



## Occurrence, distribution and possible sources of organochlorine pesticides in agricultural soil of Shanghai, China

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### ABSTRACT

Surface soil samples from agricultural soil of Shanghai were collected and analyzed for 24 organochlorine pesticides (OCPs). The concentrations were in the ranges of nd–10.38 ng g<sup>-1</sup> for HCHs (sum of  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -HCH), 0.77–247.45 ng g<sup>-1</sup> for DDTs (sum of *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, and *o,p'*-DDT), 0.84–10.08 ng g<sup>-1</sup> for CHLs (sum of heptachlor, heptachlor epoxide, *cis*-chlordane, *trans*-chlordane, and *trans*-nonachlor), nd–3.68 ng g<sup>-1</sup> for endosulfan (sum of  $\alpha$ - and  $\beta$ -endosulfan), 0.10–3.62 ng g<sup>-1</sup> for HCB and nd–5.69 ng g<sup>-1</sup> for other OCPs (sum of aldrin, dieldrin and endrin). The total OCPs concentrations ranged from 3.16 to 265.24 ng g<sup>-1</sup> and the main contaminated areas were distributed in the south regions of Shanghai (including Fengxian, Nanhui and Jinshan districts). According to the measured concentrations and detection frequencies, HCHs, DDTs, HCB and heptachlor epoxide were the most dominant compounds among the 24 OCPs. The different compositions of DDT, HCH, chlordane and endosulfan indicated that the residues of these compounds in most soil samples originated from historical application, besides slight recent introduction at some sampling locations. The correlation analysis showed no significant relationship between TOC and OCPs. The quality of Shanghai agricultural soil was classified as low pollution by OCPs.

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### 1. Introduction

Persistent organic pollutants (POPs) are typical organic compounds with high bioaccumulation, toxicity, and persistence in the environment [1,2]. They easily accumulate in organism to levels that can injure human health as well as the living creatures [1]. Persistent organochlorine pesticides (OCPs), one class of the ubiquitous POPs, have been a major environmental issue, drawing extensive attention from environmental scientists and the public. Some OCPs have been identified as endocrine disruptors which are capable of affecting the normal function of endocrine and reproductive systems of humans and wildlife [3]. They were the most widely used pesticides around the world before the 1970s [4]. Among the persistent OCPs, aldrin, dieldrin, endrin, chlordane, heptachlor, hexachlorobenzene (HCB) and DDT were listed in Stockholm Convention on POPs by the United Nations Environment Program (UNEP) [5]. Because of meeting all the screening criteria for POPs under the Stockholm Convention: persistence, bioaccumulation, potential for long-range environmental trans-

port and toxicity, hexachlorocyclohexane (HCH, including lindane), methoxychlor, and endosulfan have been proposed as potential POP candidates by the World Wide Found [5]. Although the application of the most OCPs has been forbidden or restricted for a considerable period of time in many countries, residues continuously induce a significant impact on the environment and ecosystems [6]. OCPs have been widely distributed by global distillation effect and are still detected in different environmental media from various regions [7,8], and the release of OCPs from soils continues to be a potential source of pollution to the environment [9].

Being a large agricultural country, China has been a major producer and consumer of OCPs. In China, OCPs were mostly used to control pests for more than three decades. Since the beginning of the 1980s, China began to prohibit the agricultural application of OCPs including DDT, HCH, aldrin, dieldrin, heptachlor, HCB, and chlordane [10]. However, small amount of DDT and HCH are still being produced as raw materials for other chemicals or for export (such as dicofol contained 3–7% DDT, lindane,  $\gamma$ -HCH > 99%) in China [11]. Recently, different levels of OCPs contamination and sources in soil have been found in China [12–15]. These studies suggested that further investigation is essential to assess the ecological and health risk and reveal the sources of these pollutants.

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Shanghai is located in the Yangtze River Delta, where OCPs were extensively used from the 1950s to 1980s [16]. As a result, the history of OCPs pollution in this area is longer, and the sources of various contaminants are complicated. Recently, several studies have shown that organic pollutants, such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), are present in various environmental media in Shanghai region [17–19]. However, information on the residue and distribution of OCPs in agricultural soil of Shanghai region is not available. Knowledge on the contamination level and spatial distribution of OCPs can provide a powerful backing for decision-makers, who may take effective measures to mitigate potential health and ecological risk. The objectives of the present study were: (1) to determine the residue levels of 24 OCPs; (2) to obtain detailed information on the spatial distribution and composition pattern; and (3) to identify possible sources of OCPs in agricultural soil from Shanghai.

## 2. Materials and methods

### 2.1. Soil sampling

A total of 36 surface soil samples from rice, bean, cotton and vegetable soil were collected from agricultural region of Shanghai in October 2007. The sampling locations evenly covered nine districts, including Chongming: CM1–CM4; Jiading: JD1–JD3; Baoshan: BS1–BS3; Qingpu: QP1–QP3; Songjiang: SJ1–SJ6; Jinshan: JS1–JS5; Fengxian: FX1–FX5; Nanhui: NH1–NH4; and Minhang: MH1–MH3 (Fig. 1). At each site, five subsamples (at the depth of 0–15 cm in 1000 m<sup>2</sup>) were collected randomly, and bulked together to form one composite sample. All the samples were air-dried at room temperature and crushed after removing stones and residual roots, and then passed 100-mesh sieve and stored in refrigerator until analysis. The total organic carbon (TOC) of the soil sample was measured according to the method described by Chen et al. [20].

