

# Composition, Distribution, and Risk Assessment of Organochlorine Pesticides in Drinking Water Sources in South China

Liangfu Wei · Yuyi Yang · Qing X. Li · Jun Wang

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**Abstract** Samples were collected from nine drinking water sources in south China and were analyzed for concentrations of 15 organochlorine pesticides (OCPs). The average concentrations of total OCPs were in the range of 12.9–43.0 ng L<sup>-1</sup> with an overall average of 25.7 ng L<sup>-1</sup>. The concentrations of HCHs ( $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH) and DDTs (*p,p'*-DDD, *p,p'*-DDT, *p,p'*-DDE) were in the range of 5.54–13.08 and 0.17–4.47 ng L<sup>-1</sup>, respectively. HCHs, endrin-aldehyde, methoxychlor and endrin were the most dominant in all samples. The input of HCHs was a mixture of technical HCH and lindane, while the DDT may be mainly derived from DDT-treated aged and weathered agricultural soils. Health risk assessment of DDTs and HCHs suggested that water quality from nine drinking water sources in south China was safe for human drinking.

**Keywords** Water source · Organochlorine pesticides · DDTs · HCHs · Health risk

## Introduction

Organochlorine pesticides (OCPs) are among important persistent organic pollutants (POPs) and have been of great concern. OCPs include hexachloro-cyclohexanes (HCHs), dichloro-diphenyltrichloroethanes (DDTs), endrin-aldehyde, heptachlor, aldrin and endrin, etc. Because of their persistence in the environment and biological accumulation, OCPs can affect human health (Colborn et al. 1996). Most OCPs were used due to their low cost in industry, agriculture, and public health (Shinsuke et al. 1994). OCPs had been widely used in agriculture and human pest control in China. The amounts of HCHs and DDTs produced in China were estimated at 4.9 and 0.4 million metric tons, accounting for 33 and 20 % of the total global production, respectively (Hua and Shan 1996).

Although the use of HCHs and DDTs in agriculture was prohibited by the Chinese government in 1983, high residue concentrations of OCPs still existed in many media (Lee 2007; Xu et al. 2007). In the recent years, the distribution of OCPs in surface waters in China has been widely studied, such as East Lake (Yang et al. 2013), Suburb of Beijing (Chen et al. 2008), Yangtze River watershed of Wuhan (Tang et al. 2008), Huangpu River (Xia et al. 2006), Pearl River Artery Estuary (Yang et al. 2004a), and Macau coastal waters (Yang et al. 2004b). South China is one of China's seven geographical divisions, including Guangxi Zhuangzu Autonomous Region, Guangdong province, Hainan province as well as Hong Kong and Macao. Guangxi is a big province with abundant water resources. Guangdong is the biggest province in the total economy and population in China. Hainan is China's fifth special economic zone and second largest island. The main object of this study was to investigate the concentrations, distribution, pollution sources and human health risk of OCPs in water in south China, providing important infor-

