

# Levels and patterns of organochlorine pesticides in agricultural soils in an area of extensive historical cotton cultivation in Henan province, China

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**Abstract** Organochlorine pesticides (OCPs) have attracted widespread concern because of their environmental persistence and toxicity. The historical influence of different agricultural land use types on soil concentrations of OCP residues was investigated by collecting a total of 52 surface soil samples from long-term cotton fields and fields with other crops in Lvdi township, Henan province, eastern central China. The concentration, composition, and possible sources of 16 OCPs were determined and a health risk assessment of these soils was conducted. Hexachlorocyclohexane (HCH), heptachlor, chlordane, and dichloro diphenyl trichloroethane plus its main metabolites (DDTs) were the most frequently detected OCPs with concentrations of 2.9–56.4 ng g<sup>-1</sup>, 4.3–14.0 ng g<sup>-1</sup>, 18.0–1254.4 ng g<sup>-1</sup>, and below detection limit (BDL)–206.1 ng g<sup>-1</sup>, respectively. Analysis of variance of p,p-DDE shows significant ( $P < 0.05$ ) differences while other OCPs show no significant differences between historical cotton fields and fields containing other crops. Compositional analysis suggests that the HCH is derived mainly from the

use of lindane and that there are recent inputs. Analysis of variance and compositional analysis indicate that the p,p-DDE in surface soil from long-term cotton fields is derived mainly from the aerobic biodegradation of historical residues. The sum of carcinogenic risk values of OCPs for soil samples were found to be  $1.58 \times 10^{-6}$ , posing a low cancer risk to the inhabitants of the region studied.

**Keywords** OCPs · Surface soils · Cotton fields · Compositional analysis · Source identification · Health risk

## Introduction

Soil contamination with organochlorine pesticides (OCPs) such as dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), chlordane, and heptachlor is of great concern due to their toxicity, bioaccumulation, and persistence in the environment (Yang et al. 2005). The wide distribution of their residues and their carcinogenic properties. They may also affect the normal function of the endocrine and reproductive systems of humans and wildlife (Xue et al. 2005). According to the Stockholm Convention, DDT, hexachlorobenzene (HCB), aldrin, chlordane, dieldrin, endrin, and heptachlor are among the twelve most persistent organic pollutants (POPs). Furthermore, HCH is considered to be a priority pollutant by the United States Environmental Protection Agency (US EPA) (UNEP 2003).

China is a major agricultural country and is the second largest producer and consumer of pesticides globally (Zhang et al. 2009). From 1952 to 1983 the country produced and consumed more than 4 million tonnes of HCH insecticides and 0.27 million tonnes of DDT (Zhang et al. 2009), amounting to 46 and 20 % respectively, of global consumption. Although the use of HCH and DDT was banned in 1983,

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a number of OCPs continue to be used in some areas. According to a report (Li et al. 2001), 3200 tonnes of lindane (at least 99 %  $\gamma$ -HCH) has been used from 1991 to 2000. Furthermore, DDT continues to be used in China to produce dicofol as an intermediate (Wong et al. 2006).

Even though their production and usage have been officially banned, OCP residues are still found in soils (Shi et al. 2005), waters (Wu et al. 2014), sediments (Yang et al. 2005; Yang et al. 2010), and the air (Qiu et al. 2004). The residue levels have declined substantially but they may still influence environmental quality, human health, and food security (Wang et al. 2007). For example, agricultural soils of the Yellow River Delta (Da et al. 2014), of the Pearl River Delta (Li et al. 2006), and of Jiangsu province (Yang et al. 2008) and Beijing (Shi et al. 2005) have also been reported to contain organochlorine pollution to varying extents. The highest residue levels of DDT ( $484.24 \mu\text{g kg}^{-1}$ ) and HCH ( $17.93 \mu\text{g kg}^{-1}$ ) have been found in cotton and paddy fields, respectively (Cai 1996), in China. These investigations involve waters, sediments, and agricultural land in general. However, the surveys concentrated in specific land use types are limited and the residue levels and human health risk are unclear after several decades of degradation. In Luoyang, a major cotton-producing area, large amounts of technical HCH and DDT were used in cotton fields to control cotton bollworms because of a lack of effective biological control measures in the 1970s, and this has resulted in severe historical environmental pollution. However, the current situation of pesticide residues in the region also requires investigation after long periods of metabolism. We therefore targeted our survey of the residue levels of historical cotton fields and fields containing other crops. The objectives of the present study were (1) to determine the concentrations and composition of 16 OCPs in agricultural soils in Lvdián township, an area of extensive historical cotton cultivation in Henan province, (2) to compare the residue levels of the 16 OCPs in two historical land use types, (3) to identify the possible sources of the DDTs and HCH, and (4) to assess the human health risk due to their residues.

## Materials and methods

### Study area and sampling

Lvdián township is located in Luoyang City in the west of Henan province and is characterized by a temperate monsoon climate and four distinct seasons typified by cold and dry winters and hot and rainy summers. The average annual temperature is  $14.5^\circ\text{C}$  and the mean annual precipitation is approximately 603 mm with most precipitation occurring from July through September. The township is mainly hilly and mountainous with two major rivers and covers an area of

$124 \text{ km}^2$ , of which there are 5934 ha of cultivated land area and the township has a population of 5.78 million.

