



# Concentrations and potential health hazards of organochlorine pesticides in shallow groundwater of Taihu Lake region, China



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## HIGHLIGHTS

- Most of OCP compounds occurred frequently in the shallow groundwater.
- DDTs and HCHs were mainly from the historical residues.
- There are fresh inputs of heptachlor, aldrin and endrin in the shallow groundwater.
- OCPs in the shallow groundwater may be posing serious cancer risks to children.

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## ABSTRACT

A total of 27 shallow groundwater samples were collected from the Taihu Lake region (TLR), to determine the concentrations of 14 organochlorine pesticide (OCP) species, identify their possible sources, and estimate health risk of drinking the shallow groundwater. All OCP species occurred in the shallow groundwater of TLR with high detection frequency except p, p'-dichlorodiphenyldichloroethane (p, p'-DDD) and p, p'-dichlorodiphenyltrichloroethane (p, p'-DDT). DDTs and hexachlorocyclohexanes (HCHs) were the dominant OCP contaminants in the shallow groundwater of TLR, and they account for 44.2% total OCPs. The low  $\alpha$ -HCH/ $\gamma$ -HCH ratio, high  $\beta$ -HCH/ $(\alpha + \gamma)$ -HCH ratio and  $\beta$ -HCH being the dominant HCH isomers for the majority of samples suggest that the HCHs were mainly from the historical use of lindane after a period of degradation. p, p'-DDE being the dominant DDT metabolite for all the samples indicated that the DDTs were mainly from the historical residues. Compositional analysis also suggested that there were fresh input sources of heptachlors, aldrins and endrins in addition to the historical residues. Correlation analysis indicated the hexachlorobenzene (HCB) impurity in the shallow groundwater of TLR was likely from the historical application of lindane and technical HCH (a mixture of HCH isomers that is produced by photochlorination of benzene). Carcinogenic risk values for  $\alpha$ -HCH, heptachlor, heptachlor epoxide, aldrins and dieldrin in the shallow groundwater in majority area of TLR were found to be  $> 10^{-6}$ , posing a potentially serious cancer risk to those dependant on shallow groundwater for drinking water.

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**Abbreviations:** OCP, organochlorine pesticide; POPs, persistent organic pollutants; DDT, dichlorodiphenyltrichloroethane; p, p'-DDE, p, p'-dichlorodiphenylethane; p, p'-DDD, p, p'-dichlorodiphenyldichloroethane; HCB, hexachlorobenzene; HCH, hexachlorocyclohexane; US EPA, United State Environmental Protection Agency; TLR, Taihu Lake region; PVC, polyvinyl chloride; PTFE, polytetrafluoroethylene; SPE, solid phase extraction; HPLC, high performance liquid chromatography; GC- $\mu$ ECD, gas chromatography equipped with a  $^{63}\text{Ni}$  electron capture detector; MDL, method detection limit; S/N, signal versus noise value; CDI, chronic daily intake; C, chemical concentration in water; IR, water ingestion rate; EF, the exposure frequency; SF, slope factor of the contaminant via oral exposure route; ED, exposure duration; BW, body weight; AT, average lifespan; R, carcinogenic risk; HQ, hazard quotient;  $R_pD$ , reference dose of the contaminant via oral exposure; CV, coefficient of variation; HCHs,  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -isomers; DDTs, p, p'-DDE, p, p'-DDD and p, p'-DDT; Heptachlors, heptachlor and heptachlor epoxide; Aldrins, aldrin and dieldrin; Endrins, endrin and endrin aldehyde.

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## 1. Introduction

Organochlorine pesticides (OCPs) are a kind of synthetic chemical pesticides composed primarily of carbon, hydrogen, and chlorine, and they are considered one of the most toxic and persistent organic pollutants (POPs) groups in the environment (Abou-Arab et al., 1995). According to the Stockholm Convention on POPs, nine OCPs (aldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, heptachlor, mirex, hexachlorobenzene (HCB) and toxaphene) are among the twelve POPs, also known as the dirty dozen. Although hexachlorocyclohexane (HCH) is not included in the Stockholm POPs, it is considered as priority pollutant by the United State Environmental Protection Agency (US EPA) (UNEP, 2003). OCPs attracted wide concern for decades because of their persistence, biomagnification, and high

toxicity to non-target organisms (Dimond and Owen, 1996; Zhang et al., 2002; Wan et al., 2005). Previous studies have suggested that some OCPs may affect the normal function of the endocrine and reproductive systems of humans and wildlife (Soto et al., 1994; Colborn and Smolen, 1996; Patlak, 1996; Xue et al., 2005). Due to their high persistence and toxic biological effects in the environment, risks of OCPs in a high residual concentration to environment still exists in some regions.

OCPs were widely used in the world from the 1950s, and they are ubiquitous in the environmental matrixes. China is a major agricultural country and a large producer and user of OCPs. Despite the ban on technical DDT (a mixture of DDT isomers that is produced by chloral hydrate, chlorobenzene, and sulfuric acid) and technical HCH (a mixture of HCH isomers that is produced by photochlorination of benzene) in 1983, dicofol (highly contaminated with DDT compounds) and lindane (almost pure  $\gamma$ -HCH) have continued to be widely used in agricultural practice in China in recent decades (Li et al., 2006; Yang et al., 2008). OCPs are still routinely found in soil, water, air and even foodstuff in some regions of China such as Taihu Lake region (TLR) (Feng et al., 2003; Qiu et al., 2004; Wang et al., 2007).