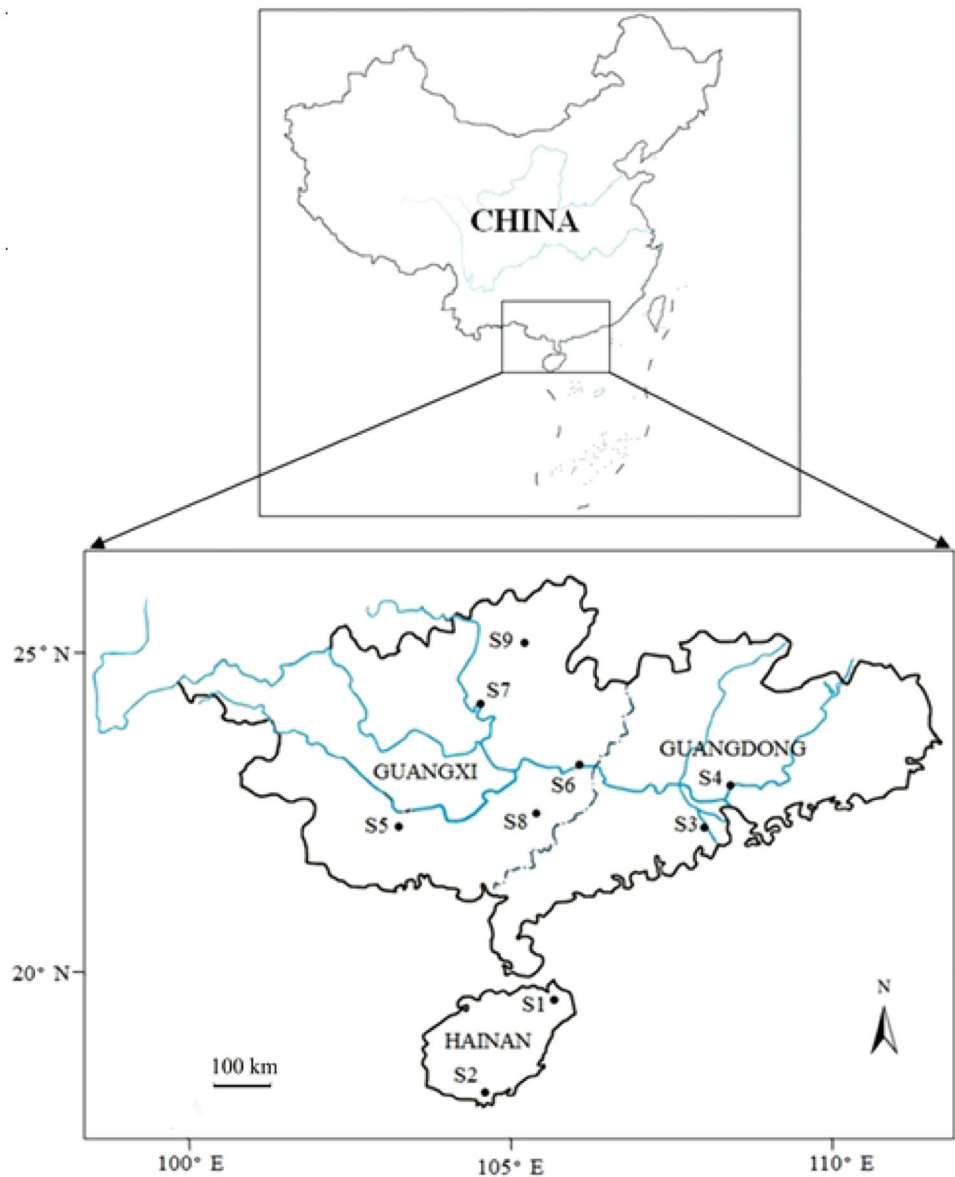
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**Fig. 1** The map of sampling sites in south China



mation for drinking water safety and management in this region.

## Materials and Method

### Study Area and Sample Collection

The study area included Guangxi, Guangdong, and Hainan provinces. During late May and early June 2013, 54 water samples were collected from nine water sources in south China. Six surface water samples were collected from each site. It was sunny in those days. Fig. 1 shows the sampling sites, including Longtang waterworks of Haikou (marked as S1) and Sanya Chitian reservoir (S2) in Hainan province, water source of Pinggang (S3), the south branch of

Dongjiang river (S4) in Guangdong province, water sources of Yongjiang river (S5), Xunjiang river (S6) and Liujiang river (S7), Suyan reservoir (S8), and waterworks of the north Guilin (S9) in Guangxi province. The land around sites S1, S2, S5, S6, S7, and S8 were mainly used for agriculture, while the land around S3, S4, S9 undergo server urbanization. All water samples were stored in a refrigerating chamber at a temperature of 4 °C and were extracted within 7 days after collection.