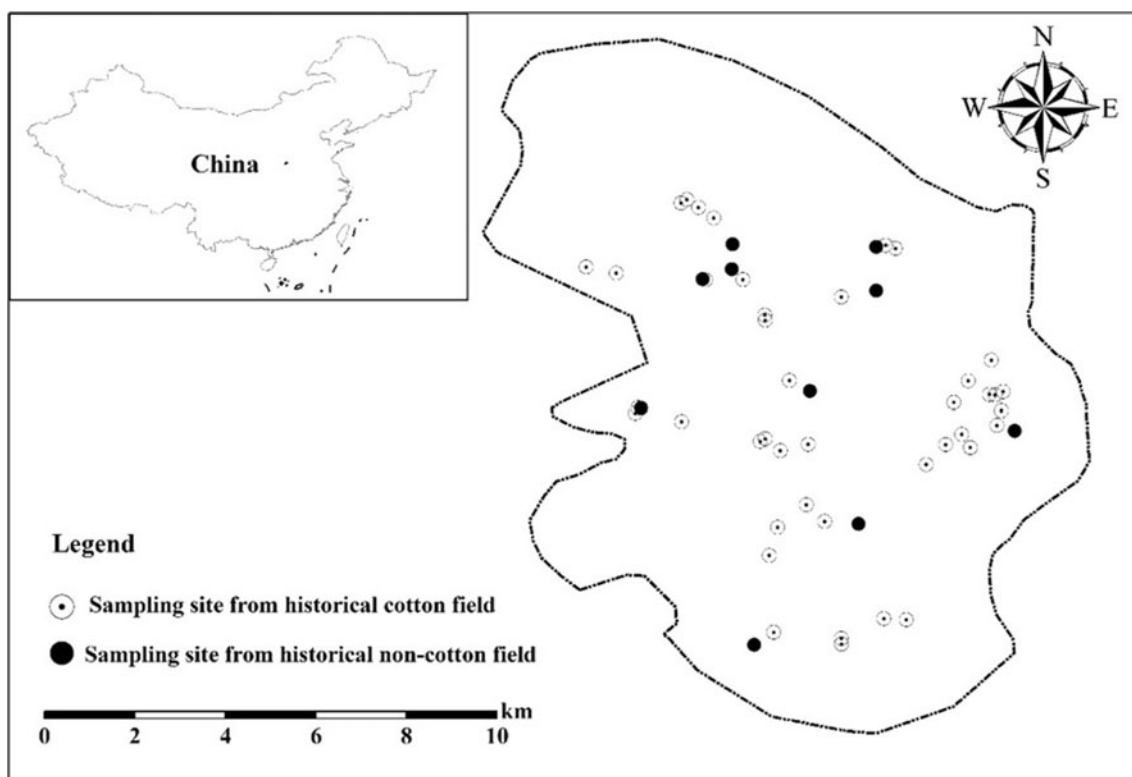
A total of 52 surface (0–20 cm depth) soil samples representing 10 field soils historically used to grow crops other than cotton and 42 historical cotton field soils were collected in May 2015. According to an earlier interview survey, representative, and extensive historical cotton cultivation fields in history were sampled as the main research areas, and the sampling points of historical non-cotton fields were sited near to the historical cotton fields. The locations of the samples were relatively evenly distributed across the region (Fig. 1) and the crops in the sampling areas were mainly wheat and rape with a small number of vegetable fields and woodlands and some fallow areas. Samples were collected using a stainless steel shovel. Approximately 500 g of soil were collected from five points at each sampling site. The samples were stored at  $4^\circ\text{C}$  for a maximum of seven days before analysis.

### Sample extraction and analysis

The soil samples were freeze-dried and sieved through a 60-mesh screen after stones and other debris were removed manually to obtain a homogeneous matrix. The extraction method was adapted from Sui et al. (2013). An aliquot of 1.00 g soil sample was extracted with 20 mL of a mixed solution of acetone and hexane (1:1 v/v) for 30 min in an ultrasonic bath followed by centrifugation and then filtered through a filter paper with 5 g anhydrous sodium sulfate into a concentration bottle. This process was repeated three times to ensure complete extraction. The sample extracts were condensed to near dryness with a rotary evaporator at 300 Pa and with the water bath temperature maintained at  $40^\circ\text{C}$ . Then 5 mL n-hexane was added for solvent exchange and further concentrated to 1 mL. The concentrated solutions were purified by upward passage through a glass column with neutral silica gel (4 g), acidic silica gel (0.5 g), and anhydrous sodium sulfate (1 g) (Zhang et al. 2009) with dichloromethane and n-hexane (4:1). The liquids collected were condensed to 1 mL and transferred to graduated test tubes. The samples were dried under a gentle stream of nitrogen and pooled together in 1 mL n-hexane.

The reagents used, n-hexane and dichloromethane were of high performance liquid chromatography (HPLC) grade and the acetone was distilled to remove impurities. Moreover, the anhydrous sodium sulfate and silica were dried at  $400^\circ\text{C}$  for 6 h in a muffle furnace before use.

The OCP residues were analyzed by gas chromatography (Agilent 7890B, Santa Clara, CA) equipped with a  $^{63}\text{Ni}$  electron capture detector (GC-ECD) and a  $30 \text{ m} \times 0.25 \mu\text{m} \times 0.25 \mu\text{m}$  HP-5 capillary column. Ultra-high purity  $\text{N}_2$  (99.9999 %) was used as the carrier gas. The oven temperature program was as follows: injector and detector temperatures were 200 and  $300^\circ\text{C}$ , respectively, initial run temperature



**Fig. 1** Map of the study area showing a relatively even distribution of sample sources

was set at 100 °C, ramped at 80 °C min<sup>-1</sup> to 200 °C, then ramped at 0.5 °C min<sup>-1</sup> to 206 °C and held for 1 min, and then ramped at 5 °C min<sup>-1</sup> to 220 °C and held for 1 min, and finally ramped at 10 °C min<sup>-1</sup> to 270 °C.

