temperature is 11.9 °C.
30 The mean annual potential evaporation is 2049 mm yr⁻¹, which far exceeds rainfall for the area.
31 The average maximum and minimum temperatures are 26 °C in July and -4 °C in January. The
32 modern YRD, which has formed since 1855, has been shaped by erosion and settling along the old
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channel. It hosts the delta's natural wetlands and is subject to environmental pollution due to extensive oil and gas exploitation as well as agricultural and industrial development in this region (Wang *et al.*, 2009b).

In September 2013, 67 surficial soil samples were collected. Sampling locations were evenly distributed across the study area of a grid ($6 \times 6 \text{ km}^2$), with the exception of some samples that were selected to be adjacent to specific chemical industries (Figure 2). Each soil sample was a composite of subsamples taken from the top 20 cm of five sites in an area of about $100 \times 100 \text{ m}^2$ (at the four corners and the center). The composite was homogenized and a subsample collected using a stainless steel shovel. Grass and other materials were removed from the surface of each sampling location before the sample was collected. The composite soil samples were air dried at room temperature ($22\text{--}25^\circ\text{C}$), sieved to $<2 \text{ mm}$, and stored at 4°C .

Twenty-six 2-L surface water samples were taken from the Yellow River, its main tributaries, old channels, irrigation ditches, and reservoirs, as well as from around cities, towns and branch afflux sites. Samples were taken using pre-cleaned brown glass bottles that had been washed with detergent and rinsed with tap water and ultra-pure water. Each 2-L glass bottle was rinsed twice with the sample and then filled just to overflowing. Upon return to the laboratory, all samples were immediately filtered through $0.45\text{-}\mu\text{m}$ organic membrane filters to remove sand and debris.

At 26 surface water sampling locations, sediment samples were also collected from top 20 cm. Homogenized subsamples were freeze-dried.

Throughout the survey, a global positioning system (GPS) was used to locate the sampling locations (Figure 2). Site descriptions, including land use type and major environmental features, were recorded at the same time as the samples were collected.

Soil pH was determined from 1:2.5 water-soil slurry by an EC/ pH meter (D23, Horiba, Japan). Total organic carbon (TOC) of soils was determined with a TOC analyzer (Vario TOC, Elementar, Germany).

[Fig. 2 here]

For extraction of pesticides from the samples, n-hexane and dichloromethane (J.T. Baker, HPLC) were used for residue analysis. Anhydrous sodium sulfate (analytical grade) was baked at 450°C and silica gel (60 mesh, for column chromatograph) was activated at 180°C for 24 h. A mixture of standard solution containing α , β , γ , δ -HCH, *op'*-DDT, *pp'*-DDT, *pp'*-DDE, and

1 *pp'*-DDD with 1 g kg⁻¹ per compound were purchased from National Research Center for
2 Certified Reference Materials of China. 2,4,5,6-Tetrachloro-m-xylene (TCMX) was used as the
3 surrogate standard (Supelco, Bellefonte, PA, USA).
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6 The microwave extraction method (USEPA Method 3546) was used to extract OCPs from
7 the soil and sediment according to the method of Wang *et al.* (1999). Each soil sample (2.0 g dry
8 weight) was mixed with 1 g anhydrous sodium sulfate. 1 mL TCMX at a concentration of 0.08 mg
9 L⁻¹ was added. The mixture was extracted twice with 30 mL of a methylene chloride–hexane
10 solvent mixture (1:1). The temperature was increased to 120 °C using the preset temperature
11 program, at which temperature the extraction was maintained for 15 minutes. The vessels were
12 then cooled to ambient room temperature. The extract was pre-concentrated to 2 ml by a rotary
13 evaporator and solvent-exchanged to hexane. The hexane extract was fractionated and cleaned by
14 solid phase extraction (SPE, 6 mL, 1 g florisil, Supelco). An SPE cartridge was loaded with 1 g
15 silica gel and 1 g anhydrous sodium sulfate, and was washed with 10 mL n-hexane before use.
16 The cartridge was then eluted with 20 mL methylene chloride–hexane (1:1, v/v) to obtain OCPs.
17 The OCP eluate was concentrated to a final volume of 1 mL for gas chromatography analysis.
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31 The SPE cartridge system was used to extract water samples according to the method of
32 Zhou et al. (2000) Before the extraction, the C18-bonded phase containing 500 mg reversed phase
33 octadecyl was first washed with 5 mL methylene chloride and conditioned by 5 mL methanol, and
34 then washed with 5 mL ultra-pure water. Each 2-L water sample was percolated through a
35 cartridge with a flow rate of 10 mL/min. The extract was eluted with 20 mL methylene chloride to
36 obtain OCPs, and then was pre-concentrated to 2 ml by a rotary evaporator and solvent-exchanged
37 to hexane. The OCPs eluate was concentrated to a final volume of 1mL for gas chromatography
38 analysis.
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47 An Agilent 7890 gas chromatograph (GC) equipped a ⁶³Ni electron capture detector (μECD)
48 (Agilent Technology Co., USA) was used for analysis. The column used for separation was a HP-5
49 silica capillary column, 30 m × 0.32 mm i.d. × 0.25 μm film thickness. The analysis was performed
50 under splitless mode. The injector and detector temperatures were 220 °C and 300 °C, respectively.
51 The oven temperature was initially set at 100 °C with a 2-min hold, ramped at 10 °C/min to
52 160 °C with a 2-min hold, then ramped at 4 °C /min to 230 °C with a 5-min hold, and finally
53 ramped at 10 °C /min to 270 °C with a 2-min hold. OCPs were identified by matching the
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retention time to standards and were quantified using peak area integration. OCPs that were measured include four DDT homologues and four HCH isomers. Concentrations of Σ DDT and Σ HCH were the sum of the four DDT homologues and four HCH isomers, respectively.