### Reagents and Standards

A 1,000 mg L<sup>-1</sup> standard solution of OCPs, including  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, *p*, *p'*-DDD, *p*, *p'*-DDT,

*p*, *p'*-DDE, heptachlor, aldrin, heptachlor-exo-epoxide,  $\alpha$ -endosulfan,  $\beta$ -endosulfan, endrin, endrin-aldehyde and methoxychlor, was purchased from AccuStandard Inc., USA and diluted to the working concentrations. Dichloromethane, ethyl acetate, methanol, and *n*-hexane were of chromatographic grade (Fisher Scientific, USA). Other chemicals were of analytical grade.

#### Extraction and Cleanup

All samples were filtered through 0.45  $\mu\text{m}$  hydrophilic filters to remove sand, debris and other suspended particles under vacuum conditions according to a published procedure (Capriotti et al. 2010; Peček et al. 2012). The samples were extracted with solid-phase extraction (SPE) cartridges. Before extraction, the C18 cartridge was first washed with 6 mL of ethyl acetate and 6 mL of dichloromethane, and then washed with methanol and ultrapure water each 10 mL, respectively. The water samples (1,000 mL) were percolated through the cartridges with a flow rate of 10 mL  $\text{min}^{-1}$  under vacuum. After extraction, the column was eluted with 10 mL of dichloromethane to yield a fraction containing OCPs. The eluents were dried by passing through anhydrous sodium sulfate and then concentrated under a gentle stream of high purity nitrogen. Finally, 100  $\mu\text{L}$  of *n*-hexane was added into the glass bottles to yield a fraction containing OCPs for gas chromatography/mass spectrometry/electron capture detection (GC-MS/ECD) analysis.

#### GC/MS/ECD Analysis

Qualitative and quantitative analysis of OCPs was carried out with an Agilent 7890A gas chromatograph equipped with an electron capture detector (GC-ECD) and a Model 5975 mass spectrometer (MS) using electron-ionization ion source (EI) in the selected ion monitoring (SIM) mode. One microliter of sample extracts was automatically injected into an HP-5 capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). Helium gas was used as the carrier gas at a constant flow of 1.0 mL  $\text{min}^{-1}$ . The injector and detector were operated at 250 and 300  $^{\circ}\text{C}$ , respectively. The ion source and interface temperatures were set to 300 and 280  $^{\circ}\text{C}$ , respectively. The GC oven temperature was programmed as follows: initial temperature was maintained at 80  $^{\circ}\text{C}$  for 1 min, and then programmed at 20  $^{\circ}\text{C}$   $\text{min}^{-1}$  to 150  $^{\circ}\text{C}$ , at 5  $^{\circ}\text{C}$   $\text{min}^{-1}$  to 300  $^{\circ}\text{C}$ , holding the final temperature for 5 min. The data were acquired and processed with Chemstation software (Hewlett-Packard).

#### Quality Assurance and Quality Control

All analytical procedures were monitored under strict quality assurance and control measures. The residue levels of OCPs were quantitatively determined by the internal stan-

dard methods using peak area of composite standards. For every set of ten samples, a procedural blank and a spiked sample with standards were used to check for interferences and eliminate cross-contaminations. Each sample was analyzed in triplicate unless otherwise noted. The limits of detection (LOD) were defined as the minimum detectable peaks of individual species with a signal-to-noise ratio (S/N) of 3:1. The average recoveries of the surrogate standard TCmX were  $76 \pm 7$  %. The recoveries of OCPs ranged from 74 to 113 %. The LODs of individual OCPs ranged from 0.14 to 0.32 ng  $\text{L}^{-1}$ . Reported 15 OCPs concentrations were corrected according to the recoveries of the standards.

#### Human Health Risk Assessment

The United States Environment Protection Agency (USEPA) recommended that toxicity data and exposure data are combined to assess chemical's carcinogenic risk and non-carcinogenic risk (USEPA 1989). A health risk assessment model proposed by USEPA was used to assess the risks of HCHs and DDTs for human health (Hamidin et al. 2008; He et al. 2012). Therefore, this study evaluated the carcinogenic and non-carcinogenic risks of  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH, total HCH, *p*, *p'*-DDT, *p*, *p'*-DDE, *p*, *p'*-DDD, and total DDT for human health.