There is a substantial body of information about OCP residues in agricultural soils (Zhu et al., 2005; Wang et al., 2007; Zhang et al., 2009), sediments and surface waters of China (Zhang et al., 2002; Zhou et al., 2006; Zhang et al., 2007; Liu et al., 2008; Sun et al., 2008; Chen et al., 2011), and there is a large body of literature on OCP residues in groundwater of other countries such as India, USA, and Portugal (Cerejeira et al., 2003; Sankararamakrishnan et al., 2005; Shukla et al., 2006; Gilliom, 2007; Jayashree and Vasudevan, 2007). However, there is little information about OCP residues in the shallow groundwater of China. Therefore, it is important to investigate the residue concentrations of OCPs in the shallow groundwater because it is an important source of drinking water and to evaluate the potential risks to human health. TLR was an important region for food production where OCPs were most extensively used to increase agricultural production from the 1950s to 1980s (Cai, 1996; Li et al., 1998, 2001; Qiu et al., 2004; Wang et al., 2005). The region is shortage of drinking water for poor surface water and therefore the shallow groundwater as an important source of drinking water. The objectives of the present study were to (1) determine the concentrations and compositions of 14 OCPs including  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -HCH and p, p'-dichlorodiphenyldichloroethane (p,p'-DDE), p, p'-dichlorodiphenylethane (p, p'-DDE), p, p'-DDT as well as heptachlor, heptachlor epoxide, HCB, aldrin, dieldrin, endrin, endrin aldehyde in the shallow groundwater of TLR, (2) to identify the possible sources of the 14 OCPs in the shallow groundwater, and (3) to estimate human health risk caused by the 14 OCPs through consumption of the shallow groundwater.

## 2. Materials and methods

### 2.1. Study area and sampling

TLR, located between the Yangtze River and the Taihu Lake, is characterized by northern sub-tropical monsoon with a temperate and humid climate throughout the year and four distinct seasons. The average annual temperature is 16.0 °C and mean annual precipitation is approximately 1181 mm, with most precipitation occurring from May through September. Floodplain, interlaced with a network of canals and ditches, is the dominant geomorphologic type. The shallow aquifer is comprised of unconsolidated sedimentary material. According to hydrogeological data, the thickness of the porous unconfined aquifer is approximately 2–5 m, and the static water table of the shallow groundwater is approximately 1.0–3.0 m below the ground surface (Chen et al., 2005). The water table fluctuates both with the seasons and years because it is affected by climatic variation and precipitation with the extent of fluctuation reaching 1 m. Shallow groundwater is an important source of drinking water in the study area because of the poor water quality of the surface waters.

A total of 27 shallow groundwater samples were collected from monitoring wells and drinking wells in April 2011 with consideration of uniform distribution, regional difference and convenience of monitoring (the locations are shown in Fig. 1). Most of the wells had depths ranging from 4 to 5 m while the remaining ranged from 5 to 8 m. The groundwater levels during sampling were 0.7–2.0 m below the ground surface. Groundwater samples were collected following this sequence: (1) pump the tube-well for several minutes; (2) wash out a clean brown glass bottle with the groundwater; (3) collect groundwater from 5 cm below the groundwater table using a polyvinyl chloride (PVC) Baylor tube and filter the water through a 0.45  $\mu$ m glass-fiber filter (Whatman, Clifton, NJ, USA) to remove sand and debris; (4) fill a 1-l brown glass bottle with filtered groundwater and acidify with ultra-pure sulfuric acid to pH < 2 to inhibit biological activity; (5) seal the bottle using a polytetrafluoroethylene (PTFE) membrane and store the sample in the dark at temperature between 0 °C and 4 °C prior to extraction within 2 days. A filtered groundwater sample was collected from each well, and a field duplicate sample was collected for every 5–8 wells to estimate sampling and laboratory analysis precision.

### 2.2. Sample extraction and analysis

The Supelco solid phase extraction (SPE) C18 cartridges (Bellefonte, PA, USA) were first washed with 5 ml of ethyl acetate and conditioned by 5 ml of methanol, then washed with 2  $\times$  5 ml of ultra-pure water. The filtered groundwater samples (500 ml) were percolated through the cartridges with a flow rate of 5 ml/min under vacuum pump. After extraction, the pesticides trapped within the cartridges were eluted by passing 6 ml ethyl acetate. Water in the extracts was eliminated by 2.5 g of anhydrous sodium sulfate (baked at 450 °C) before evaporation. The eluates were dried under a gentle stream of nitrogen and pooled together in 1 ml n-hexane.

All reagents used (ethyl acetate, methanol cyclohexane and n-hexane) were high performance liquid chromatography (HPLC) grade purchased from Tedia Company, Inc., Fairfield, OH. The anhydrous sodium sulfate (analytical grade, Shanghai Chemical Reagent Co.) was baked at 450 °C for 4 h.

The OCPs residues were analyzed by a gas chromatography (Varian 3800, Salt Lake City, UT) equipped with a <sup>63</sup>Ni electron capture detector (GC- $\mu$ ECD) and a DB-5MS (Agilent) column 30 m  $\times$  0.25 mm i.d. and 0.25  $\mu$ m film thickness. Ultra-high purity N<sub>2</sub> (>99.9999%) was used as the carrier gas. The oven temperature program was as follows: injector and detector temperatures were 250 °C and 300 °C respectively, initial run temperature was set at 80 °C, ramped at 30 °C min<sup>-1</sup> to 220 °C, then ramped at 5 °C min<sup>-1</sup> to 280 °C and held for 1 min. The concentrations of OCPs were determined by comparing the peak height of the samples and the calibration curves of the standards. The correlation coefficient of calibration curves of OCPs were all greater than 0.999. Peak identification was conducted by the accurate retention time of each standard ( $\pm$  1%) and also confirmed by GC-MS (Agilent 5975).