### 2.2. Reagents and glassware

The standard mixture solution of 22 OCPs including *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT,  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -HCH, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide, *trans*-nonachlor, *cis*-nonachlor, *trans*-chlordane, *cis*-chlordane, methoxychlor, endrin aldehyde, endrin ketone,  $\alpha$ -,  $\beta$ -endosulfan and endosulfan sulfate at a concentration of 2000 mg L<sup>-1</sup> in isooctane was obtained from Supelco (Bellefonte, PA, USA). The single standard solutions of HCB and *o,p'*-DDT each at a concentration of 50 mg L<sup>-1</sup> in *n*-hexane were purchased from the National Research Center for Certified Reference Materials of China. 2,4,5,6-Tetrachloro-*m*-xylene (TCmX) was also purchased from Supelco (Bellefonte, PA, USA) and used as a surrogate. Silica gel (100–200 mesh) purchased from Qingdao Haiyang Chemical Co. (Shandong, China) was activated at 130 °C for 16 h, then deactivated by purified water (3.3%) and stored in a desiccator. Anhydrous sodium sulfate was baked at 600 °C for 6 h before use. All solvents were of HPLC grade (Fisher Chemical Company, USA). The glass apparatus were washed successively with detergent, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>–H<sub>2</sub>SO<sub>4</sub> solution, running water, deionized water and acetone, and baked at 400 °C for 3.5 h before use.

### 2.3. Sample extraction and cleanup

Sample extraction and cleanup were performed according to the previously reported literature with a modification [21]. Ten grams of the soil sample was weighed precisely and mixed with 10 g of anhydrous sodium sulfate. The mixture was spiked with surrogate, and then was Soxhlet-extracted for 24 h with 200 mL mixture of hexane/acetone (1:1, v/v). The crude extracts were concentrated by rotary vacuum evaporation, and then solvent-exchanged to hexane. A silica gel column (25 cm × 1 cm i.d.) containing 6 g of deactivated silica gel topped with 2 cm anhydrous sodium sulfate was pre-eluted by 40 mL of hexane. After introduction of extract, the column was eluted with 80 mL of *n*-hexane and 35 mL of *n*-

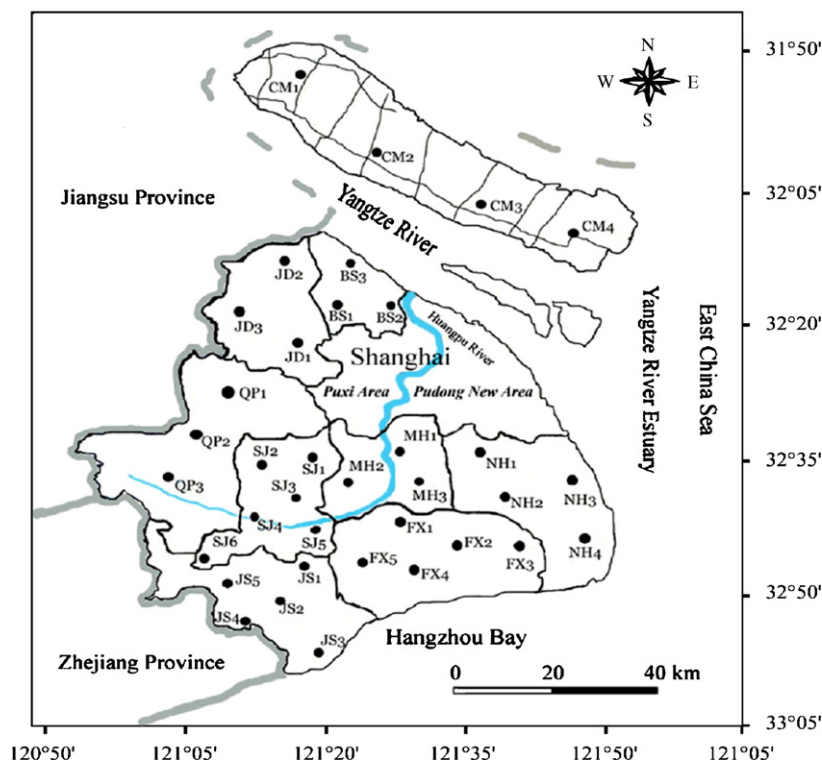


Fig. 1. The map of sampling sites in Shanghai agricultural areas.

**Table 1**  
The limit of detections, spiked recoveries and RSD of the method.

Analysts	LODs (ng g <sup>-1</sup> )	Recovery (%)	RSD (%)	Analysts	LODs (ng g <sup>-1</sup> )	Recovery (%)	RSD (%)
<i>p,p'</i> -DDD	0.016	94.15	6.72	Heptachlor	0.025	84.36	4.38
<i>p,p'</i> -DDE	0.019	84.39	8.79	Heptachlor epoxide	0.015	94.32	4.58
<i>p,p'</i> -DDT	0.027	89.58	5.36	<i>trans</i> -Nonachlor	0.020	68.87	7.82
<i>o,p'</i> -DDT	0.015	86.21	8.13	<i>cis</i> -Chlordane	0.020	78.34	6.68
$\alpha$ -HCH	0.007	91.43	6.66	<i>trans</i> -Chlordane	0.015	78.80	5.54
$\beta$ -HCH	0.005	82.37	7.32	Endrin aldehyde,	0.030	81.34	6.25
$\gamma$ -HCH	0.010	89.89	7.98	Endrin ketone	0.032	78.18	8.17
$\delta$ -HCH	0.012	81.32	5.32	$\alpha$ -Endosulfan	0.016	69.27	6.15
HCB	0.005	92.35	4.74	$\beta$ -Endosulfan	0.018	89.54	6.42
Aldrin	0.046	78.84	5.35	Endosulfan sulfate	0.025	85.25	7.47
Dieldrin	0.036	72.45	9.78	Endrin	0.030	75.54	9.88
<i>cis</i> -Nonachlor	0.035	71.47	9.80	Methoxychlor	0.025	78.84	6.88

hexane/DCM (2:3, v/v). The two fractions were combined as a single fraction, then concentrated and solvent-exchanged to isoctane, and reduced to 0.2 mL under a gentle stream of nitrogen before analysis.