### Quality control and quality assurance

Quantification of OCPs was determined from an external standard comparing peak area. The correlation coefficients (*r*) of calibration curves of OCPs were all higher than 0.999. A procedural blank sample and a spiked sample with standards were run to check for interference and cross-contamination every 10 samples. The standard solutions were purchased from J&K Scientific Ltd., Beijing, China. The pesticide recoveries were determined relative to the ratio of direct injection of extract and the working standards (10 µg L<sup>-1</sup>) prepared in n-hexane. Five clean soils were spiked with the standard solution, extracted and analyzed in the same way as the samples. The results are listed in Table 1. The recovery values ranged from 55 to 110 %, of which the recovery of α-HCH was 55 %, lower than those of other HCH isomers due to its low boiling point and volatility.

### Statistical analysis

Differences in OCP concentrations between historical cotton fields and other fields were compared by analyzing the

variances of the two land use types by one-way analysis of variance (ANOVA) using the SPSS 17.0 software package.

### Health risk assessment

Most organochlorine pesticide residues have led to growing concern regarding their potential for contamination of the environment and also associated effects on human health (Shi et al. 2005). Ordinarily, humans may be exposed to OCPs in agricultural soils via ingestion, dermal contact, and inhalation of soil particles. They were estimated based on the following Eqs. (1), (2), and (3), which have been adapted from the U.S. Environmental Protection Agency (USEPA 1997, 2009).

$$CR_{\text{ingestion}} = \frac{(C \times \text{IngR} \times \text{EF} \times \text{ED}) \times \text{CF} \times \text{SF}}{\text{BW} \times \text{AT}} \quad (1)$$

$$CR_{\text{dermal}} = \frac{(C \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED}) \times \text{CF} \times \text{SF}}{\text{BW} \times \text{AT}} \quad (2)$$

$$CR_{\text{inhal}} = \frac{(C \times \text{InhR} \times \text{BF} \times \text{EF} \times \text{ED}) \times \text{IUR}}{\text{PEF} \times \text{AT}} \quad (3)$$

where *C* (mg kg<sup>-1</sup>) is the concentration of OCPs in soil; *CR*<sub>ingestion</sub> is the cancer risk via accidental ingestion of soil; *CR*<sub>dermal</sub> is the cancer risk via dermal contact with soil; *CR*<sub>inhal</sub> is the cancer risk via inhalation of soil; IngR is the ingestion rate, 100 mg day<sup>-1</sup> for adults (USEPA 2001). EF is the exposure frequency, 350 days yr<sup>-1</sup> (USEPA 1989). ED is the exposure duration, 70 yr for adult and 12 yr for children (USEPA

**Table 1** Recoveries in the analysis of organochlorine pesticides by GC-ECD

Compound	Recovery (%)	RSD (%)	Compound	Recovery (%)	RSD (%)
α-HCH	55	4.21	o,p-DDT	90	5.78
β-HCH	67	2.36	p,p-DDT	89	0.75
γ-HCH	57	3.97	Heptachlor	66	0.15
δ-HCH	67	1.69	γ-Chlordane	95	3.05
o,p-DDE	81	1.57	Endosulfan I	81	3.68
p,p-DDE	110	3.84	α-Chlordane	72	1.24
o,p-DDD	70	6.46	Dieldrin	78	6.15
p,p-DDD	71	1.26	Endosulfan sulfate	80	5.60

RSD relative standard deviation

1989). CF is the conversion factor,  $1 \times 10^{-6} \text{ kg mg}^{-1}$  (USEPA 1997). SF is the oral slope factor, in this study,  $2 \text{ kg day mg}^{-1}$  (Ge et al. 2013). BW is the average body weight, in this study, 56.8 kg (MEP 2014). AT is the averaging time, 25,550 days (Ge et al. 2013; USEPA 2001). SA is the exposed skin area, in this study,  $5700 \text{ cm}^2$  (Qu et al. 2015). AF is the skin adherence factor,  $0.2 \text{ mg cm}^{-2} \text{ day}^{-1}$  (USEPA 2001). ABS is the dermal absorption factor, for DDT, DDE, and DDD 0.2, for HCH 0.1, for heptachlor 0.2, and for chlordane 0.05 (Health Canada 2004). GIABS is the fraction of contaminant absorbed in the gastrointestinal tract, 1 (Ge et al. 2013; USEPA 1989). InhR is the inhalation rate,  $15.8 \text{ m}^3 \text{ d}^{-1}$  (USEPA 1989). BF is the absorption factor for the lungs, 1 (Ge et al. 2013; USEPA 1989). IUR is the inhalation unit risk,  $0.57 \text{ mg}^{-1} \text{ m}^{-3}$  (Ge et al. 2013; USEPA 1989). and PEF is the particle emission factor,  $1.36 \times 10^9 \text{ m}^3 \text{ kg}^{-1}$  (Ge et al. 2013; USEPA 1989).