Non-carcinogenic risk (HI) equation is as follows:

$$\text{HI} = E/\text{RfD} \quad (1)$$

and carcinogenic risk (R) is as follows:

$$\text{R} = \text{SF} \cdot E \quad \text{R} < 0.01 \quad (2)$$

$$\text{R} = 1 - e^{-(\text{SF} \cdot E)} \quad \text{R} \geq 0.01 \quad (3)$$

where RfD and SF are reference dose ( $\text{mg kg}^{-1}\text{day}^{-1}$ ) and slope factor [ $(\text{mg kg}^{-1}\text{day}^{-1})^{-1}$ ], respectively. The RfD values of  $\gamma$ -HCH, total HCH, *p*, *p'*-DDT and total DDT were 0.0004, 0.0004, 0.0005, and 0.0005, respectively. The SF values of  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH, total HCH, *p*, *p'*-DDT, *p*, *p'*-DDE, *p*, *p'*-DDD and total DDT were 6.3, 1.8, 1.3, 0.35, 0.34, 0.34, 0.24 and 0.35, respectively (USEPA 2012). *E* is exposure level (or intake) expressed as mass of a substance contacted per unit body weight per unit time ( $\text{mg kg}^{-1}\text{day}^{-1}$ ), it was calculated with two exposure approaches as follows:

$$E_1 = (C \cdot IR_W \cdot \text{EF} \cdot \text{ED})/(\text{BW} \cdot \text{AT}) \quad (4)$$

$$E_2 = (6\tau \cdot \text{TE}/\pi)^{0.5} \cdot (C \cdot k \cdot A_{sb} \cdot \text{EF} \cdot \text{FE} \cdot \text{ED})/500/\text{BW}/\text{AT}/f \quad (5)$$

where  $E_1$  and  $E_2$  are exposure levels to water for drinking and bathing, respectively. *C* is the concentration of HCHs and DDTs in water ( $\text{mg L}^{-1}$ );  $IR_W$  is water intake rate (2 L  $\text{day}^{-1}$ ); EF is exposure frequency (365 days  $\text{year}^{-1}$ ); ED is exposure duration (the carcinogenic equation employs 70

**Table 1** Concentrations of OCPs in all water samples from nine water sources in south China (ng L<sup>-1</sup>)

Compounds	Sampling sites								
	S1	S2	S3	S4	S5	S6	S7	S8	S9
α-HCH	1.52	3.17	1.42	1.71	3.24	3.86	2.48	0.88	1.01
β-HCH	1.63	2.51	1.42	1.88	3.07	3.44	1.39	0.33	0.29
γ-HCH	1.3	1.17	0.93	nd	1.67	1.6	nd	0.68	nd
δ-HCH	3.22	3.04	1.93	1.95	2.03	4.18	1.92	6.99	5.61
<i>p</i> , <i>p'</i> -DDD	2.41	1.03	0.4	nd	1.56	1.92	1.03	0.11	0.1
<i>p</i> , <i>p'</i> -DDE	nd	0.36	0.17	0.23	0.55	0.65	0.27	0.04	0.07
<i>p</i> , <i>p'</i> -DDT	nd	nd	nd	nd	nd	nd	3.17	1.76	nd
Methoxychlor	4.56	3.51	3.39	9.23	nd	nd	3.6	1.12	2.05
α-Endosulfan	0.47	1.16	0.57	0.48	0.55	1.62	0.22	0.02	nd
β-Endosulfan	nd	nd	nd	1.85	nd	nd	nd	0.15	0.15
Heptachlor	1.99	1.63	1.66	2.28	2.32	3	2.11	1.12	1.03
Heptachlor-exo-epoxide	0.4	0.38	0.76	0.49	1.23	1.84	0.45	nd	nd
Aldrin	1.09	2.42	1.74	1.23	1.38	4.74	2.05	0.78	0.89
Endrin	1.97	1.91	2.33	2.09	4.01	4.39	2.15	0.53	0.58
Endrin-aldehyde	1.73	8.14	1.89	6.18	11.18	11.75	5.9	0.45	1.11
∑HCHs	7.67	9.89	5.7	5.54	10.01	13.08	5.79	8.88	6.91
∑DDTs	2.41	1.39	0.57	0.23	2.11	2.57	4.47	1.91	0.17
∑OCPs	22.29	30.43	18.61	29.6	32.79	42.99	26.74	14.96	12.89