#### 2.4. OCPs analysis

The determination of OCPs was performed on an Agilent 6890 gas chromatograph equipped with <sup>63</sup>Ni micro-electron capture detector (GC- $\mu$ ECD). The separation was performed on a fused silica capillary column (DB-XLB, 30 m  $\times$  0.25 mm i.d., and 0.25  $\mu$ m film thickness). Helium was used as carrier gas at a constant flow of 1.0 mL/min and high purity nitrogen was used as make-up gas (30 mL/min). The temperature program was as follows: initial temperature of 60 °C was held for 2 min, increased to 190 °C at a rate of 5 °C/min, and then increased to 280 °C at a rate of 10 °C/min. The injector and detector temperatures were set at 250 °C and 290 °C, respectively. One microliter of each sample was injected in the splitless mode. Identification of individual OCPs was based on comparison of retention time between samples and the standard solution. Quantification was performed by five-point calibration method (from 2.5 to 500 ng mL<sup>-1</sup>,  $r^2 > 0.992$ ). To confirm the results, typical samples selected were confirmed with an Agilent 6890GC-5975MSD system. The GC parameters were the same as described above. The MS was operated in electron impact ionization mode with electron energy of 70 eV. The ion source, quadruple and trans-

fer line temperatures were held at 230, 150 and 280 °C, respectively. Target compounds were monitored in selected ion monitoring (SIM) mode.

#### 2.5. Quality control and quality assurance

The procedure was checked for recovery efficiencies by analyzing uncontaminated soil spiked with OCPs standard ( $n=5$ ). The limits of detection (LODs) were detected with a signal-to-noise (S/N) of three. The LODs, recoveries of analysts and relative standard deviations (RSDs) were showed in Table 1. The spike blanks, solvent blanks and duplicate samples were analyzed in each 12 samples. In addition, surrogate standard was added to each of the sample to monitor procedural performance and matrix effects. The recoveries of surrogate spiked in soil samples ranged from 84.07% to 111.85% and the variation of OCPs in duplicate samples was less than 15%. All of results were expressed on dry weight basis and were not corrected for recoveries.

#### 2.6. Statistical analysis

Pearson correlation analysis and factor analysis were performed using STATISTICA 7.0 (StatSoft Inc.) and the results have been graphically displayed as loading plots. In the case of samples with the concentrations below LOD, zero was set for calculations.

**Table 2**  
The concentration (ng g<sup>-1</sup>) of individual OCPs in agriculture soil of Shanghai.

	Mean	Standard deviation	Minimum	Maximum	Detection frequencies	RV
<i>p,p'</i> -DDT	3.26	2.93	nd	24.52	69%	-
<i>p,p'</i> -DDE	16.14	18.47	0.17	77.76	100%	-
<i>p,p'</i> -DDD	4.56	3.51	0.15	124.67	100%	-
<i>o,p'</i> -DDT	1.66	0.97	nd	21.01	75%	-
DDTs	21.41	22.43	0.44	247.45	-	2.5
$\alpha$ -HCH	0.48	0.38	nd	1.46	97%	2.5
$\beta$ -HCH	1.19	1.81	nd	9.52	88%	1
$\gamma$ -HCH	0.36	0.78	nd	4.15	83%	0.5
$\delta$ -HCH	0.38	0.34	nd	1.76	83%	-
HCHs	2.41	2.32	nd	10.38	-	10
Aldrin	0.32	1.13	nd	6.62	36%	-
Dieldrin	0.09	0.24	nd	1.38	39%	-
Endrin	0.24	0.77	nd	4.32	19%	1
Heptachlor	1.05	1.36	nd	6.07	72%	-
Heptachlor epoxide	0.92	0.84	nd	4.78	89%	-
<i>trans</i> -Chlordane	0.10	0.23	nd	1.21	33%	-
<i>cis</i> -Chlordane	0.20	0.39	nd	1.41	39%	-
<i>trans</i> -Nonachlor	0.21	0.31	nd	1.28	53%	-
CHLs	2.47	2.14	nd	10.38	-	2.5
HCB	0.64	0.79	0.10	3.62	100%	2.5
$\alpha$ -Endosulfan,	0.13	0.30	nd	1.77	47%	-
$\gamma$ -Endosulfan	0.19	0.54	nd	2.33	25%	-

nd, not detected; RV, reference values of unpolluted soil according to soil protection guideline of the Netherlands.

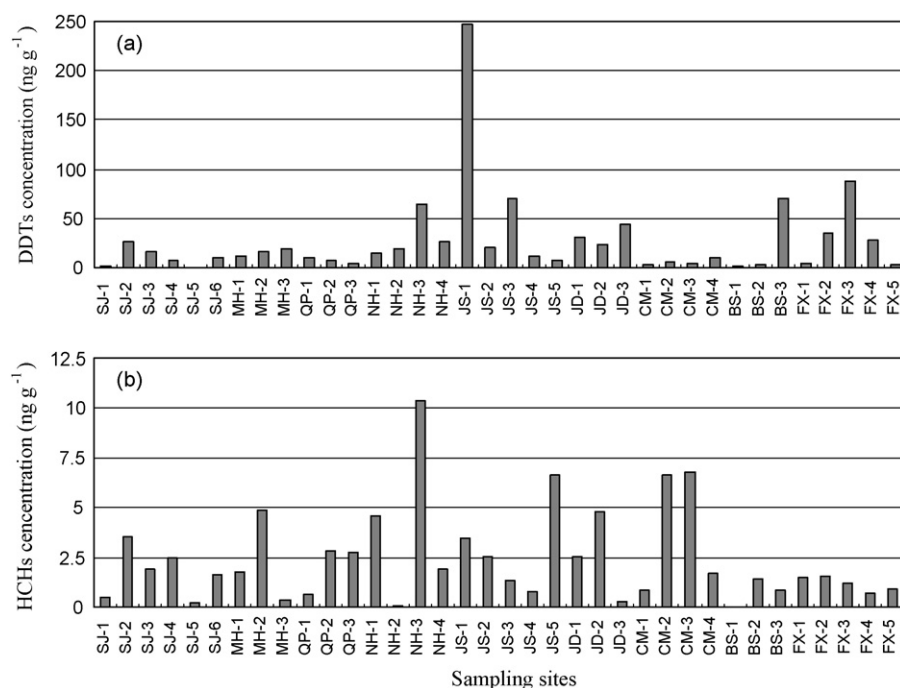


Fig. 2. The total concentrations of DDTs and HCHs in each sampling sites.