## Results and discussion

### Soil OCP concentrations in the study area

Concentrations of OCPs detected in the surface soils from historical cotton fields and other fields are shown in Table 2. The total concentration of OCPs ranged from 85 to  $1392 \text{ ng g}^{-1}$  with an average value of  $213 \text{ ng g}^{-1}$  in historical cotton fields and the corresponding values for other fields were 101 to  $394 \text{ ng g}^{-1}$  with a mean value of  $173 \text{ ng g}^{-1}$ . HCH, heptachlor, and g-chlordane were detected in all of the soil samples with detection rate up to 100 %. DDTs were detected in all the historical cotton fields and in all but one of the other fields. The concentration of HCH ranged from 6.5 to  $56.4 \text{ ng g}^{-1}$ , with a mean value of  $19.0 \text{ ng g}^{-1}$  in historical cotton fields, and ranged from 2.9 to  $53.2 \text{ ng g}^{-1}$  with a mean of  $21.6 \text{ ng g}^{-1}$  in other fields. The mean residue level of heptachlor was  $9.6 \text{ ng g}^{-1}$  in historical cotton fields and  $10.3 \text{ ng g}^{-1}$  in other fields. The largest residues of g-chlordane were found in historical cotton fields with concentration up to  $1254 \text{ ng g}^{-1}$ , higher than the levels of other types of organochlorine pesticide but the average ( $110 \text{ ng g}^{-1}$ ) was

close to that ( $99.7 \text{ ng g}^{-1}$ ) of other fields. The average concentration of DDTs ( $71.3 \text{ ng g}^{-1}$ ) in historical cotton fields was higher than that ( $38.5 \text{ ng g}^{-1}$ ) in other fields, while the average content of p,p-DDE was  $50.3 \text{ ng g}^{-1}$  in historical cotton fields and  $18.9 \text{ ng g}^{-1}$  in other fields.

Technical DDT and HCH were produced and consumed widely in China and they have therefore been generally considered to be representative of the composition of OCPs in assessing pollution levels (Zhao et al. 2009). Some survey results of agricultural soils in other regions are listed in Table 3 for comparison with the present study. The soil concentrations of DDTs in our study are somewhat higher than those reported in soils in Fujian but lower than those in soils of Beijing, the northwest and cotton soils of Jiangsu province in east China. According to the Environmental Quality Standard for soils (GB15618-1995), the second grade value for DDTs and HCHs is proposed to be  $<500 \text{ ng g}^{-1}$  for arable land and the first grade tolerance concentration of both DDTs and HCH is  $<50 \text{ ng g}^{-1}$ . The GB15618-1995 standard may need to be reviewed in the long-term. If we compare the concentrations of DDTs and HCH in our study with soil environmental quality standard for agricultural land (draft for comment), about 23 % of soil samples in our area exceed the standard value for DDTs and the content of HCH is below standard value. Other organochlorine pesticides have no clear standards for arable land. Consequently, the soils in this area can be considered to be slightly polluted by OCPs.

### Comparison of OCPs residues in different historical land use types

The mean concentrations of OCPs in historical cotton fields and other fields were compared by one-way analysis of variance. According to the results listed in Table 4, p,p-DDE showed a difference at the 5 % level of significance. The DDTs almost reached significance at the 5 % level with a probability of 0.069 but other components showed no significance differences.

Generally, p,p-DDT is the active ingredient in DDTs and is degraded to p,p-DDE under aerobic conditions and to p,p-

**Table 2** Concentrations (ng g<sup>-1</sup>) of individual organochloride pesticides in surface soils from historical cotton fields and other fields

Compound	Range		Mean		Detection rate (%)	
	Historical cotton fields	Historical non-cotton fields	Historical cotton fields	Historical non-cotton fields	Historical cotton fields	Historical non-cotton fields
α-HCH	BDL–12.8	BDL–3.4	1.7	0.7	40.5	20.0
β-HCH	BDL–3.9	BDL–2.2	0.3	0.4	21.4	30.0
γ-HCH	2.7–19.5	2.9–15.0	7.0	7.3	100.0	100.0
δ-HCH	BDL–28.0	BDL–45.0	10.0	13.2	95.2	90.0
HCH	6.5–56.4	2.9–53.2	19.0	21.6	100.0	100.0
o,p-DDE	BDL–5.8	BDL–3.4	0.7	1.0	23.8	30.0
p,p-DDE	8.4–176.7	BDL–46.0	50.3	18.9	100.0	90.0
o,p-DDD	BDL–2.2	BDL	0.1	0	2.4	0
p,p-DDD	BDL–10.5	BDL–3.6	0.5	0.4	7.1	10.0
o,p-DDT	BDL–25.4	BDL–6.9	4.3	3.4	59.5	60.0
p,p-DDT	6.3–43.6	BDL–59.5	15.3	14.8	100.0	90.0
DDTs	20.0–206.1	BDL–79.2	71.3	38.5	100.0	90.0
Heptachlor	4.3–14.0	6.5–13.5	9.6	10.3	100.0	100.0
g-Chlordane	18.0–1254.4	48.5–317.8	109.9	99.7	100.0	100.0
Endosulfan I	BDL–3.3	BDL	0.4	0	14.3	0
α-Chlordane	BDL	BDL	0	0	0	0
Dieldrin	BDL	BDL	0	0	0	0
Endosulfan sulfate	BDL	BDL	0	0	0	0
OCPs	85.0–1392.1	101.3–393.8	212.7	173.3	100.0	100.0

BDL below detection limit; HCH sum of α-, β-, γ-, and δ-HCH isomers; DDTs sum of DDT plus its main metabolites o,p-, p,p-DDE and o,p-, p,p-DDD; OCPs, sum of 16 organochloride pesticides