For quality assurance and quality control, procedural blanks and matrixes spiked with the standard solution were analyzed. None of the target compounds were detected in the procedural blanks. Each replicate sample was analyzed twice by GC- μ ECD, and the relative standard deviation (RSD) of replicate samples was less than 20%. Extraction efficiency, as indicated by recovery of the surrogate standards (TCMX), was consistently $75\% \pm 10\%$.

OCP residue levels in the soil, surface water, groundwater and sediment samples from the YRD are summarized in Table 2. Soil was the largest sink in the environment and has a large influence on a variety of human health functions. In China, OCPs are one of the most frequently studied persistent organic pollutants (POPs) in soil (Cai *et al.*, 2008), and concentrations of OCPs in soil have been increasing for 100–150 years, especially in urban areas (Jones *et al.*, 1989).

[Table 2 here]

Soil Σ HCH was detected in 100% of the surface soil samples, and Σ DDT was detected in 95.5%. As shown in Table 2, Σ HCH concentrations in the 67 soil samples ranged from 0.51 to 208.48 ng/g dry weight (dw), with an average of 9.66 ng/g dw. This average was higher than those in some remote regions and green plant base station in China, such as Tibet (1.97 ng/g dw) (Fu *et al.*, 2001) and green food production base in Liaoning province (7.0 ng/g dw) (Zhang *et al.*, 2001), while lower than those in Beijing orchard soils (32 ng/g dw) (Shi *et al.*, 2005), Tianjin surface soils (45.8 ng/g dw) (Gong *et al.*, 2004a; Gong *et al.*, 2004b), Romanian surface soils (26.1 ng/g dw) (Covaci *et al.*, 2001) and a paddy soil in the India Dehradun (326 ng/g dw) (Babu *et al.*, 2003) (Table 3). Total DDT concentrations in the topsoil samples from the study area ranged from undetectable to 109.12 ng/g dw, with an average of 8.39 ng/g dw. This average was higher than that in remote and clean regions, such as Tibet (1.13 ng/g dw) (Fu *et al.*, 2001), while lower than averages in farmland soil in the Pearl River Delta (20.1 ng/g dw) (Li *et al.*, 2006) and green food production basement in Liaoning province (22.0 ng/g dw) (Zhang *et al.*, 2001), and much lower than averages in Beijing orchard soils (381.3 ng/g dw) (Shi *et al.*, 2005), Tianjin surface soils (56 ng/g dw) (Gong *et al.*, 2004a; Gong *et al.*, 2004b), Romanian surface soils (62.5 ng/g dw) (Covaci *et al.*, 2001), a paddy soil in the India Dehradun (326 ng/g dw) (Babu *et al.*, 2003) and farmland

soil in Hanoi, Vietnam (89.86 ng/g dw) (Toan *et al.*, 2007). According to National Environmental Quality Standards for Soils of China (GB15618-1995), with the exception of the concentration of Σ HCH in 1.5% sample that was between the first (50 ng/g dw) and the second grade (500 ng/g dw), those in remaining 98.5% samples were lower than the first grade. Σ DDT displayed the same pattern, indicating that there is no extensive OCP soil pollution in the YRD.