### 3. Results and discussion

#### 3.1. Residues of OCPs

##### 3.1.1. The residues of total OCPs

The mean, minimum, maximum concentrations and detection frequencies of various OCPs in Shanghai agricultural soil were shown in Table 2. Most of OCPs were found in soil samples except for endrin aldehyde, endrin ketone, *cis*-nonachlor, methoxychlor and endosulfan sulfate, which were not discussed later. According to the concentrations and detection frequencies, HCHs, DDTs, HCB and heptachlor epoxide were the most dominant compounds among the OCPs. The total OCPs concentrations ( $\Sigma$ OCPs) in soil samples were in the range of 3.16–265.24 ng g<sup>-1</sup>. The highest level of total OCPs were detected in soil samples from the south of Shanghai region, which is possibly explained by historical application and global distillation effect in these region.

##### 3.1.2. DDTs

*p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD and *o,p'*-DDT were all detected in Shanghai agricultural soil. The total concentrations of DDTs (sum of *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD and *o,p'*-DDT) ranged from 0.44 to 247.45 ng g<sup>-1</sup> with a mean of 21.41 ng g<sup>-1</sup>. The highest concentration of DDTs (247.45 ng g<sup>-1</sup>) was found at JS1, and the lowest concentration was detected at BS1 and SJ5 (Fig. 2a). The high concentration of DDTs was found in soil samples mainly from the south of Shanghai such as Jinshan, Jiading, Fengxian and Nanhui districts. As the famous rice and vegetable bases, the relatively higher OCPs residues may originate from agricultural usage in these areas. Among DDT and its metabolites, *p,p'*-DDE was the most dominant, and its concentrations were in the range of 0.17–77.76 ng g<sup>-1</sup> with a mean value of 16.14 ng g<sup>-1</sup>, accounting for 65% (in the range of 14–97%) of the total DDTs. *p,p'*-DDT was the second highest in the range of nd–124.67 ng g<sup>-1</sup>, with a mean value of 4.56 ng g<sup>-1</sup>, accounting for 3–50% of the total DDTs. The mean of *p,p'*-DDD and *o,p'*-DDT was 3.26 and 1.66 ng g<sup>-1</sup>, respectively. In our study, the level of DDTs was obviously lower than that reported previously (84 ± 31 ng g<sup>-1</sup>) [17], which suggested a decreasing trend

in agricultural soil DDT contamination of Shanghai. Compared to other regions and countries, it was lower than those in some typical agricultural areas in China such as Pearl River Delta region (37.6 ng g<sup>-1</sup>) [22], Taihu Lake region (50.23 ± 28.70 ng g<sup>-1</sup>) [11], northern Jiangsu province (4.2–678.6 ng g<sup>-1</sup>) [14], and in agricultural soil of Argentina (26.3 ± 165 ng g<sup>-1</sup>), Poland (4.3–2400 ng g<sup>-1</sup>) and German (23.7–173 ng g<sup>-1</sup>) [21,23,24].

##### 3.1.3. HCHs

HCHs were found in all soil samples except for QP3. The concentrations of HCHs (sum of  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -HCH) ranged from nd to 10.38 ng g<sup>-1</sup>, with a mean of 2.41 ng g<sup>-1</sup>. The highest concentration of HCHs (10.38 ng g<sup>-1</sup>) was found at NH3, and the lowest concentration was detected at QP3. Relatively higher levels of HCHs were observed in soil samples from the Nanhui and Jinshan districts (the south of Shanghai, Fig. 2b), which were probably attributed to the more agricultural activities in these areas. As far as HCH isomers are concerned, the concentration was in an order:  $\beta$ -HCH >  $\alpha$ -HCH >  $\gamma$ -HCH >  $\delta$ -HCH. The most dominant  $\beta$ -HCH varied from nd to 9.52 ng g<sup>-1</sup> with a mean of 1.19 ng g<sup>-1</sup>.  $\alpha$ -,  $\gamma$ - and  $\delta$ -HCH had similar concentration levels and the mean values were 0.48, 0.36 and 0.38 ng g<sup>-1</sup>, respectively (Table 2). In this study, the concentration of HCHs was similar to those in agricultural soil of Shanghai (2.4 ± 0.72 ng g<sup>-1</sup>) reported previously [17], in archived background soils in UK (0.1–10 ng g<sup>-1</sup>) [25], rice growing and industrial areas in Korea (<3 ng g<sup>-1</sup>) [8], and European high altitude mountains (0.08–0.49 ng g<sup>-1</sup>) [26]. However, it was much lower than those in vegetable soil of Liaoning province (7–25 ng g<sup>-1</sup>), Pearl River Delta region (12.2 ng g<sup>-1</sup>) and in rural soil of Hong Kong (6.19 ± 1.31 ng g<sup>-1</sup>) in China [21,27,28]. By comparison with other reports, HCHs pollution in agricultural soil of Shanghai was lower.

##### 3.1.4. Chlordane-related compounds

Technical chlordane is generally used as insecticide, herbicide and termiticide, and is still being used against termites in China nowadays [29,30]. It is a mixture of over 140 different components, and among them, *trans*-chlordane (13%), *cis*-chlordane (11%), and

heptachlor (5%) and *trans*-nonachlor (5%) are the most abundant components [15]. In this study, the concentrations of chlordanes-related compounds (CHLs) (sum of heptachlor, heptachlor epoxide, *cis*-chlordanes, *trans*-chlordanes, and *trans*-nonachlor) in soil samples ranged from 0.84 to 10.08 ng g<sup>-1</sup> with 2.47 ng g<sup>-1</sup> as the mean. The concentrations of chlordanes (sum of *trans*-chlordanes and *cis*-chlordanes) were in the range of nd–1.86 ng g<sup>-1</sup>.