### 2.3. Quality control and quality assurance

The concentrations of OCPs were quantitatively determined by the external standard method using peak height. For every set of 10 samples, a procedural blank and spike sample consisting of all reagents was run to check for interference and cross contamination. The detection limits of OCPs were determined as the concentration of analyses in a sample that gives rise to a peak with a signal-to-noise ratio (S/N) of 3. The pesticides recoveries were determined relative to the ratio of direct injection of extract and the working standards (5  $\mu$ g l<sup>-1</sup>) prepared in n-hexane. The mean recovery of OCPs was estimated at mean

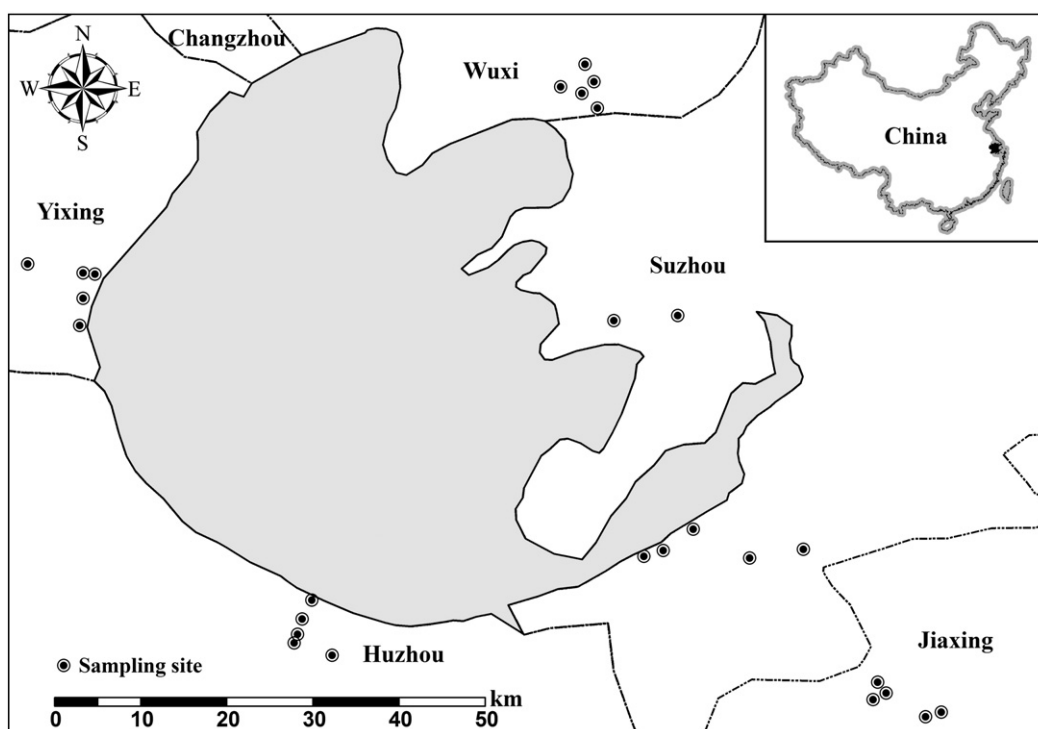


Fig. 1. Study area and locations of sampling sites.

concentration levels. A strict regime of quality control was employed before the onset of the sampling and analysis program. OCPs recovery studies were undertaken to demonstrate the efficiency of the method. The standard solution of the 14 OCPs was purchased from National Research Center of certified reference material in China. Five separate ultra-pure waters were spiked with the working solution ( $5 \mu\text{g l}^{-1}$ ) containing all the 14 OCPs, then extracted and analyzed in the same way as the real samples ( $5 \text{ ng l}^{-1}$ ). Mean recovery of OCPs ( $n = 5$ ) ranged from 78% to 93% for water samples. Details on the recovery and method detection limits (MDL) for the 14 OCPs were listed in Table 1.

**Table 1**  
Recoveries and method detection limits (MDL) for the analysis of the 14 organochlorine pesticides by GC- $\mu$ ECD.<sup>a</sup>

Pesticide	Recovery (%)	RSD (%)	MDL ( $\text{ng l}^{-1}$ )
$\alpha$ -HCH	83	4.3	0.06
$\beta$ -HCH	92	2.2	0.24
$\gamma$ -HCH	90	4.1	0.08
$\delta$ -HCH	93	1.9	0.10
p, p'-DDE	86	5.9	0.28
p, p'-DDD	84	5.7	0.54
p, p'-DDT	90	3.5	0.62
Heptachlor	79	6.2	0.35
Heptachlor epoxide	78	4.7	0.30
Hexachlorobenzene	85	7.4	1.10
Aldrin	84	5.4	0.55
Dieldrin	82	3.6	0.35
Endrin	88	6.1	0.45
Endrin aldehyde	85	4.4	0.51

<sup>a</sup> RSD, relative standard deviation.

#### 2.4. Health risk assessment model

Health risk assessment is the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media, now or in the future. Individuals can be exposed to OCPs through several pathways, but oral exposure route is considered to be the most important one (Phan et al., 2010; Hu et al., 2011). In this study, a health risk assessment model derived from US EPA is applied to estimate the carcinogenic and non-carcinogenic risks for adults and children consuming the shallow groundwater as their drinking water source (IRIS, 2005). The chronic daily intake (CDI) is used to estimate human exposure to contaminants (US EPA, 1989), and is calculated using the following formula.

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (1)$$

$C$  = chemical concentration in water ( $\text{mg l}^{-1}$ );  $IR$  = water ingestion rate ( $1 \text{ day}^{-1}$ ) (for children:  $IR = 1.0$ ; for adults:  $IR = 2.0$ );  $EF$  = the exposure frequency ( $350 \text{ days year}^{-1}$ );  $ED$  = exposure duration (year) (for children:  $ED = 6$ ; for adults:  $ED = 70$ );  $BW$  = body weight (kg) (for children:  $BW = 14$ ; for adults:  $BW = 60$ );  $AT$  = average lifespan (days) (for children:  $AT = 2190$ ; for adults:  $AT = 25,550$ ).