DDD under anaerobic conditions (Zhao et al. 2009). Over recent decades the majority of DDT in soils has degraded to DDE and DDD, resulting in the differences between historical cotton fields and other fields. Moreover, the residual quantity of DDE was greater than that of DDT in historical cotton fields (Table 2) and this confirms that the DDT was metabolized to DDE. The residues of DDE in historical cotton fields appear to be larger than those in non-cotton fields. In the environment, α- and γ- HCH can be converted to β-HCH, which is more stable than the other HCH isomers (Kim et al. 2007). However, photochemical transformation and biodegradation may transform γ-HCH to α-HCH (Strandberg et al. 1998). DDTs are more persistent than HCH in soil and the residues

of HCH were lower than DDTs in surface soil (2.93 to 56.41 ng g<sup>-1</sup> for HCH, and from BDL to 206.13 ng g<sup>-1</sup> for DDTs). In addition, the content of HCH in soil dramatically decreased and showed no significance differences (Table 4) between historical cotton fields and other fields due to the effects of degradation over the long periods. Moreover, the OCPs such as heptachlor and chlordane were widely used in croplands to protect the crops from insect pests. In addition, local farmers cultivated many cotton crops at the tops of hills to obtain increased economics from a large-scale textile mill. As would be expected, the level terrain and areas of slight depression were relatively fertile land and were used to grow food crops. The similar content of other OCPs in historical

**Table 3** Comparison of DDT and HCH levels (ng g<sup>-1</sup>) in the agricultural soils with the levels reported in other regions

Area	Land use types	DDTs		HCH		Reference
		Range	Mean	Range	Mean	
Beijing	Agricultural	7.2–2910.0	381.3	2.0–760.3	32.0	(Shi et al. 2005)
Northwestern	Agricultural	67.1–79.4	74.4	86.1–93.9	91.1	(Wang et al. 2006)
Jiangsu	Agricultural	4.2–678.6	190.4	– <sup>a</sup>	–	(Yang et al. 2008)
Fujian	Agricultural	0.6–78.1	3.9	0.7–30.2	9.8	(Yang et al. 2012)
This study	Agricultural	0–206.1	65.0	2.9–56.4	19.5	

<sup>a</sup> no given value

**Table 4** Analysis of variance of individual organochloride pesticides comparing historical cotton fields and fields with other cropping histories

Component	Significance	Component	Significance
α-HCH	0.226	p,p-DDT	0.886
β-HCH	0.822	DDTs	0.069
γ-HCH	0.832	Heptachlor	0.505
δ-HCH	0.177	γ-Chlordane	0.885
HCH	0.440	Endosulfan I	0.214
o,p-DDE	0.632	α-Chlordane	– <sup>a</sup>
p,p-DDE	0.049*	Dieldrin	–
o,p-DDD	0.63	Endosulfan sulfate	–
p,p-DDD	0.817	OCPs	0.594
o,p-DDT	0.631	–	–

\**p*<0.05

<sup>a</sup>no given value;

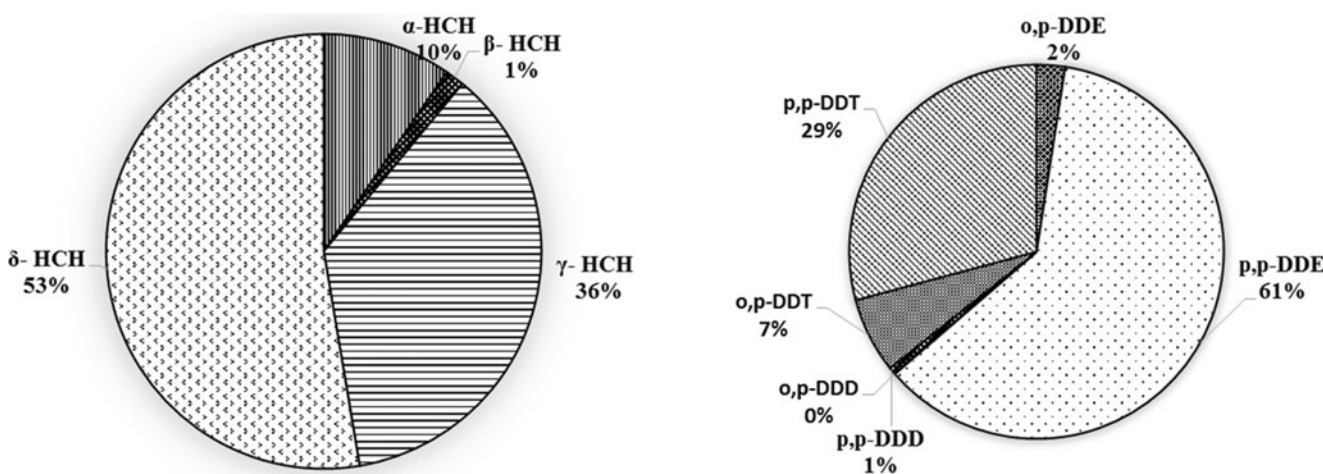
cotton fields and other fields may be attributable to the wide use of OCPs historically and perhaps also to transfer due to rainfall.

**Composition and source identification**

Generally, technical HCH consists mainly of 55–80 % α-HCH, 5–14 % β-HCH, 8–15 % γ-HCH, and 2–10 % δ-HCH and lindane mostly comprises >99 % γ-HCH (Ge et al. 2013). If there were no fresh inputs of technical HCH, β-HCH was usually the predominant isomer in soils owing to its resistance to hydrolysis and environmental degradation as well as the transformation of α-HCH and γ-HCH. As can be seen in Fig. 2, the proportion of HCH isomers followed the order δ-HCH>γ-HCH>α-HCH>β-HCH and their corresponding contributions were approximately 53, 36, 10, and 1 %, respectively. The percentages of α-HCH and β-HCH decreased compared with the primitive components but the