As far as the single component, *trans*-chlordanes was detected in 33% soil samples, while *cis*-chlordanes was detected in 39% soil samples. The concentrations of *trans*-chlordanes and *cis*-chlordanes were in the range of nd–1.41 and nd–1.21 ng g<sup>-1</sup>, respectively (Table 2). The high concentrations of *trans*-chlordanes and *cis*-chlordanes were found in soil samples collected from Jinshan and Nanhui districts. The levels of *trans*-chlordanes and *cis*-chlordanes obtained in the study were similar to that in archived soil in UK (range from <0.05 to 1.6 and from <0.07 to 1.0 ng g<sup>-1</sup>) [25], and was lower than that of soil from US (mean, 0.49 and 0.43 ng g<sup>-1</sup>) and soil from Pearl River Delta (mean, 0.75 and 0.78 ng g<sup>-1</sup>) [31,32]. The levels of *trans*-nonachlor varied from nd to 1.28 ng g<sup>-1</sup> with the detection frequency of 53% (Table 2), and *trans*-nonachlor was the most abundant component detected in Jinshan and Nanhui districts. Heptachlor was detected in 72% soil samples with the concentration range of nd–6.07 ng g<sup>-1</sup>, and heptachlor epoxide was in the range of nd–4.78 ng g<sup>-1</sup>. Higher concentrations and detection frequencies of heptachlor and heptachlor epoxide were observed in Jinshan, Nanhui and Jiading districts, the northwest and the south of Shanghai region.

### 3.1.5. HCB

HCB was mainly used for producing pentachlorophenol sodium and as pesticide on prevention and cure of schistosomiasis in China. It was also used on wood preservation. Although there are no current commercial uses of HCB as an end product so far, it is still being unintentionally produced as a by-product or impurity in several chemical processes, such as the manufacturing of chlorinated solvents, chlorinated aromatics, and some pesticides. In this study, HCB was detected in all soil samples collected, and the concentrations ranged from 0.10 to 3.62 ng g<sup>-1</sup> with a mean of 0.64 ng g<sup>-1</sup>. The higher concentrations were detected in soil samples from JS1 (3.62 ng g<sup>-1</sup>), JS4 (1.93 ng g<sup>-1</sup>), NH2 (1.66 ng g<sup>-1</sup>) and MH1 (2.42 ng g<sup>-1</sup>), and the lower concentrations were found in soil samples collected from Songjiang and Chongming (<0.30 ng g<sup>-1</sup>).

### 3.1.6. Endosulfan

Endosulfan is a cyclodiene pesticide extensively used throughout the world to control a wide variety insects and mites. It consists of  $\alpha$ - and  $\beta$ -isomers.  $\alpha$ - and  $\beta$ -endosulfan are fairly resistant to photo-degradation, but the metabolites endosulfan sulfate and endosulfan diol are susceptible to photolysis [33]. Because of their high toxicity, technical endosulfan was restricted in many countries. However, it is still being used on cotton and crops in China. In this study, the total concentrations of endosulfan (sum of  $\alpha$ - and  $\beta$ -endosulfan) in soil samples were between nd and 3.68 ng g<sup>-1</sup>.  $\alpha$ - and  $\beta$ -isomer were detected only in a few soil samples with the levels from nd to 1.77 and nd to 2.33 ng g<sup>-1</sup>, respectively. The concentration of  $\beta$ -isomer was higher than that of  $\alpha$ -isomer, which can be explained by the more rapid degradation of  $\alpha$ -isomer in soil [34]. Endosulfan sulfate, which is a major degradation product of endosulfan, is known to be as toxic as parent compound. However, it was below the limit of detection in most of soil samples, which can be explained that endosulfan sulfate is susceptible to photolysis in the environment [33].

### 3.1.7. Aldrin, dieldrin, endrin and its metabolites

Apart from the organochlorine pesticides mentioned above, the other OCPs, including aldrin, dieldrin and endrin, were also found in lower detection frequencies. Their total concentrations (sum of

aldrin, dieldrin and endrin) were in the range of nd–5.69 ng g<sup>-1</sup>. Although these chemicals had never been produced and used for agriculture in China, they were detected in PM<sub>2.5</sub> and PM<sub>10</sub> in Beijing [15], surface water and sediments from Guanting Reservoir of Beijing [35], and most water samples from Qiantang River [36]. As the three compounds are still being used in some developing countries around the tropical belt, they are possibly transported by air parcels from abroad by global distillation effect.

In this study, aldrin, dieldrin and endrin were detected with 36%, 39% and 19% of detection frequencies, respectively. The level of aldrin varied from nd to 6.62 ng g<sup>-1</sup> and that of dieldrin ranged from nd to 1.38 ng g<sup>-1</sup>. Endrin was found in a range of nd–4.32 ng g<sup>-1</sup> and its metabolites, both endrin aldehyde and endrin ketone, were below their limits of detection in this study. The higher detection frequencies with the higher levels of aldrin, dieldrin and endrin were mainly distributed in Jinshan and Nanhui districts.