From the US EPA exposure factors handbook (US EPA, 1997), carcinogenic risk ( $R$ ) is calculated as follows:

$$R = CDI \times SF \quad (2)$$

where  $CDI$  is the chronic daily intake from the oral exposure route ( $\text{mg kg}^{-1}$  per day),  $SF$  is the slope factor of the contaminant via oral exposure route [ $(\text{mg kg}^{-1}$  per day) $^{-1}$ ].

**Table 2**  
Toxicological parameters of the 14 organochlorine pesticides.<sup>a</sup>

Parameter	SF/[(mg kg <sup>-1</sup> per day) <sup>-1</sup> ]	R <sub>D</sub> /[(mg kg <sup>-1</sup> per day)
α-HCH	6.3	5.0E-4
β-HCH	1.8	2.0E-4
γ-HCH	1.3	3.0E-4
δ-HCH	/	/
p, p'-DDE	0.34	/
p, p'-DDD	0.24	2.0E-3
p, p'-DDT	0.34	5.0E-4
Heptachlor	4.5	5.0E-4
Heptachlor epoxide	9.1	1.3E-5
Hexachlorobenzene	1.6	8.0E-4
Aldrin	17	3.0E-5
Dieldrin	16	5.0E-5
Endrin	/	3.0E-4
Endrin aldehyde	/	3.0E-4

<sup>a</sup> /, no given parameter value.

To estimate non-carcinogenic risk, hazard quotient (HQ) is calculated using the following equation:

$$HQ = \frac{CDI}{R_f D} \quad (3)$$

where R<sub>D</sub> (mg kg<sup>-1</sup> per day) is the reference dose of the contaminant via oral exposure route. The values of slope factor and reference dose (Table 2) for OCPs are obtained from the US EPA Integrated Risk Information System (US EPA, 1986).

### 3. Results and discussion

#### 3.1. Occurrence of OCPs in shallow groundwater

A summary description of detection frequency (equivalent to the ratio of the number of samples that the pollutant could be detected to the number of analysis samples), range, mean and median concentration for the 14 OCPs in the shallow groundwater is presented in Table 3. OCP compounds that occurred frequently in the shallow groundwater samples in TLR were HCHs (α-, β-, γ-, and δ-HCH), p, p'-DDE, heptachlor, heptachlor epoxide, HCB, aldrin, dieldrin, endrin and endrin aldehyde. Particularly, HCHs, p, p'-DDE, heptachlor and HCB residues were ubiquitous in the shallow groundwater of TLR, indicating these compounds were very serious in the shallow groundwater of TLR. The detection frequencies of p, p'-DDD and p, p'-DDT were relatively low. Although aldrin, dieldrin, endrin, endrin aldehyde and heptachlor epoxide were only from synthetic experiment carried out in China and there was no industrial production (MEP, 2007), these OCP species in the shallow groundwater of TLR had a high detection frequency (77.8%–96.3%). Although agricultural use of most OCPs have been banned in China for more than 30 years, these OCPs residues in the shallow groundwater of TLR were very still serious, indicating the persistence of these OCPs in the shallow groundwater is very strong.

Previous studies showed that OCP compounds also occurred frequently in surface water and sediment of Taihu Lake (Yuan et al., 2003; Wang et al., 2012), and indicated that OCPs in the surface water and sediment of Taihu Lake may have influenced the concentrations of OCPs in the shallow groundwater in surrounding area of Taihu Lake. The study area is a floodplain interlaced with a network of canals and ditches, and the shallow groundwater and surface water interactions in the study area are difficult to observe and measure (Chen et al., 2005). To study the impact of the shallow groundwater and surface water interactions on the quality of the shallow groundwater in surrounding area of Taihu Lake, we compared the concentrations of the 14 OCPs in some shallow groundwater samples from the same

sub-study area with different distance to Taihu Lake. The results showed that the influence of the interaction on the shallow groundwater quality to some extent was limited (Fig. 2), and the interaction was not the major pathway of OCP entering into the shallow groundwater.

HCHs (α-, β-, γ-, and δ-isomers) and DDTs (p, p'-DDE, p, p'-DDD and p, p'-DDT) could be the most two important contaminants in this area due to their relatively higher fractions in the total OCPs (21.26% for HCHs and 22.94% for DDTs). The concentrations of the HCHs and DDTs in the shallow groundwater of TLR had a wide range for HCHs, 11.31–189.4 ng l<sup>-1</sup> with a mean of 43.71 ng l<sup>-1</sup>; and DDTs, 0.72–482.3 ng l<sup>-1</sup> with a mean of 52.46 ng l<sup>-1</sup>. The concentrations of the other OCPs in the shallow groundwater of TLR also had a wide range with a high coefficient of variation (CV). It indicated that all the 14 OCPs residues in the shallow groundwater of TLR had strong spatial variability.

#### 3.2. Compositions and source identification of OCPs

Differences in composition of OCP isomers/metabolites in the environment can reveal different pollution sources (Doong et al., 2002; Zhou et al., 2006) and various ratios have been used to identify the sources of OCPs (Strandberg et al., 1998; Bidleman, 1999; Hong et al., 1999; Covaci and Hurab, 2001). However, the OCPs in groundwater are not derived from direct inputs and the ratios of OCP isomers/metabolites will change during transport due to differences in their physical and chemical properties. Some ratios may be inadequate for the evaluation of old and new sources of OCPs in groundwater despite their widespread use to identify old and new OCP sources in other environment media such as soils, sediments and surface waters.