nd not detected

∑HCHs=α-HCH+β-HCH+γ-HCH+δ-HCH; ∑DDTs=*p*, *p'*-DDE+ *p*, *p'*-DDD+*p*, *p'*-DDT

years; the non-carcinogenic equation employs 30 years); BW is average of body weight (60 kg for Chinese people); AT is average time (the carcinogenic equation employs 70 years × 365 days year<sup>-1</sup>; the non-carcinogenic equation employs 30 years × 365 days year<sup>-1</sup>); τ is lag time for each pollutant in the body (assuming a value of 1 h); *TE* is bathing time (0.4 h); *k* is a skin permeability parameter (0.001 cm h<sup>-1</sup>); *A<sub>sb</sub>* is body surface area (16,600 cm<sup>2</sup>); *FE* is bathing frequency (0.3 times day<sup>-1</sup>); and *f* is the intestinal absorption ratio (1) (Wan et al. 2009; Wang et al. 2009).

## Results and Discussion

### Concentrations of OCPs in the Water

Concentrations of 15 OCPs in all water samples of nine water sources from south China are shown in Table 1. Concentrations of total OCPs in all water samples from south China ranged from 12.9 to 43.0 ng L<sup>-1</sup> with a mean value of 25.7 ng L<sup>-1</sup>. The highest concentrations of total OCPs were found in water source of XunJiang River (S6) and the lowest value occurred at sampling site 9 located in waterworks of north Guilin. This may be due to the higher level of agricultural and industrial activity near sampling site 6.

Table 2 shows the concentration ranges, medians and mean values of compounds in all water samples of nine water

**Table 2** The concentration ranges, medians, and mean values of compounds in all water samples from nine water sources in south China (ng L<sup>-1</sup>)

Compounds	Mean	Median	Range
∑HCHs	8.16	7.67	5.54–13.08
Endrin-aldehyde	5.37	5.9	0.45–11.75
Methoxychlor	3.05	3.39	nd–9.23
Endrin	2.22	2.09	0.53–4.39
Heptachlor	1.9	1.99	1–3
Aldrin	1.81	1.38	0.78–4.74
∑DDTs	1.76	1.91	0.17–4.47
∑Other OCPs <sup>a</sup>	0.72	0.38	nd–1.85
∑OCPs	25.7	26.74	12.89–42.99
∑Other OCPs <sup>a</sup> = α-Endosulfan + β-Endosulfan + Heptachlor-exo-epoxide			

sources from south China. It can be seen that the concentrations of HCHs (sum of α-HCH, β-HCH, γ-HCH, δ-HCH), endrin-aldehyde and methoxychlor were higher than those of DDTs (sum of *p*, *p'*-DDD, *p*, *p'*-DDT, *p*, *p'*-DDE) and other OCPs. Several compounds, such as endrin, heptachlor, aldrin, and heptachlor-exo-epoxide were detected at high concentrations in some water samples. The concentrations of DDTs and HCHs ranged from 0.17 to 4.47 and 5.54 to 13.1 ng L<sup>-1</sup>, respectively, which were much lower than that

**Table 3** Comparison of HCHs and DDTs concentrations in all water samples from nine water sources in south China and other areas in the world (ng L<sup>-1</sup>)