The average soil pH in the study area was 8.69 (8.08-9.26). The content of soil TOC ranged from 0.24% to 2.76% with a mean of 0.72%. Spearman correlation analyses showed that there was no significant correlation between pH and concentrations of HCH and DDT, the same as the TOC. It indicated that soil pH and TOC levels have no obvious effect on HCH and DDT distributions in the study area, and the residue levels of HCH and DDT were mainly affected by OCP inputs rather than air-soil equilibrium (Wang *et al.*, 2009a).

[Table 3 here]

Σ HCH and Σ DDT were detected in all of the surface water and groundwater samples. Groundwater samples were relatively higher in Σ HCH, with values ranging from 3.95 to 154.45 ug/L and a mean value of 34.74 ug/L, while surface water sample values ranged from 1.10 to 62.15 ug/L, with a mean value of 18.57 ug/L. A similar situation was noted with respect to Σ DDT residue in surface water and groundwater samples. Σ DDT in groundwater samples ranged from 1.16 to 30.89 ug/L, with a mean value of 10.78 ug/L, while values in surface water samples ranged from 1.46 to 35.52 ug/L, with a mean value of 9.79 ug/L. The factors influence the concentrations of OCPs in the groundwater were complex, including not only the pollution sources, but also the environmental factors such as physical and chemical properties of soil/sediment and other effects (Ahel, 1991; Chen *et al.*, 2014).

Σ HCH concentrations of the 29 surface water samples were higher than those in Peacock River, Xin Jiang Province (nd–19.00 ug/L) (Chen *et al.*, 2011) and Huaihe River (0.47–6.13 ug/L) (Feng *et al.*, 2011), while lower than those in the Yangtze River (0.55–28.07 ug/L) (Tang *et al.*, 2008), Qiantang River (0.74–543.1 ug/L) (Gong *et al.*, 2004a; Gong *et al.*, 2004b), Nestos River, Greece (nd–68.00 ug/L) (Golfinopoulos *et al.*, 2003) and much lower than those in the Gomti River, India (0.02–4846.00 ug/L) (Malik *et al.*, 2007) (Table 4). Σ DDT concentrations in surface water samples were higher than that in Ebro River, Spain (3.40 ug/L) (Fernandez *et al.*, 1999), while lower than those in the Yangtze River (nd–16.71 ug/L) (Tang *et al.*, 2008), Huaihe River

(4.44–33.59) (Feng *et al.*, 2011) and Nestos River, Greece (nd–64.00 ug/L) (Golfinopoulos *et al.*, 2003), and much lower than those in the Qiantang River (nd–204.1 ug/L) (Zhou *et al.*, 2006), Gomti River, India (0.20–4578.00 ug/L) (Malik *et al.*, 2007), and Kucuk Menderes River, Turkey (72–120 ug/L) (Turgut, 2003).

[Table 4 here]

Sediment Σ HCHs was detected in 100% of the samples, and Σ DDTs was detected in 95.7%. As shown in in Table 2, Σ HCH concentrations of the 26 sediment samples ranged from 0.56 to 232.60 ng/g dw, with an average of 19.59 ng/g dw. This was similar with the value in Dalian Bay (21.25 ng/g dw) (Li and Fu, 1998), higher than those in other two deltas in China, the Yangtze Delta (6.0 ng/g dw) (Liu *et al.*, 2008) and Pearl River Estuary (0.68 ng/g dw) (Hong *et al.*, 1999), but was lower than values in Liaodong Bay (68.6 ng/g dw) (Lu *et al.*, 2008) and Tianjin Dagu Drainage Canal (87.74 ng/g dw) (Yang *et al.*, 2005). Total DDT concentrations in the sediment samples in the study area ranged from undetectable to 52.03 ng/g dw, with an average of 7.20 ng/g dw. This was similar to the value in the Yangtze Delta (8.2 ng/g dw) (Liu *et al.*, 2008), lower than the values in Liaodong Bay (42.8 ng/g dw) (Lu *et al.*, 2008), Dalian Bay (21.75 ng/g dw) (Li and Fu, 1998) and the Tianjin Dagu Drainage Canal (87.74 ng/g dw) (Yang *et al.*, 2005), while higher than those in the Pearl River Estuary, China (2.84 ng/g dw) (Hong *et al.*, 1999), Wu-Shi River estuary, Taiwan (2.51 ng/g dw) (Doong *et al.*, 2002a), Ulsan Bay, Korea (2.34 ng/g dw) (Khim *et al.*, 2001), Andes Lake (Borghini *et al.*, 2005) and James Stuart Island in Antarctica (Klanova *et al.*, 2008) (Table 5). Furthermore, according to National Marine Sediment Quality Standards of China (GB18668-2002) , all of the sediment samples were unpolluted by Σ HCHs (<500 ng/g dw), and 91.6% of the sediment samples were unpolluted by Σ DDTs (<20 ng/g dw).