##### 3.2.1. HCHs and HCB

Generally, technical HCH consists of 60–70% α-HCH, 5–12% β-HCH, 10–15% γ-HCH, and 6–10% δ-HCH and the α-HCH/γ-HCH ratio is in the range of 4–7 (Iwata et al., 1993; Buser and Müller,

**Table 3**

Summary statistics for the concentrations of the 14 organochlorine pesticides (ng l<sup>-1</sup>) in the shallow groundwater.<sup>a</sup>

Pesticide	Range	Mean	Median	SD	CV (%)	DF (%)
α-HCH	0.92–41.77	5.85	2.71	8.13	139	100
β-HCH	0.94–107.6	14.53	9.60	20.13	139	100
γ-HCH	1.38–56.05	8.77	4.03	12.11	138	100
δ-HCH	3.69–80.58	14.56	9.60	16.76	115	100
ΣHCHs	11.31–189.4	43.71	30.83	35.83	88.1	100
p, p'-DDE	0.72–453.5	46.77	11.89	98.84	211	100
p, p'-DDD	BDL–6.95	1.04	BDL	2.22	212	22.2
p, p'-DDT	BDL–60.28	4.64	BDL	12.56	270	40.7
ΣDDTs	0.72–482.3	52.46	13.18	108.9	208	100
Heptachlor	4.97–189.2	21.98	12.09	35.44	161	100
Heptachlor epoxide	BDL–47.12	12.31	8.02	13.76	112	96.3
ΣHeptachlors	5.12–228.9	34.29	20.01	44.32	129	100
Hexachlorobenzene	3.05–65.24	16.53	12.43	13.40	81.1	100
Aldrin	BDL–356.5	27.59	5.61	70.06	254	85.2
Dieldrin	BDL–257.9	13.37	2.79	49.26	369	77.8
ΣAldrins	BDL–359.3	40.95	10.26	84.20	206	96.3
Endrin	BDL–129.2	11.53	4.79	25.08	217	81.5
Endrin aldehyde	BDL–78.79	6.15	1.42	15.76	256	74.1
ΣEndrins	1.04–159.3	17.68	5.68	33.81	191	100
Total OCPs	31.36–1241	205.6	104.4	272.2	132	100

<sup>a</sup> Min, minimum; Max, maximum; SD, standard deviation; CV, coefficient of variation; DF, detection frequency; BDL, below detection limit; ΣHCHs, sum of α-, β-, γ- and δ-HCH isomers; ΣDDTs, sum of p, p'-DDE, p, p'-DDD and p, p'-DDT; ΣHeptachlors, sum of heptachlor and heptachlor epoxide; ΣAldrins, sum of aldrin and dieldrin; ΣEndrins, sum of endrin and endrin aldehyde.

1995; Li and Macdonald, 2005). In contrast, lindane consists almost entirely of  $\gamma$ -HCH. The average percentages of HCH isomers in the shallow groundwater of TLR were  $\alpha$ -HCH: 13.38%,  $\beta$ -HCH: 33.24%,  $\gamma$ -HCH: 20.06%, and  $\delta$ -HCH: 33.31% and the  $\alpha$ -HCH/ $\gamma$ -HCH ratio was in the range of 0.02–3.18 with a mean of 1.00. The low  $\alpha$ -HCH/ $\gamma$ -HCH ratio for the majority of groundwater samples collected from TLR were further below the  $\alpha$ -HCH/ $\gamma$ -HCH ratio in technical HCH (Fig. 3).  $\beta$ -HCH was the predominant HCH isomers in the shallow groundwater, and the  $\beta$ -/( $\alpha + \gamma$ )-HCH ratio of the 89% shallow groundwater samples were greater than 0.5. These observations indicated that the sources of the HCHs were mainly from the historical use of lindane after a period of degradation (Liu et al., 2012), an earlier study also demonstrated lindane was used in this region (Qiu et al., 2004).

HCb has never been used directly as a pesticide in China, but has been used to produce pentachlorophenol (PCP) and pentachlorophenol-Na (PCP-Na), reagent and fireworks (Wei et al., 2007). Most PCP-Na produced through HCB was used as amolluscicide in limnological regions of south China such as Taihu (Wang et al., 2010), and the historical use of PCP-Na may be an important source of HCB in the shallow groundwater of TLR. Previous studies showed that HCB was a trace contaminant in several pesticides containing chlorine such as lindane, technical HCH, pentachlorophenol (PCP) and pentachlorophenol-Na (PCP-Na), pentachloronitrobenzene (PCNB), atrazine, simazine, picloram, chlorothalonil, dimethyl tetrachloroterephthalate (DCPA) (US EPA, 1998; Benazon, 1999; Pacyna et al., 2003; Barber et al., 2005). The Spearman non-parametric correlation coefficients were calculated between HCB and four HCH isomers in the shallow groundwater, and the results showed that the concentration of HCB had significant correlation with the concentration of  $\alpha$ -HCH ( $r = 0.60$ ) and  $\beta$ -HCH ( $r = 0.41$ ). It indicated that HCB impurity was likely from the historical application of technical HCH and lindane. It is consistent with the results of earlier studies that the use of PCP-Na and other pesticides containing HCB impurity were the main source of HCB in agricultural soils in TLR (Gao et al., 2005; Wang et al., 2007).

### 3.2.2. DDTs

Among the three DDT isomers/metabolites (p, p'-DDE, p, p'-DDD, and p, p'-DDT) that were analyzed, p, p'-DDE dominated among the DDT isomers/metabolites in the shallow groundwater of TLR, while the other DDT isomers/metabolites (p, p'-DDD, and p, p'-DDT) had low detection frequency, indicating that historical residues were the main source of DDTs in the shallow groundwater. A higher amount of DDE than DDD in the shallow groundwater of TLR, this probably reflects the aerobic shallow groundwater environment (Vryzas et al., 2009; Sun et al., 2008).

### 3.2.3. Heptachlors (heptachlor and heptachlor epoxide)

Heptachlor is a pesticide primarily used against soil insects and termites although it had also been used in controlling malaria mosquitoes. Heptachlor epoxide is a more stable breakdown product of heptachlor and would normally be assessed together with heptachlor. In the majority (81.5%) shallow groundwater samples, the concentrations of heptachlor were higher than that of heptachlor epoxide, indicating that there may be some fresh input sources of heptachlor in addition to the historical residues, and the application of heptachlor may have been one of the main fresh input sources of heptachlor in the shallow groundwater of TLR.