### 3.2. Sources and fate of DDT, HCH, chlordanes and endosulfan

The ratios between the parent compound and its metabolite can provide some useful information on the pollution source. *p,p'*-DDE and *p,p'*-DDD were the two main products of *p,p'*-DDT dechlorination and the ratios between *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD have been regarded as an indication of increasing or decreasing inputs to the environment. A small ratio of *p,p'*-DDT/(*p,p'*-DDE + *p,p'*-DDD) indicates historical DDT while a value much greater than 1.0 indicates fresh application. In the present study, the ratios of *p,p'*-DDT/(*p,p'*-DDE + *p,p'*-DDD) were much smaller than 1 except for JS1, especially the *p,p'*-DDT was not detected in soil samples from Songjiang, Minhang and Chongming districts, implying that there is no recent introduction of technical DDT to the soil of Shanghai region (Table 3). The ratio of *o,p'*-DDT/*p,p'*-DDT can be also used to distinguish DDT pollution caused by technical DDT from that by dicofol [13,14]. Generally, *o,p'*-DDT/*p,p'*-DDT ranges from 0.2 to 0.3 in technical DDT and from 1.3 to 9.3 or higher in dicofol [37]. In the present study, the ratios of *o,p'*-DDT/*p,p'*-DDT ranged from 0 to 13.58. Higher ratios of *o,p'*-DDT/*p,p'*-DDT (>1.3) were found in soil samples from Fengxian, Nanhui, Jinshan, Qingpu and Chongming districts, which suggested the application of dicofol in these areas. According to the ratios of *p,p'*-DDT/(*p,p'*-DDE + *p,p'*-DDD) and *o,p'*-DDT/*p,p'*-DDT, it could be concluded that DDT residues in Shanghai agricultural soil originate from recent input of dicofol and historical application of technical DDT.

Technical HCH contains 60–70%  $\alpha$ -HCH, 5–12%  $\beta$ -HCH, 10–12%  $\gamma$ -HCH, and 6–10%  $\delta$ -HCH. Alternatively, it was available in its pure form as lindane (>99%  $\gamma$ -HCH) (UNEP). Technical HCH has been forbidden for application, but lindane is still being used in China. Among the four HCH isomers,  $\beta$ -HCH is easily adsorbed to the soil organic matter and more difficult to evaporate from the soil than other HCH isomers [38]. In addition,  $\alpha$ - and  $\gamma$ -HCH can be transformed into  $\beta$ -HCH in the environment [39]. Furthermore, the spatial arrangement of chlorine atoms in the molecular structure of  $\beta$ -HCH was supposed to more resistant to microbial degradation in soil [40], which may lead to an accumulation of  $\beta$ -HCH in soil. The mean percentage of  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -HCH to HCHs in soil samples in our study is 28%, 38%, 12% and 22%, respectively. Compared with that in technical HCH, the relatively higher percentages of  $\beta$ -HCH in all of the samples indicated no new HCH sources in the surface soil of Shanghai region. The ratio of  $\alpha$ -/ $\gamma$ -HCH could be used to monitor whether the source was from technical HCH or lindane. Because the ratio of  $\alpha$ -/ $\gamma$ -HCH is relatively stable with a value of 4.64–5.83 for the technical HCH and nearly zero for lindane [41], which might increase during their degradation process in the environment. Based on the compositions, a

**Table 3**  
Ratios of OCPs for source identification in Shanghai agricultural soil.

	$p,p'$ -DDT/ $p,p'$ -DDD + $p,p'$ -DDE	$o,p'$ -DDT/ $p,p'$ -DDT	$\alpha$ -/ $\gamma$ -HCH	Heptachlor/heptachlor epoxide	<i>cis</i> -Chlordane/ <i>trans</i> -chlordane
SJ1	0	nd	–	0	0.67
SJ2	0	nd	2.43	0.57	nd
SJ3	0.04	0	13.67	0	0
SJ4	0	nd	3.90	0	nd
SJ5	0	nd	–	0	nd
SJ6	0	nd	5.17	0.73	nd
MH1	0	nd	6.80	0.92	0
MH2	0	nd	–	0	nd
MH3	0	nd	0.45	1.11	nd
JS1	1.21	0.17	1.79	–	0
JS2	0.16	0.48	3.83	3.06	–
JS3	0.03	1.33	7.68	2.94	0
JS4	0.06	1.51	1.79	6.19	nd
JS5	0.38	0.65	0.70	–	1.69
QP1	0.03	5.73	0.56	0	nd
QP2	0.12	2.32	4.69	1.43	nd
QP3	0	–	–	0.42	–
BS1	0.33	0	0.55	0.78	nd
BS2	0.08	0.46	0.42	0.74	1.55
BS3	0.03	0.56	0.22	2.67	nd
JD1	0.49	0.08	0.71	–	nd
JD2	0.18	0.38	–	40.47	3.43
JD3	0.04	0.96	1.12	0.80	2.62
FX1	0.04	13.58	3.00	0.79	3.75
FX2	0.02	2.39	0.38	0.89	–
FX3	0.06	0.46	1.32	1.02	0
FX4	0.04	0.69	2.26	0	–
FX5	0.07	2.47	–	1.01	–
NH1	0	–	–	0	0
NH2	0.24	1.15	1.51	–	–
NH3	0.04	1.03	1.54	1.61	–
NH4	0.08	1.07	2.77	–	–
CM1	0	–	2.13	0	nd
CM2	0.03	6.60	–	0.20	nd
CM3	0.08	1.66	3.75	1.43	nd
CM4	0.02	1.67	2.33	2.08	0

nd, means both two compounds not detected; “–”, the compound as denominator is not detected.

high ratio of  $\alpha$ -/ $\gamma$ -HCH (>5.83) in soil indicates the historical usage of technical HCH, and a low ratio (nearly zero) suggests recent input of lindane. The ratios of  $\alpha$ -/ $\gamma$ -HCH in Shanghai soil samples ranged from 0.22 to 13.67 (Table 3). The higher ratios of  $\alpha$ -/ $\gamma$ -HCH were only found in soil samples collected from Songjiang district, but for other sampling sites, the ratios of  $\alpha$ -/ $\gamma$ -HCH were lower than 4.64. It can be concluded that the HCHs in the soil samples investigated might originate from technical HCH usage in the past in Songjiang district and new input of lindane in other sampling sites.