[Table 5 here]

Technical DDT and dicofol containing high DDT-related compound impurities were the main sources of DDT pollution in China (Wang *et al.*, 2005). Technical DDT is typically composed of 77.1% *p, p'*-DDT, 14.9% *o, p'*-DDT, 4% *p, p'*-DDE and some other trace impurities (Kannan *et al.*, 1995). In this study, *o, p'*-DDT was the predominant metabolite in the sediment samples (31%), and was the second most common isomer in soil (29%) and surface water samples (28%; Figure 3). However, the characteristic of “dicofol type DDTs contamination” was a higher *o, p'*-DDT/*p, p'*-DDT ratio than for technical DDTs. Generally, the *o, p'*-DDT /*p, p'*-DDT ratio

1 ranged from 0.2 to 0.3 in technical DDTs and from 1.3 to 9.3 or higher in dicofol (Qiu *et al.*, 2005).
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3 Therefore, sources of DDTs (from technical DDT or dicofol impurities or both) can be identified
4 according to the ratio of *o,p'*-DDT/*p,p'*-DDT (Yang *et al.*, 2008). In this study, the ratios of
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6 *o,p'*-DDT/*p,p'*-DDT in soil, surface water, groundwater and sediment samples were 7.48, 2.19,
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8 4.02, and 3.83, respectively, showing the source to be dicofol.
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10 DDT degrades to DDE and DDD in aerobic and anaerobic conditions, respectively (Doong *et*
11 *al.*, 2002b). In general, a ratio of (DDE + DDD)/DDTs of more than 0.5 indicates long-term
12 biotransformation of DDT to DDE and DDD, while a ratio of less than 0.5 may indicate recent
13 input of DDT (Hitch and Day, 1992). The ratios of (DDE + DDD)/DDTs found in the YRD were
14 1.48, 1.35, 17.10 and 0.63 for soil, surface water, groundwater and sediment samples, respectively.
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16 The finding that all values were higher than 0.5 indicates that much of the degradation occurred
17 after the official ban of DDT in 1983, and that the DDT compounds in YRD may be mainly
18 derived from DDT-treated aged and weathered agricultural sources. Moreover, a higher ratio of
19 *p,p*-DDE/*p,p*-DDT can be used to indicate the long range atmospheric transport of DDT
20 compounds because *p,p*-DDE is transported more efficiently than *p,p*-DDT (Iwata *et al.*, 1993).
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22 The ratios of *p,p*-DDE/*p,p*-DDT varied from 1.62 to 7.02 in the multiple environments of the
23 YRD, indicating that the DDTs in this area may also come from atmospheric deposition (Dai *et al.*,
24 2011). As a result, DDT pollution in the multiple environments of the YRD not only came from
25 the residue of dicofol in the environment but also from atmospheric deposition.
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40 **[Fig.3 here]**

41 Technical HCH and lindane were two types of HCH products manufactured and used in
42 China. Technical HCH contains about 55% to 80% α -HCH, 5% to 14% β -HCH, 8% to 15%
43 γ -HCH and minor proportions of other isomers, while the major component of lindane is γ -HCH
44 (>99%) (Wang *et al.*, 2009a). Hence, the α/γ -ratio might be between 4 and 7 for the technical
45 mixture, and nearly zero for lindane (Dai *et al.*, 2011). In this study, β -HCH was the predominant
46 isomer in the groundwater samples (42%), and the second most common isomer in the soil (24%)
47 and sediment samples (31%; Figure 4). β -HCH is the most stable isomer in HCHs because of its
48 lower vapor pressure. The abundance of β -HCH indicates that most HCHs come from older
49 residues in the study area (Dai *et al.*, 2011). In surface water samples, α -HCH was the
50 predominant isomer (41%). The α/γ -HCH ratio was highest in surface water samples (8.55),
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Lower α/γ -HCH ratios were measured in soil (0.69), groundwater (3.73), and sediment samples (0.25). These observations may be explained by greater transportability of α -HCH than of γ -HCH or photochemical transformation and the new input of the technical mixture in surface water and lindane in the soil (Strandberg *et al.*, 1998). This indicates that the early usage pattern of HCHs was a mixture of technical HCHs and lindane (Iwata *et al.*, 1993).