### 3.2.4. Aldrins (aldrin and dieldrin) and Endrins (endrin and endrin aldehyde)

Aldrin has been manufactured commercially since 1950 and used to control soil pests and in the protection of wooden structures against termites. It is readily metabolized to dieldrin. There were 18(66.7%) shallow groundwater samples with a higher concentration of aldrin than that of dieldrin, indicating that there may be some fresh input sources

of aldrin in addition to the historical residues, and the application of aldrin may have been one of the main fresh input sources of aldrin in the shallow groundwater of TLR.

Endrin is used against a wide range of agricultural pests and as rodenticide. Endrin may be metabolized to endrin aldehyde and endrin ketone. There were 19(70.4%) shallow groundwater samples with a higher concentration of endrin than that of endrin aldehyde, indicating that there may be some fresh input sources of endrin in addition to the historical residues, and the application of endrin may have been one of the main fresh input sources of endrin in the shallow groundwater of TLR.

### 3.3. Health risk assessment of OCPs in shallow groundwater

Health risks from drinking local shallow groundwater for adults and children were calculated according to the health risk assessment model (US EPA, 1997). Since the concentrations of the 14 OCPs in the shallow groundwater of TLR had a wide range, the health risk levels caused by the 14 OCPs groups whether for adults or for children through drinking local shallow groundwater also had wide range. Summary statistics for the health risks caused by the 14 OCPs groups for adults and children is presented in Table 4. For adults, the average cancer risks from drinking local shallow groundwater were  $1.18 \times 10^{-6}$  for  $\alpha$ -HCH,  $3.16 \times 10^{-6}$  for heptachlor,  $3.58 \times 10^{-6}$  for heptachlor epoxide,  $1.50 \times 10^{-5}$  for aldrin,  $6.84 \times 10^{-6}$  for dieldrin and  $3.27 \times 10^{-5}$  for all the OCPs. While for children, the average cancer risks from drinking local shallow groundwater were  $2.53 \times 10^{-6}$  for  $\alpha$ -HCH,  $1.79 \times 10^{-6}$  for  $\beta$ -HCH,  $1.09 \times 10^{-6}$  for p, p'-DDE,  $6.78 \times 10^{-6}$  for heptachlor,  $7.67 \times 10^{-6}$  for heptachlor epoxide,  $1.81 \times 10^{-6}$  for HCB,  $3.21 \times 10^{-5}$  for aldrin,  $1.47 \times 10^{-5}$  for dieldrin and  $6.91 \times 10^{-5}$  for all the OCPs.

In the majority of the shallow groundwater samples, cancer risk caused by  $\alpha$ -HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin for children and adults through drinking was greater than the acceptable risk level ( $1 \times 10^{-6}$ ) recommended by US EPA for carcinogens. This indicated that the current concentrations of these OCPs in the shallow groundwater in majority of the areas of TLR may pose serious cancer risk to the local population, especially to children, and that the shallow groundwater in majority of the areas of TLR was not suitable for drinking water. It is necessary to control the fresh input sources of these OCPs in the shallow groundwater and to carry out valid shallow groundwater remediation. Cancer risk from each pollutant in the shallow groundwater of TLR was in the order of aldrin > dieldrin > heptachlor epoxide > heptachlor >  $\alpha$ -HCH > HCB >  $\beta$ -HCH > p, p'-DDE >  $\gamma$ -HCH > p, p'-DDT > p, p'-DDD, the predominance of aldrin and dieldrin suggested that the two OCPs were the main cancer risk factor in the shallow groundwater of TLR. In all the shallow groundwater samples of TLR, cancer risk from p, p'-DDD and p, p'-DDT in the shallow groundwater were lower than the acceptable risk level ( $1 \times 10^{-6}$ ) recommended by US EPA for carcinogens, indicating the carcinogenic risk levels caused by them were acceptable.

The HQs of the 14 OCPs through drinking shallow groundwater for individuals were also calculated according to the assessment model. According to the standards (US EPA, 1986), when the ratio exceeds 1, it means that it has an adverse human health effect. The non-carcinogenic risks from all the 14 OCPs for adults and children were much less than 1, suggesting that these OCPs in the shallow groundwater of TLR were considered unlikely to pose any non-carcinogenic effects to individuals. Non-carcinogenic risk from each pollutant in the shallow groundwater of TLR was in the order of heptachlor epoxide > aldrin > dieldrin >  $\beta$ -HCH > heptachlor > endrin >  $\gamma$ -HCH > HCB > endrin aldehyde >  $\alpha$ -HCH > p, p'-DDT > p, p'-DDD.

In this study, cancer and non-carcinogenic risk assessments utilize the following conventional assumptions regarding human exposure to the 14 OCPs: (1) The shallow groundwater was the sole source of drinking water. This assumption may overestimate health risks for shallow

groundwater was only one important source of drinking water in the rural area. (2) Risk estimates assume that the concentrations of the 14 OCPs in the shallow groundwater of TLR remain unchanged during the whole exposure duration (6 years for children and 70 years for adults). This assumption could lead to overestimation of potential health risks if pollution levels decline over time. (3) Risk values do not incorporate chemical-specific uptake factors for each pollutant, but rather assume 100% of the oral dose is absorbed into the body. This

could be a source of overestimation of risks. (4) Exposures to the 14 OCPs through other media, such as food and inhalation, are not taken into account. Omission of these exposures may underestimate potential human health risks. These default assumptions are based on science policy decisions to address uncertainties in the risk assessment process. Therefore, the results of cancer and non-carcinogenic risk assessment should not be interpreted as an accurate prediction of observed health outcomes, and it only provide a way to screen for those pollutants