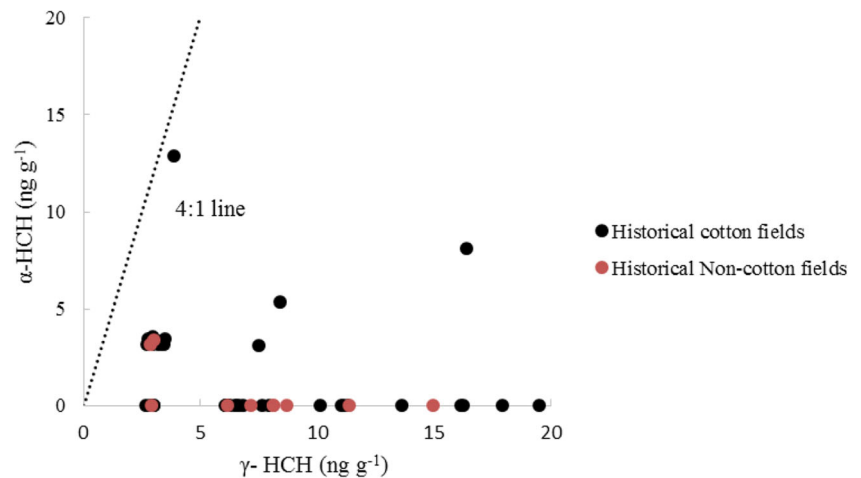
percentages of δ-HCH and γ-HCH increased. Generally, α-, β- and γ-HCH are the most common isomers of HCHs in the environment but much higher concentrations of δ-HCH were detected in our present study, similar to the results obtained from the Beijing Guanting reservoir (Xue et al. 2006) and surface sediments of Taihu Lake (Zhao et al. 2009). However, the explanations require further study. Technical HCH usually possesses a α-HCH/γ-HCH ratio of 4–7 and a β-/(α+γ)-HCH ratio of 0.06–0.17. For lindane, the α-HCH/γ-HCH ratio is nearly zero and the β-/(α+γ)-HCH ratio is less than 0.06. Therefore, the values of α-/γ-HCH in soil samples can be used to identify the sources of HCHs. As shown in Fig. 3, the ratio of α-HCH/γ-HCH lay between 0 and 3.30 with a mean value of 0.41 in this study area, much lower than that of technical HCH. This indicates that the source of HCH might be the use of lindane (Yang et al. 2010). The β-/(α+γ)-HCH ratio can be used to identify the history of HCH use, and 0.5 has been used as a threshold (Liu et al. 2012). According to the analysis in the present study, the β- / (α+γ) -HCH ratios of the all soil samples were 0.5, suggesting some recent use of lindane or the existence of an atmospheric source for the input (Liu et al. 2012).

As shown in Figs. 2 and 3, δ-HCH and γ- HCH are the main residues of HCH in all soil samples, and the residue contents in the most samples of historical cotton fields are larger than that in historical non-cotton fields although the analysis of variance showed no significant differences (Table 4). The α-HCH/γ-HCH ratio was <4 for all samples, while the value of 80 % of non-cotton field points is 0, which indicating that the HCH in non-cotton fields was mostly derived from lindane. The α-/γ-HCH for the majority of historical cotton fields was >0, implying that the source of HCH was the application of technical HCH and lindane. This phenomenon may result from the wide application of technical HCH in cotton fields for prevention of insect infestation. After several decades of degradation, the residues of HCH in cotton fields



**Fig. 2** Average composition of HCHs and DDTs in the surface soils

**Fig. 3** Relationship between  $\alpha$ -HCH and  $\gamma$ -HCH in the surface soils tested



were still detectable and showed a high content versus historical non-cotton fields.

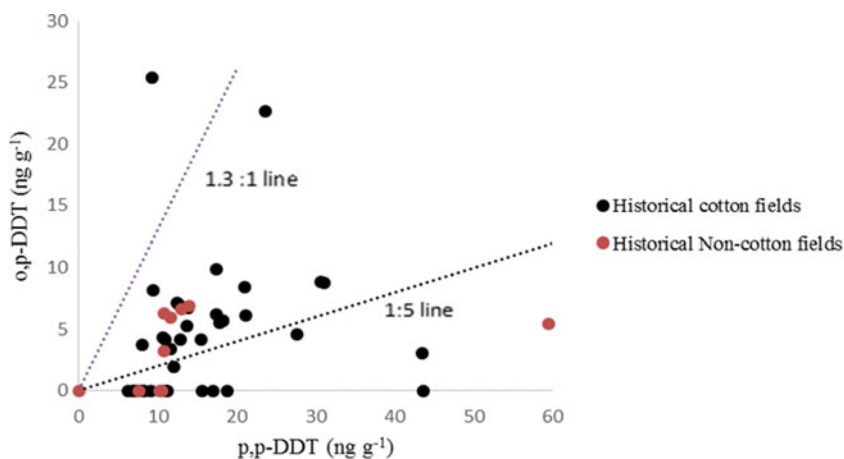
Although the use of technical DDT in China was officially banned in 1983, about 4000–6000 tonnes of DDT continued to be produced annually for export and for use as an intermediate in the production of dicofol (Wei et al. 2007). There remain currently two DDT technical production enterprises and one DDT processing enterprise together with three to five factories producing dicofol in China (NIP 2007). DDT is usually degraded to the stable and toxic metabolites DDE and DDD in soils. As shown in Fig. 2, p,p-DDE was the predominant residue and this may reflect the degradation of DDT under aerobic conditions in the surface soils over a period of several years. It is also noteworthy that  $\alpha$ -chloro-DDT, one of the components of dicofol, can also be degraded to p,p-DDE (Brown et al. 1986). The sources of the DDTs may be evaluated by analyzing their components in the study area. Technical DDT consists of p,p-DDT (85 %) and o,p-DDT (15 %) while dicofol often contains impurities in the form of DDTs. The ratios of o,p-DDT / p,p-DDT ranged from 0.2 to 0.3 in technical DDT and ranged from 1.3 to 9.3 in dicofol (Qiu et al. 2005; Yang et al. 2010). Therefore, a o,p-DDT / p,p-DDT ratio of <0.2 indicates that technical DDT was the main source while a high ratio is thought to indicate pollution by dicofol (Qiu et al. 2005). The o,p-DDT/p,p-DDT ratios found are shown in Fig. 4 and range from 0 to 2.7 with an average value of 0.28. All the ratios were 1.3 except for one sample, suggesting that the detectable DDTs were derived from both technical DDT and dicofol. A (DDE+DDD)/DDTs ratio of >0.5 can be judged to indicate aged DDTs and a ratio much lower than 0.5 can be considered to show recently input DDT (Li et al. 2006). According to Fig. 5, the values in most samples were 0.5, indicating that long-term weathering of DDTs was the primary source and a minority of samples contained newly input DDTs. DDT can be degraded to DDE under