[Fig.4 here]

Potential exposures to OCPs through soil, surface water and groundwater were assessed by use of the United States Environmental Protection Agency (USEPA) residential scenario (USEPA, 2002). The Excess Lifetime Cancer Risk (ELCR) calculated for direct exposure to OCPs from soil was estimated by applying existing methods to make probabilistic estimates of risk of excess cancer due to intake of chemicals through ingestion (Equation 1), inhalation (Equation 2) (USEPA, 1991), and dermal contact (Equation 3) (Chen and Liao, 2006),

$$ELCR_o = \frac{SF_o \times C_s \times EF \times ED \times IR_{soil}}{BW \times AT} \quad (1)$$

$$ELCR_i = \frac{SF_i \times C_s \times EF \times ED \times IR_{air} \times (1/PEF)}{BW \times AT} \quad (2)$$

$$ELCR_j = \frac{SF_j \times C_s \times SA \times FE \times RAF \times EF \times ED}{BW \times AT} \quad (3)$$

where SF_o represents the oral cancer slope factor (mg/kg d^{-1}); C_s , pollutant concentration in soil (mg/kg); EF , exposure frequency, 350 day/year (USEPA, 1991); ED , exposure duration, triangular type (50%: 9; 90%: 30), yr; IR_{soil} , soil ingestion rate (mg/day); BW , average body weight, as lognormal type (m: 60.2, sd: 2.9) kg (Li *et al.*, 2010); AT , averaging time, for non-carcinogens, 30 yr; SF_i , inhalation cancer slope factor (mg/kg d^{-1}); IR_{air} , inhalation rate (m^3/day); PEF , particulate emission factor (m^3/kg); SF_j , dermal cancer slope factor (mg/kg d^{-1}); SA , exposed skin area, 2,800 cm^2 ; FE , dermal adsorption fraction (unitless); and RAF , adherence factor of soil to skin (mg/cm^2).

The sum estimation of ELCR ($\sum ELCR$) from multiple routes of exposure to OCPs was calculated using Equation 4 (USEPA, 1991).

$$\sum ELCR = ELCR_o + ELCR_i + ELCR_j \quad (4)$$

The risks of exposure to contaminants in surface water and groundwater environment are through the two main routes of exposure – ingestion (Equation 5) and dermal absorption (Equation 6) (Song *et al.*, 2013).

$$ELCR_o = \frac{SF_o \times C_w \times IRW \times EF \times ED}{BW \times AT} \quad (5)$$

$$ELCR_j = \frac{SF_j \times C_w \times SA \times K_p \times ABS \times ET \times EF \times ED \times CF}{BW \times AT} \quad (6)$$

where C_w represents the pollutant concentration in water (mg/L); IRW , drinking water ingestion rate, 2 L/day; K_p , dermal permeability constant, cm/h; ABS , dermal absorption factor, 0.001; ET , exposure time, 0.6 h/day; and CF , unit conversion factor for water: 1 L/1,000 cm³.

A Monte Carlo analysis was conducted based on probability distributions for each parameter (USEPA, 1991). The probability of exceedance of the specified probability of effect was calculated (Table 6), and the resulting ELCRs were compared to acceptable guideline values. The USEPA has defined the target risk levels for contaminants in soils to be below a one-in-a-million (1×10^{-6}) excess lifetime cancer risk for carcinogens (USEPA, 2002).

Predicted values of pathway-specific ELCR due to oral, inhalation and dermal exposure to POPs in soils, surface water and groundwater for adults are shown in Table 6. Ingestion is the predominant pathway of exposure to residues from soil, surface water and groundwater; inhalation and dermal exposure of organic chemicals can be disregarded, especially if there data were insufficient or not readily available for inhalation or dermal exposure under residential land use (USEPA, 1991). Ingestion ELCR from surface water was greater than from groundwater and soil.