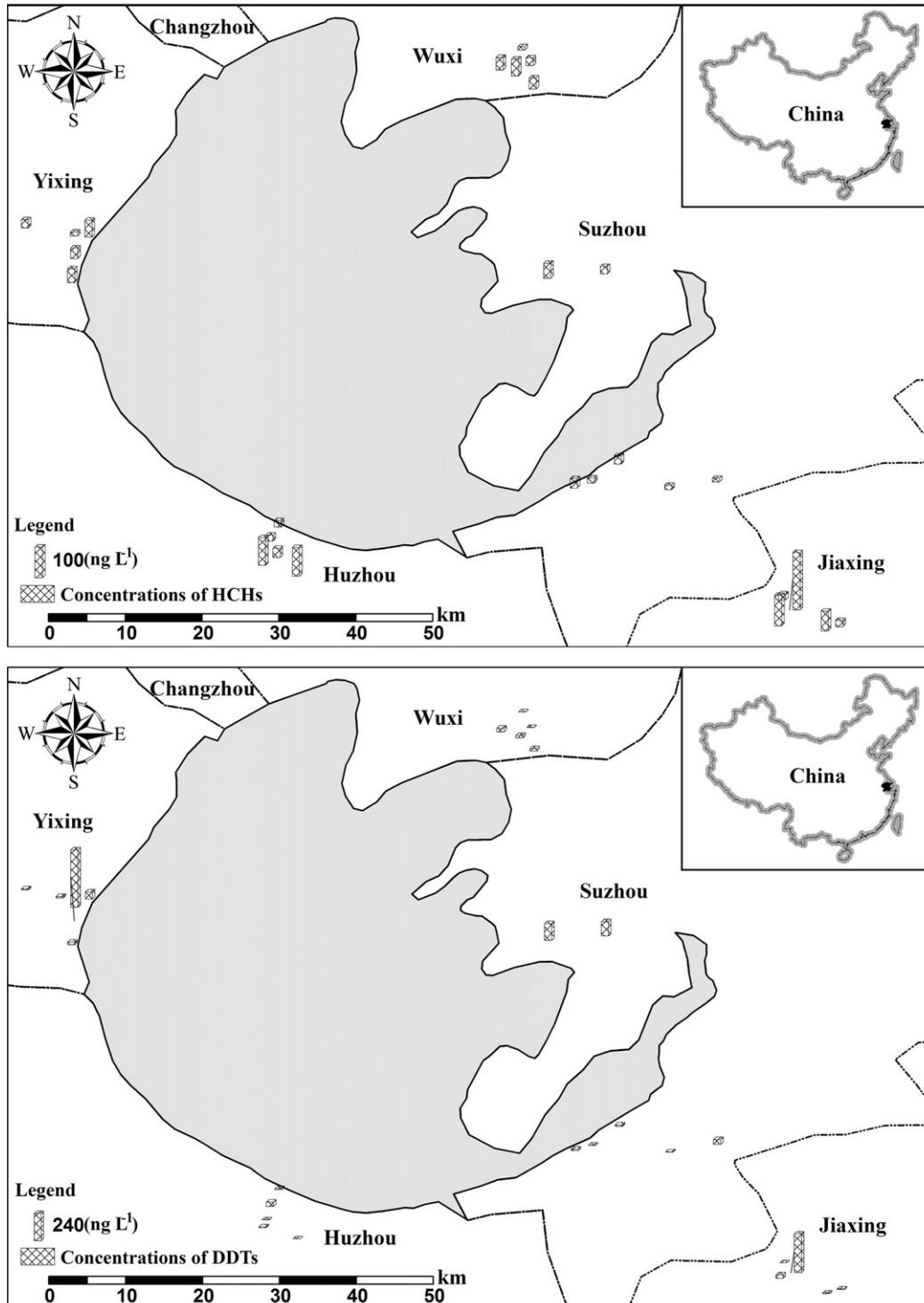


Fig. 2. The column charts of the concentrations of HCHs, DDTs and the 14 organochlorine pesticide (OCPs) in the 27 shallow groundwater samples in the study area.

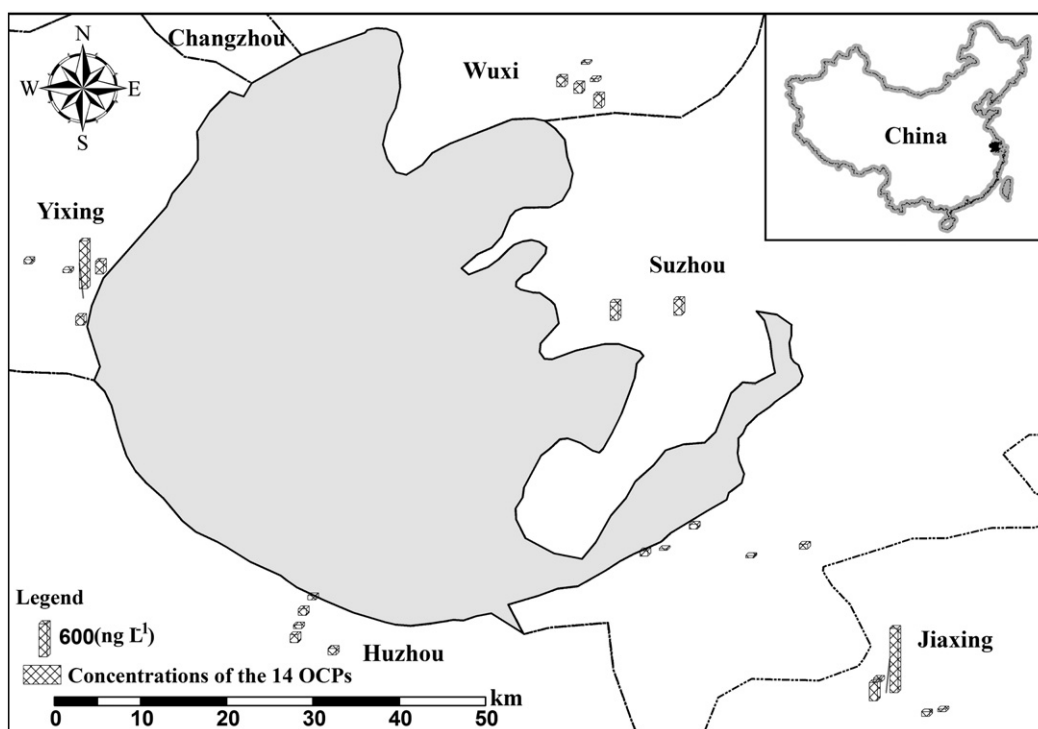


Fig. 2. (continued).

that are of public health significance in order to prioritize research and regulatory intervention efforts.