aerobic conditions and to DDD under anaerobic conditions. Hence, the p,p-DDD/p,p-DDE ratio can reflect the biodegradation conditions of p,p-DDT in the region. A p,p-DDD/p,p-DDE ratio of <1 implies the predominant occurrence of aerobic degradation (Wu et al. 2013). In the present study the p,p-DDD/p,p-DDE ratio ranged from 0 to 0.94 with a mean of 0.03, suggesting that the parent DDTs decomposed mainly under aerobic conditions and this is consistent with the plowing method used locally.

According to Fig. 2, the predominant metabolites, DDE and DDD, accounted for 70 % in DDT residues. Moreover, analysis of variance of p,p-DDE shows significant ( $P < 0.05$ ) differences between the two land use types (Table 4). In addition, as can be seen in Figs. 4 and 5, the content of DDT and DDE+DDD in the majority of samples from historical cotton fields was larger than that in non-cotton fields except for one sample. However, the o,p-DDT/p,p-DDT ratio in most samples ranged from 0.2 to 1.3, suggesting that the source of DDTs was technical DDT combined with dicofol and was undergoing long-term weathering. This could be attributed to vast usage of technical DDT in cotton fields and degradation in the soil. DDE and DDD, the main metabolites of DDT, accumulate in the environment, leading to DDD and DDE becoming the main components of DDTs in the study region.

Heptachlors were produced and used in China in the 1960s and 1970s as a pesticide primarily used against soil insects and termites (Wu et al. 2014) as well as termite control in railway sleepers, and production was halted in 1978. In the present study, the content of heptachlor ranged from 4.30 to 13.95 ng g<sup>-1</sup> with a mean value of 9.64 ng g<sup>-1</sup> in historical cotton fields and 6.49–13.5 ng g<sup>-1</sup> with an average of 10.3 ng g<sup>-1</sup> in other fields. In all soil samples tested, the concentrations of heptachlor were much higher than that of heptachlor epoxide (below detection limit, BDL), indicating that

**Fig. 4** Concentration of o,p-DDT versus the concentration of p,p-DDT in surface soils from Lvodian township



recent applications of heptachlor might be the primary source of fresh inputs of heptachlor.

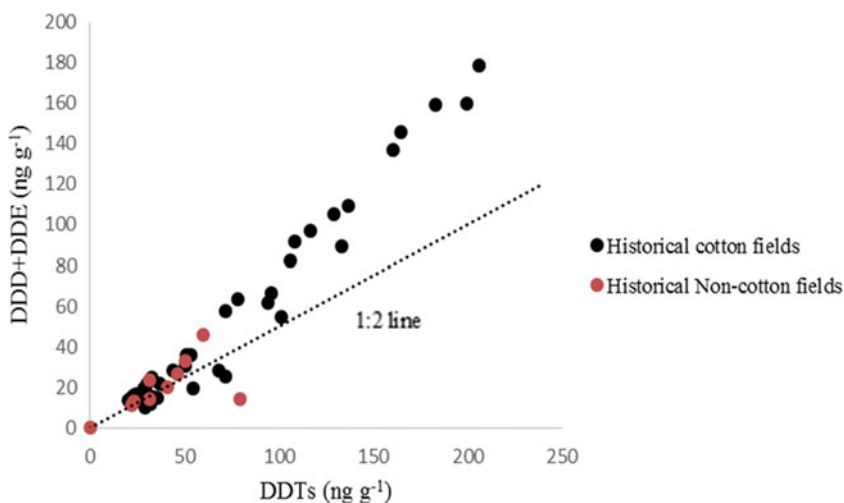
Chlordane was also widely used against infestation by insects (Boonyatumanond et al. 2002) such as mole crickets, cutworms and white ants. Chlordane was produced at a rate of 9000 tonnes per annum since the 1950s, and it is still produced and applied. In general, it is a mixture of  $\gamma$ -chlordane,  $\alpha$ -chlordane, and heptachlor and the ratio of  $\alpha$ -chlordane/ $\gamma$ -chlordane is about 0.77 (Zhang et al. 2006). An  $\alpha$ -chlordane/ $\gamma$ -chlordane ratio 1.0 suggests that the chlordane is derived mainly from legacy use (Zhao et al. 2013). The ratio in all of our samples was far below 1.0, implying that the chlordane was derived primarily from new inputs in the survey area.

Endosulfan is one of the few organochlorine insecticides that are still in use globally (Qiu et al. 2004). Technical endosulfan typically contains 70 % endosulfan I and 30 % endosulfan II, and endosulfan sulfate is the dominant component in the environment as a result of the photolysis and biodegradation of endosulfan. The detection rate of endosulfan I in our study area was very low at

14.3 % with none detected in historical cotton fields or other fields and no endosulfan sulfate was detected in the surface soils. Dieldrin (which was not produced or used in China) was not detected in this region.