Calculations were made for the chemical-specific ELCR of the two classes of OCPs, HCH and DDT, as well as the sum of the two ELCR values based on intake from all exposure routes (Table 6). The mean Σ ELCRs were estimated to be 5.21E-08, 1.99E-06 and 1.66E-06 for adults' exposure to OCPs in soil, surface water and groundwater, respectively. Those values exceed the generally acceptable risk level recommended by USEPA for carcinogenic chemicals of 10^{-6} , not being greater than 10^{-4} , which indicates that the adsorption of OCPs may present little or no health threat. Due to the greater cancer slope factors, the contribution of Σ HCH to the Σ ELCR was greater than that of Σ DDT. Among the five OCP isomers (α -HCH, β -HCH, p , p' -DDE, p , p' -DDD and p , p' -DDT), the relative proportion contributed by α -HCH to the Σ ELCR was the greatest,

with an average value in soil of 72%; surface water, 80%; and groundwater, 49%. Due to the higher cancer slope factors and the greater concentrations, the contribution to the Σ ELCR of *p, p'*-DDE in soil (6%), β -HCH in surface water (17%) and in groundwater (47%) were larger.

[Table 6 here]

In summary, the residue characteristics of OCPs in the YRD were studied using comprehensive surveys in September 2013. A total of 67 soil, 26 surface water, 16 groundwater and 26 sediment samples were collected. The risk of residents' exposure to OCPs was assessed by a human health assessment model recommended by the USEPA. The main conclusions of this study are: (1) Σ HCH concentration in soil, surface water, groundwater and sediment varied from 0.51–208.48 ng/g dw, 1.10–62.15 ug/L, 3.95–154.45 ug/L, and 0.56–232.60 ng/g dw, respectively; Σ DDT concentrations ranged from undetectable – 109.16 ng/g dw, 1.46–35.52 ug/L, 1.16–30.89 ug/L and undetectable – 52.03 ng/g dw, respectively. (2) Compared with reported studies, OCP concentrations were at low levels in the YRD; compared with related environmental quality standards, 1.5% soil samples and 8.4% sediment samples were polluted by OCPs. (3) Composition of OCPs (DDT metabolites and HCH isomers) showed that DDTs in the multiple environments of the YRD not only came from residues of dicofol in the environment but also from atmospheric deposition, while HCH pollution results from the historical usage of a mixture of technical HCH and lindane. (4) Ingestion is the predominant pathway of OCP exposure to residues in all exposure routes, and the relative contribution of α -HCH to the Σ ELCR was the greatest due to higher cancer slope factors. Σ ELCR exposure to OCPs in surface water and groundwater exceeded the generally acceptable risk level of 1.0E-06 recommended by the USEPA for carcinogenic chemicals.

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Conflicts of Interest

The authors declare no conflict of interest.

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Table 1. OCP application in China from 1950-1990 (t) (Wang *et al.*, 2005)

Year	HCHs	DDTs	Gross pesticides
1950			213
1960	68310	8100	81415
1970	171672	18992	227314
1980	241613	16428	348847
1990			163586

Table 2. Concentration of OCPs in soil, water and sediment

	N	Min.	Max.	Mean	CV	Detection Rate
Surface soil (ng/g dw)						
α -HCH	67	0.10	14.80	1.79	1.91	100.0%
β -HCH	67	nd	8.36	0.37	3.60	16.7%
γ -HCH	67	nd	9.12	3.33	0.67	90.9%
δ -HCH	67	nd	200.70	4.32	5.64	97.0%
Σ HCH	67	0.51	208.48	9.66	2.60	100.0%
<i>p, p'</i> -DDE	67	nd	34.19	3.75	1.58	81.8%
<i>p, p'</i> -DDD	67	nd	3.88	0.30	2.33	28.8%
<i>o, p'</i> -DDT	67	nd	82.40	2.79	3.78	34.8%
<i>p, p'</i> -DDT	67	nd	10.91	1.51	1.39	93.9%
Σ DDT	67	nd	109.16	8.39	1.82	95.5%
Surface water (ug/L)						
α -HCH	26	0.19	27.39	7.52	1.15	100.0%
β -HCH	26	0.22	33.27	5.54	1.45	100.0%
γ -HCH	26	nd	6.43	1.97	0.94	95.2%
δ -HCH	26	0.25	14.80	3.53	1.08	100.0%
Σ HCH	26	1.10	62.15	18.57	0.79	100.0%
<i>p, p'</i> -DDE	26	0.18	11.28	2.10	1.37	100.0%
<i>p, p'</i> -DDD	26	nd	6.27	0.92	1.69	61.9%
<i>o, p'</i> -DDT	26	nd	16.56	2.76	1.49	66.7%
<i>p, p'</i> -DDT	26	0.05	23.41	4.01	1.38	100.0%
Σ DDT	26	1.46	35.52	9.79	0.96	100.0%
Groundwater (ug/L)						
α -HCH	16	0.64	11.09	3.84	0.89	100.0%
β -HCH	16	0.63	56.10	12.95	1.41	100.0%
γ -HCH	16	0.19	12.39	3.16	1.46	100.0%
δ -HCH	16	0.28	82.21	14.71	1.98	100.0%
Σ HCH	16	3.95	154.45	34.74	1.48	100.0%
<i>p, p'</i> -DDE	16	nd	28.16	6.75	1.52	88.9%
<i>p, p'</i> -DDD	16	nd	1.68	0.40	1.32	88.9%
<i>o, p'</i> -DDT	16	nd	1.11	0.42	1.05	66.7%
<i>p, p'</i> -DDT	16	0.82	10.06	3.21	0.98	100.0%
Σ DDT	16	1.16	30.89	10.78	1.06	100.0%
Sediment (ng/g dw)						
α -HCH	26	0.09	9.69	1.01	2.01	100.0%
β -HCH	26	nd	3.50	0.33	2.74	13.0%
γ -HCH	26	nd	5.73	1.42	1.33	39.1%
δ -HCH	26	nd	232.43	16.83	3.23	95.7%
Σ HCH	26	0.56	232.60	19.59	2.79	100.0%
<i>p, p'</i> -DDE	26	nd	6.44	1.97	0.93	82.6%
<i>p, p'</i> -DDD	26	nd	10.28	1.21	1.91	52.2%