#### 4. Conclusion

OCPs residues in the shallow groundwater of TLR were frequently detected at high concentrations. All OCP species occurred in the shallow groundwater of TLR with high detection frequency except *p*, *p'*-DDD and *p*, *p'*-DDT. DDTs and HCHs were the dominant OCP species in the shallow groundwater of TLR, and they account for 44.2% total OCPs. Compositional analysis of OCPs indicated that the sources of the HCHs were mainly from the historical use of lindane after a period of degradation; the DDTs were mainly

from the historical residues; and there were fresh input sources of heptachlors, aldrins and endrins in addition to the historical residues. Correlation analysis indicated that HCB had similar source with HCHs and the historical application of technical HCH and lindane containing HCB impurity was one important source of HCB in the shallow groundwater of TLR.

The health risks from drinking local shallow groundwater for adults and children were estimated. The results show the current concentrations of  $\alpha$ -HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin in the shallow groundwater in majority of the areas of TLR may pose serious cancer risk to the local population, especially to children, and the aldrin and dieldrin were the main cancer risk factors in the shallow groundwater of TLR. Aldrins, heptachlors and HCHs residues in the shallow groundwater of TLR should be controlled urgently and effectively.

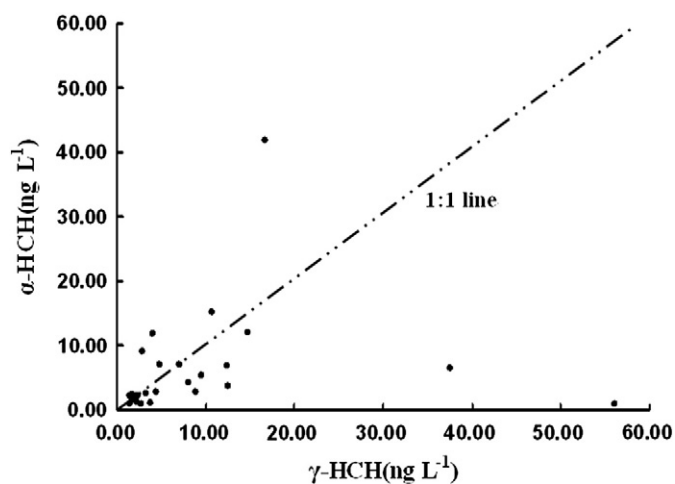


Fig. 3. Concentrations of  $\gamma$ -HCH ( $\text{ng L}^{-1}$ ) versus the concentrations of  $\alpha$ -HCH ( $\text{ng L}^{-1}$ ) in shallow groundwater samples from Taihu Lake Region.

#### Conflict of interest

We are the authors of the manuscript entitled "Levels and potential health hazards of organochlorine pesticides in shallow groundwater of Taihu Lake region, east China", and we declared that no conflict of interest was existed among us.

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**Table 4**  
Summary statistics for the health risks due to the 14 organochlorine pesticides for adults and children in Taihu Lake region through drinking shallow groundwater.<sup>a</sup>

Pesticide	Cancer risk ( $10^{-6}$ )				Hazard quotient ( $10^{-2}$ )			
	Range		Mean		Range		Mean	
	Adults	Children	Adults	Children	Adults	Children	Adults	Children
$\alpha$ -HCH	0.19–8.41	0.40–18.03	1.18	2.53	0.01–0.27	0.01–0.57	0.04	0.08
$\beta$ -HCH	0.05–6.19	0.12–13.26	0.84	1.79	0.02–1.72	0.03–3.68	0.23	0.50
$\gamma$ -HCH	0.06–2.33	0.12–4.99	0.36	0.78	0.01–0.60	0.03–1.28	0.09	0.20
$\delta$ -HCH	/	/	/	/	/	/	/	/
p, p'-DDE	0.01–4.93	0.02–10.56	0.51	1.09	/	/	/	/
p, p'-DDD	0–0.05	0–0.11	0.01	0.02	0–0.011	0–0.024	0.002	0.004
p, p'-DDT	0–0.66	0–1.40	0.05	0.11	0–0.39	0–0.83	0.03	0.06
Heptachlor	0.71–27.22	1.53–58.32	3.16	6.78	0.03–1.21	0.07–2.59	0.14	0.30
Heptachlor epoxide	0–13.71	0–29.37	3.58	7.67	0–11.59	0–24.83	3.03	6.48
Hexachlorobenzene	0.16–3.34	0.33–7.15	0.85	1.81	0.01–0.26	0.03–0.56	0.07	0.14
Aldrin	0–193.7	0–415.1	14.99	32.12	0–37.98	0–81.38	2.94	6.30
Dieldrin	0–131.9	0–282.6	6.84	14.65	0–16.48	0–35.32	0.85	1.83
Endrin	/	/	/	/	0–1.38	0–2.95	0.12	0.26
Endrin aldehyde	/	/	/	/	0–0.84	0–1.80	0.07	0.14
Total	1.73–207.9	3.71–445.6	32.26	69.12	0.18–40.92	0.39–87.7	7.61	16.30

<sup>a</sup> /, no given reference dose of the contaminant via oral exposure route parameter value.

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