In summary, source analysis indicates that the OCP residues are derived not only from historical use but also occur in new inputs, especially heptachlor and chlordane. HCH and DDTs were applied mainly as pesticides in cotton fields and they may still have an impact on the environment despite several decades of decomposition. Although current levels of HCH are below the first standard permissible value at the majority of sampling sites, the residue contents in most samples from historical cotton fields are larger than those in historical non-cotton fields. The HCH residue is derived from lindane for most non-cotton fields but technical HCH mixed with lindane for the majority of historical cotton. DDE residues showed significant differences with the residual quantities apparently higher in historical cotton fields than in fields with other cropping histories, and this may be attributed to the widespread application of DDTs in cotton fields.

**Fig. 5** Relationship between DDD+DDE and DDTs in surface soils





**Table 5** Total cancer risks from human exposure via ingestion, dermal absorption, and inhalation

Exposure pathways		Minimum	Maximum	Mean
Heptachlor	CR <sub>ingestion</sub>	1.45E-08	4.71E-08	3.30E-08
	CR <sub>dermal</sub>	3.31E-08	1.07E-07	7.52E-08
	CR <sub>inhal</sub>	2.73E-11	8.86E-11	6.20E-11
	∑ CR <sup>a</sup>	4.77E-08	1.55E-07	1.08E-07
Chlordane	CR <sub>ingestion</sub>	6.09E-08	4.24E-06	3.64E-07
	CR <sub>dermal</sub>	3.47E-08	2.41E-06	2.08E-07
	CR <sub>inhal</sub>	1.14E-10	7.97E-09	6.86E-10
	∑ CR	9.57E-08	6.66E-06	5.73E-07
HCH	CR <sub>ingestion</sub>	9.90E-09	1.90E-07	6.59E-08
	CR <sub>dermal</sub>	1.13E-08	2.17E-07	7.51E-08
	CR <sub>inhal</sub>	1.86E-11	3.58E-10	1.24E-10
	∑ CR	2.12E-08	4.08E-07	1.41E-07
DDTs	CR <sub>ingestion</sub>	0	6.96E-07	2.19E-07
	CR <sub>dermal</sub>	0	1.59E-06	5.00E-07
	CR <sub>inhal</sub>	0	1.31E-09	4.12E-10
	∑ CR	0	2.28E-06	7.20E-07
OCPs	CR <sub>ingestion</sub>	2.87E-07	4.70E-06	6.93E-07
	CR <sub>dermal</sub>	3.24E-07	3.26E-06	8.82E-07
	CR <sub>inhal</sub>	5.40E-10	8.84E-09	1.30E-09
	∑ CR	6.66E-07	7.97E-06	1.58E-06

<sup>a</sup>∑ CR, the sum of CR<sub>ingestion</sub>, CR<sub>dermal</sub>, and CR<sub>inhal</sub>

## Health risk assessment

The results of human risk assessment for OCPs are shown in Table 5. The ATSDR (Agency for Toxic Substances and Disease Registry) (1995) standard proposes the following qualitative ranking of cancer risk: very low (value < 10<sup>-6</sup>), low (10<sup>-6</sup> ≤ value < 10<sup>-4</sup>), moderate (10<sup>-4</sup> ≤ value < 10<sup>-3</sup>), high (10<sup>-3</sup> ≤ value < 10<sup>-1</sup>), and very high (value ≥ 10<sup>-1</sup>). The cancer risk values of heptachlor and HCH are all < 10<sup>-6</sup>, implying that they represent a very low cancer risk in this region. There are three sampling sites with a CR for chlordane of > 10<sup>-6</sup>, illustrating that chlordane may pose a low CR. Although the CR via ingestion and inhalation of DDTs are all < 10<sup>-6</sup>, the summation of the three exposure pathways for 14 sampling points are > 10<sup>-6</sup> though the average CR value is 0.7198. As shown in Table 5, there are 35 sampling points where the ∑ CR value of OCPs is 10<sup>-6</sup>, accounting for 67 % of the total number of samples.

## Conclusions

The present study examined the contents and distribution of OCP residues in 52 surface soil samples from the Lvdiian region. The OCP concentrations varied from 85 to

1392 ng g<sup>-1</sup> with a mean of 205 ng g<sup>-1</sup>. HCH, heptachlor, and chlordane showed a 100 % detection rate. The main pesticides, HCH and DDT, were detected in historical cotton fields and fields with other cropping histories, with mean concentrations of 19.0, and 21.6 ng g<sup>-1</sup> for HCH, and 71.3, and 38.5 ng g<sup>-1</sup> for DDTs. The composition and source identification of HCH show that the contribution of δ-HCH was approximately 53 %, the source of HCH might be attributed mainly to the use of lindane. Moreover, a recent usage of lindane or an atmospheric source for the input is indicated. Though there has been no cotton cultivation for decades, the residue of DDE in historical cotton fields are significantly higher (*P* < 0.05) than those in other fields, and this can be attributable to the degradation of the extensively used DDT for cotton in historically. Also, p,p-DDE was the predominant component of DDTs, resulting from the degradation of DDT under aerobic conditions. The source identification shows that DDTs are derived mainly from historical residues of DDT and a few samples contained newly input DDT. Moreover, the ∑ CR average value of OCPs is 1.58 × 10<sup>-6</sup>, indicating that current levels of OCP residues in agricultural soils pose a relatively low cancer risk in Lvdiian region.

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