<i>o, p'</i> -DDT	26	nd	35.32	2.26	3.26	30.4%
<i>p, p'</i> -DDT	26	nd	11.13	1.76	1.42	91.3%
Σ DDT	26	nd	52.03	7.20	1.52	95.7%

Values less than LOD (limit of detection) were set to zero for statistical purposes.

Σ HCH = α -HCH + β -HCH + γ -HCH + δ -HCH; Σ DDT = *p, p'*-DDE + *p, p'*-DDD + *o, p'*-DDT + *p, p'*-DDT

nd = not detected

Table 3. OCPs residues in the soil in selected areas in China and abroad (ng/g dw)

Region	Land use	N	Date	Σ HCHs	Σ DDTs	Reference
Beijing, China	orchard	17	2003	2–760.3 (32)	7.2–2910 (381.3)	(Shi <i>et al.</i> , 2005)
Tianjin, China	urban and rural soils	188	2001	1.3–1095 (45.8)	0.7–972.2 (56.0)	(Gong <i>et al.</i> , 2004a; Gong <i>et al.</i> , 2004b)
Tibet, China	surface soils	15	1993	0.18–5.38 (1.97)	0–2.83 (1.13)	(Fu <i>et al.</i> , 2001)
Pearl River Delta	farmland soil	37	2002	0.05–24.1 (2.94)	0.52–414 (20.1)	(Li <i>et al.</i> , 2006)
Haihe River Estuary	surface soils	31	2007	ND–1728 (93.9)	ND–288 (34.4)	(Zhao <i>et al.</i> , 2009)
Green food production base in Liaoning	paddy soil	122	1998	3–16 (7)	6–51 (22)	(Zhang <i>et al.</i> , 2001)
Central Germany	farmland soil	11	1995	4.60–11.50 (7.52)	23.7–173 (72.0)	(Manz <i>et al.</i> , 2001)
Romania	surface soils	26	2000	2.8–89.5 (26.1)	9–187.4 (62.5)	(Covaci <i>et al.</i> , 2001)
Hanoi, Vietnam	farmland soil	31	2006	0.05–20.57 (8.03)	0.02–171.83 (89.86)	(Toan <i>et al.</i> , 2007)
India Dehradun	paddy soil	10	2001	122–638 (326)	13–238 (117)	(Babu <i>et al.</i> , 2003)

Table 4. OCP residues in the surface water in China and abroad (ng/L)

Region	Date	Σ HCHs	Σ DDTs	Reference
Yangtze River	2005	0.55–28.07	nd–16.71	(Tang <i>et al.</i> , 2008)
Qiantang River	2005–2006	0.74–543.1	nd–204.1	(Zhou <i>et al.</i> , 2006)
Peacock River	2006	nd–19.00	nd–176	(Chen <i>et al.</i> , 2011)
Huaihe River	2007	0.47–6.13	4.44–33.59	(Feng <i>et al.</i> , 2011)
Ebro River, Spain	1995–1996	3.38	3.40	(Fernandez <i>et al.</i> , 1999)
Nestos River, Greece	1996–1998	nd–68.00	nd–64.00	(Golfonopoulos <i>et al.</i> , 2003)
Gomti River, India	1996–1998	0.02–4846.00	0.20–4578.00	(Malik <i>et al.</i> , 2007)
Kucuk Menderes River, Turkey	2002–2003	187–337	72–120	(Turgut, 2003)