It was reported that the ratio of *cis*-chlordane/*trans*-chlordane in technical mixtures is about 0.77 [42]. Previous studies showed that *trans*-chlordane is easier to degrade than *cis*-chlordane in the environment [43], and a ratio of *cis*-chlordane/*trans*-chlordane >1 is generally indicative of aged chlordane [44]. In the present study, *cis*-chlordane and *trans*-chlordane were only detected in a few soil samples from Jiading, Fengxian and Nanhui districts. In the study, the soil concentration of *cis*-chlordane was either equal to or higher than that of *trans*-chlordane, which indicated that chlordane residues in these districts were from “old” usage. In most samples, the concentration of heptachlor epoxide was higher than that of heptachlor, suggesting no fresh introduction in most agricultural fields of Shanghai. However, the higher level of heptachlor was found in the soil samples from Jinshan, Nanhui and Chongming districts, suggesting that there still is recent introduction of heptachlor to soil in these areas.

$\alpha$ - and  $\beta$ -endosulfan in technical endosulfan accounts for 70% and 30%, respectively [34] and the ratio of  $\alpha$ -/ $\beta$ -isomer in technical product is about 2.33. Because  $\alpha$ -endosulfan decomposes more easily than  $\beta$ -endosulfan in soil, the ratio of  $\alpha$ -/ $\beta$ -endosulfan

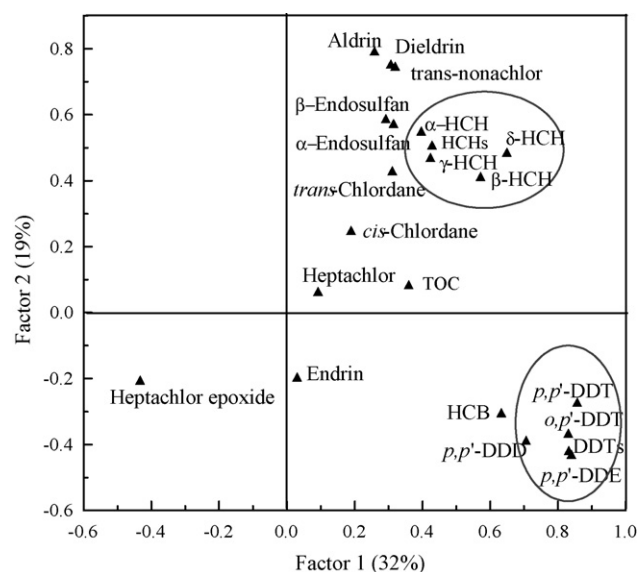
<2.33 can be used to judge the age of their residues in soil. The  $\alpha$ -/ $\beta$ -isomer ratios in this study ranged from 0.08 to 0.92 in 8 out of 36 soil samples in which  $\alpha$ - and  $\beta$ -isomer were simultaneously detected, indicating there are no recent application of technical endosulfan in the investigated area from Shanghai region.

### 3.3. Correlation among TOC and individual OCPs

Organochlorine pesticides are inclined to bind with soil organic matter because of their hydrophobicity. The increase of organic matter content in soil can supply more carbon source to facilitate microbial degradation of organochlorine pesticides [45]. As a result, the content of TOC could make an impact on the residue of organochlorine pesticides in soil [40,46]. In this study, there was a positive but weak correlations between TOC contents and residues of  $\alpha$ -HCH (0.494), HCHs (0.358),  $p,p'$ -DDT (0.326), HCB (0.301) (Table 4), indicating that soil organic matter could enhance adsorption of these compounds. However, there was a poor correlation between TOC and other individual OCPs, which can be explained that land use, particle size of soil, organic matter composition and physicochemical characteristics of OCPs can also affect the retention of individual OCPs in soil. Additionally, there was a significant correlation between  $\Sigma$ OCPs and CHLs, HCB, DDTs, suggesting high contribution of these contaminants to OCPs pollution. A significant correlation was also observed among HCH isomers, and DDT isomer and its metabolites. Moreover, HCB and CHLs were significantly related with DDTs, which suggested that they were probably originated from similar contamination sources.

**Table 4**  
Correlation coefficient matrix for individual OCPs and TOC ( $n = 36$ ,  $P < 0.01$ ).

	$p,p'$ -DDD	$p,p'$ -DDE	$o,p'$ -DDT	$p,p'$ -DDT	DDT's	$\alpha$ -HCH	$\gamma$ -HCH	$\beta$ -HCH	$\delta$ -HCH	HCHs	HEPC	HEPX	CC	TC	CN	CHLs	HCB	$\Sigma$ OCPs	TOC
$p,p'$ -DDD	1.000																		
$p,p'$ -DDE	0.592	1.000																	
$o,p'$ -DDT	0.765	0.833	1.000																
$p,p'$ -DDT	0.593	0.894	0.879	1.000															
DDT's	0.958	0.778	0.902	0.789	1.000														
$\alpha$ -HCH	0.064	0.399	0.268	0.377	0.185	1.000													
$\gamma$ -HCH	-0.188	-0.032	-0.130	-0.071	-0.163	0.386	1.000												
$\beta$ -HCH	0.151	0.059	0.003	0.039	0.117	0.279	0.080	1.000											
$\delta$ -HCH	0.265	0.182	0.248	0.298	0.284	0.441	0.157	0.172	1.000										
HCHs	0.105	0.129	0.041	0.114	0.109	0.579	0.485	0.876	0.408	1.000									
HEPX <sup>a</sup>	0.174	-0.041	0.028	0.037	0.125	0.055	-0.081	0.043	0.097	0.097	1.000								
HEPX <sup>a</sup>	-0.064	-0.263	-0.271	-0.319	-0.161	-0.368	-0.140	-0.214	-0.272	-0.315	0.242	1.000							
CC <sup>a</sup>	0.061	0.029	0.012	0.027	0.051	-0.075	0.007	0.489	0.000	0.370	0.081	-0.228	1.000						
TC <sup>a</sup>	0.011	0.077	-0.043	-0.039	0.005	0.372	0.013	0.150	0.213	0.215	0.058	-0.172	0.079	1.000					
CN <sup>a</sup>	0.329	0.442	0.351	0.280	0.371	0.353	-0.060	0.286	0.127	0.280	0.009	-0.303	0.473	0.715	1.000				
CHLs	0.591	0.737	0.621	0.699	0.687	0.225	0.057	0.054	0.116	0.119	-0.017	-0.181	0.119	0.116	0.394	1.000			
HCB	0.387	0.647	0.600	0.600	0.519	0.317	-0.188	-0.085	-0.028	-0.080	-0.118	-0.321	-0.053	0.038	0.437	1.000			
$\Sigma$ OCPs	0.879	0.831	0.860	0.814	0.948	0.224	-0.104	0.093	0.209	0.107	0.055	-0.090	0.096	0.055	0.427	0.875	1.000		
TOC	-0.022	0.286	0.261	0.326	0.105	0.494	0.106	0.281	0.147	0.358	0.031	-0.074	0.044	-0.040	0.092	0.104	0.301	1.000	

<sup>a</sup> HEPC, heptachlor; HEPX, heptachlor epoxide; CC, *cis*-chlordane; TC, *trans*-chlordane; TN, *trans*-nonachlor.**Fig. 3.** Loading plot of factor analysis based on concentration of OCPs and TOC content.

### 3.4. Factor analysis

Factor analysis (FA) was performed to determine the structure of OCPs data, and to make the results more easily interpretable. Factor loading plot (Fig. 3) showed loadings for individual OCP and soil TOC on the principal component plane (Factor 1 vs Factor 2). Two factors were considered in the FA analysis, accounting for 51% of the total variances. Along the axis Factor 1, the compounds were found on the positive-coordinate side (except for heptachlor epoxide). Factor 1 was associated mainly with compounds such as *p,p'*-DDE (0.857), *o,p'*-DDT (0.832), *p,p'*-DDT (0.831), *p,p'*-DDD (0.706), DDTs (0.840) and HCB (0.649), which were generally high correlated with the  $\Sigma$ OCPs (Table 4). Meanwhile, HCH group also had medium loading on Factor 1, which explained over 32% of the total variance. This fact that DDT and its metabolites were the highest loading of all the elements, suggested that DDT and its metabolites appeared to have the similar contributions to OCPs and originate from the similar source. The Factor 2 was associated mainly with  $\alpha$ - and  $\beta$ -endosulfan, aldrin, dieldrin, while HCH isomers also had medium loadings on the axis, which explained about 19% of the total variance. This can be explained that the most of OCPs have similar physicochemical properties such as low water solubility and high hydrophobicity, resistibility to photo-oxidation, and low vapor pressure as well as bioaccumulation and persistence in the environment [8]. In Fig. 3, heptachlor epoxide, *cis*-chlordane, endrin and heptachlor were separated from others, suggesting different source and fate of these contaminants.

### 3.5. Pollution assessment

According to national environmental quality standards for soils of China (GB15618-1995), the soil quality was classified as three levels: first level (residual concentration  $\leq 50 \text{ ng g}^{-1}$ ), second level (residual concentration between 50 and  $500 \text{ ng g}^{-1}$ ), and third level (residual concentration between 500 and  $1000 \text{ ng g}^{-1}$ ) for DDTs and HCHs. In the present study, total HCHs concentrations in all soil samples were lower than the guideline of first level ( $50 \text{ ng g}^{-1}$ ). While for total DDTs, the concentrations in 31 out of 36 soil samples were lower than the first level ( $50 \text{ ng g}^{-1}$ ), and those in five soil samples collected from NH3, JS1, JS3, BS3 and FX3 were between the first and the second level ( $500 \text{ ng g}^{-1}$ ), and no samples exceeded the third level ( $1000 \text{ ng g}^{-1}$ ) in this study.

In terms of the soil protection guideline of the Netherlands (Table 1) [47], the concentrations of HCHs in soil samples collected in this study were significantly lower than the target value for unpolluted soil ( $<10 \text{ ng g}^{-1}$ ) except one soil sample from NH3 area ( $10.38 \text{ ng g}^{-1}$ ). Nevertheless, the concentrations of  $\beta$ -HCH in most samples were higher than the target value for unpolluted soil. For total DDTs, the concentrations in 33 of 36 soil samples in the present study were higher than the value for unpolluted soil ( $<2.5 \text{ ng g}^{-1}$ ). Meanwhile, the target values of HCB ( $<2.5 \text{ ng g}^{-1}$ ), endrin ( $<1 \text{ ng g}^{-1}$ ) and CHLs ( $<2.5 \text{ ng g}^{-1}$ ) for unpolluted soil in the soil protection guideline of the Netherlands were higher than corresponding OCPs concentrations in most of agricultural soil samples from Shanghai.

In comparison with soil quality standards of China and the Netherlands, HCH pollution in the agricultural soil of Shanghai may be categorized as nonexistence, but the level of DDTs was classified as low pollution, while HCB, endrin and CHLs were classified as no pollution for the majority of soil samples, and only in a few samples they were classified as low pollution. Although no remediation measures were required with respect to the soil OCPs residues in Shanghai, the ecological and health effects of these endocrine disruptive pollutants through food chain should deserve concern in light of their possible biological magnifications in higher trophic organisms including human beings.

#### 4. Conclusions

The present study examined the occurrence, distribution and possible sources of 24 OCPs in agricultural soil of Shanghai, China. Although the use of most OCPs ceased in China from 1982, residues of some OCP species still existed in agricultural soil and the notable contaminated region was found in south region of Shanghai. HCHs, DDTs, HCB and heptachlor epoxide were the most dominant compounds in the soil. However, the concentrations of DDTs and HCHs in the most agricultural soil samples from Shanghai were lower than the target values of soil quality standard of China and the Netherlands, and the agricultural soil quality of Shanghai was classified as low OCPs pollution. The residues of OCPs in most soil samples originated from historical application, but there is still recent introduction of lindane, DDT and heptachlor at some sampling sites in Shanghai.

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