Table 5. OCP residues in the sediment in selected areas in China and abroad (ng/g dw)

Region	N	Date	ΣHCHs	ΣDDTs	Reference
Liaodong Bay, China	3	2006	20.1–103.0 (68.6)	7.7–76.9 (42.80)	(Lu <i>et al.</i> , 2008)
Dalian Bay, China	30	1996	7.54–92.30 (21.25)	20.12–72.3 (21.75)	(Li and Fu, 1998)
Tianjin Dagu Drainage Canal	9	2003	33.24–141.03 (87.74)	3.60–83.49 (35.52)	(Yang <i>et al.</i> , 2005)
Yangtze Delta, China	10	2004	0.5–17.5 (6.0)	0.9–33.1 (8.2)	(Liu <i>et al.</i> , 2008)
Pearl River Estuary, China	20	1998	0.28–1.23 (0.68)	1.36–8.99 (2.84)	(Hong <i>et al.</i> , 1999)
Wu-Shi River estuary, Taiwan	19	1998	0.99–14.5 (3.79)	0.53–11.4 (2.51)	(Doong <i>et al.</i> , 2002a)
Ulsan Bay, Korea	32	2000	0.02–4.55 (0.64)	0.02–41.9 (3.34)	(Khim <i>et al.</i> , 2001)
Andes Lake	17	1999	nd–0.23	0.019–4.1	(Borghini <i>et al.</i> , 2005)
James Stuart Island in Antarctica	25	2005	0.14–0.76	0.19–1.15	(Klanova <i>et al.</i> , 2008)

Table 6. Characterization of cancer risk for local residents by exposure route

	α -HCH	β -HCH	p, p' -DDE	p, p' -DDD	p, p' -DDT	HCHs	DDTs	OCPs
Soil								
Ingestion	3.84E-08	2.30E-09	3.07E-09	3.49E-10	1.75E-09	4.07E-08	5.17E-09	4.59E-08
Inhalation	8.25E-13	4.93E-14	6.58E-14	7.50E-15	3.76E-14	8.74E-13	1.11E-13	9.85E-13
Dermal	5.19E-09	3.10E-10	4.15E-10	4.72E-11	2.37E-10	5.50E-09	6.99E-10	6.20E-09
Sum	4.36E-08	2.61E-09	3.48E-09	3.96E-10	1.99E-09	4.62E-08	5.87E-09	5.21E-08
Surface water								
Ingestion	1.58E-06	3.32E-07	1.68E-08	1.04E-08	4.55E-08	1.91E-06	7.27E-08	1.99E-06
Dermal	1.27E-09	2.67E-10	1.35E-11	8.38E-12	3.66E-11	1.54E-09	5.84E-11	1.60E-09
Sum	1.58E-06	3.33E-07	1.68E-08	1.04E-08	4.55E-08	1.91E-06	7.27E-08	1.99E-06
Groundwater								
Ingestion	8.07E-07	7.77E-07	2.90E-08	4.53E-09	3.63E-08	1.58E-06	6.99E-08	1.65E-06
Dermal	6.49E-10	6.25E-10	2.33E-11	3.64E-12	2.92E-11	1.27E-09	5.62E-11	1.33E-09
Sum	8.08E-07	7.78E-07	2.90E-08	4.53E-09	3.64E-08	1.59E-06	6.99E-08	1.66E-06

Figure Captions

Figure 1. DDT outputs from 1951 to 2003 in China

Figure 2. Locations of sampling sites

Figure 3. Percentage composition of DDTs in soil, surface water, groundwater and sediment

Figure 4. Percentage composition of HCHs in soil, surface water, groundwater and sediment

Figure 1. DDT outputs from 1951 to 2003 in China ^a (MEP, 2007)

^a No data about DDT outputs are available before 1951.

Figure 2. Locations of sampling sites

Figure 3. Percentage composition of DDTs in soil, surface water, groundwater and sediment

Figure 4. Percentage composition of HCHs in soil, surface water, groundwater and sediment