Area	Time	HCHs	DDTs	Reference
		Range (mean)	Range (mean)	
South China <sup>a</sup>	2013	5.54–13.08 (8.16)	0.17–4.47 (1.76)	This study
East Lake, China <sup>b</sup>	2012	6.96–28.65 (7.40)	3.74–57.92 (5.70)	(Yang et al. 2013)
Suburb of Beijing, China <sup>c</sup>	2006	3.87–146.42 (34.20)	0.39–13.98 (5.21)	(Chen et al. 2008)
Yangtze River watershed of Wuhan, China <sup>c</sup>	2005	0.55–28.07 (6.66)	nd–16.71 (1.48)	(Tang et al. 2008)
Huangpu River, China <sup>d</sup>	2004	42.13–75.47 (55.37)	3.83–20.90 (11.97)	(Xia et al. 2006)
Pearl River Artery Estuary, China <sup>b</sup>	2001	5.8–99.7 (28.97)	0.52–9.53 (4.33)	(Yang et al. 2004a)
Macau coastal waters, China <sup>b</sup>	2001	8.71–27.02 (18.06)	8.66–29.76 (18.02)	(Yang et al. 2004b)
Lake Burullus, Egypt <sup>e</sup>	2006	nd–495.55 (96.46)	0.03–726.77 (144.40)	(Said et al. 2008)
Northeastern part of São Paulo State, Brazil <sup>c</sup>	2005	20–600	20–580	(Rissato et al. 2006)
Northern Indo-Gangetic alluvial plains, India <sup>c</sup>	2003	1880–1950	nd–230	(Singh et al. 2006)
Küçük Menderes River, Turkey <sup>f</sup>	2001–2002	187–337	72–120	(Turgut 2003)
Nestos River, Greek <sup>f</sup>	1996–1998	nd–68.00	nd–64.00	(Spyros et al. 2003)

<sup>a</sup> HCHs=α-HCH+β-HCH+γ-HCH+δ-HCH, DDTs=p, p'-DDE+p, p'-DDD+p, p'-DDT;

<sup>b</sup> HCHs=α-HCH+β-HCH+γ-HCH+δ-HCH, DDTs=o, p'-DDE+p, p'-DDE+o, p'-DDD+p, p'-DDD+o, p'-DDT+p, p'-DDT;

<sup>c</sup> HCHs=α-HCH+β-HCH+γ-HCH+δ-HCH, DDTs=p, p'-DDE+p, p'-DDD+o, p'-DDT+p, p'-DDT;

<sup>d</sup> HCHs=α-HCH+β-HCH+γ-HCH, DDTs=p, p'-DDE+p, p'-DDD+p, p'-DDT;

<sup>e</sup> HCHs=α-HCH+β-HCH+γ-HCH, DDTs=o, p'-DDE+p, p'-DDE+o, p'-DDD+p, p'-DDD+o, p'-DDT+p, p'-DDT;

<sup>f</sup> HCHs=α-HCH+β-HCH+γ-HCH+δ-HCH, DDTs=p, p'-DDE+p, p'-DDD+p, p'-DDT

of drinking water quality standards (DDTs up to 8.11 ng L<sup>-1</sup>, HCHs up to 75.2 ng L<sup>-1</sup>, GB3838 – 2002) in China. The mean values of HCHs and DDTs were 8.16 and 1.76 ng L<sup>-1</sup>, respectively, accounting for 31.8 and 6.8 % of the total OCPs. It can be also found that the detection frequencies of DDTs, HCHs, heptachlor, aldrin, endrin, and endrin-aldehyde in the study were up to 100 %, indicating a common occurrence of these compounds in different regions of south China.

Table 3 shows the comparison of HCHs and DDTs concentrations in water samples of nine water sources from south China with those in other surface water in China and some other areas in the world. It can be seen that the ranges of DDTs and HCHs concentrations were much narrower than other areas. The level of HCHs in this study was higher than that in the East Lake of central China (Yang et al. 2013) and Yangtze River watershed of Wuhan city in China (Tang et al. 2008), lower than that in the other areas listed in Table 3. The level of DDTs in water of south China was higher than that in Yangtze River watershed of Wuhan in China (Tang et al. 2008), lower than that in the other areas listed in Table 3. When it was compared with some other areas in the world, the concentrations of DDTs and HCHs of this study were relatively lower.

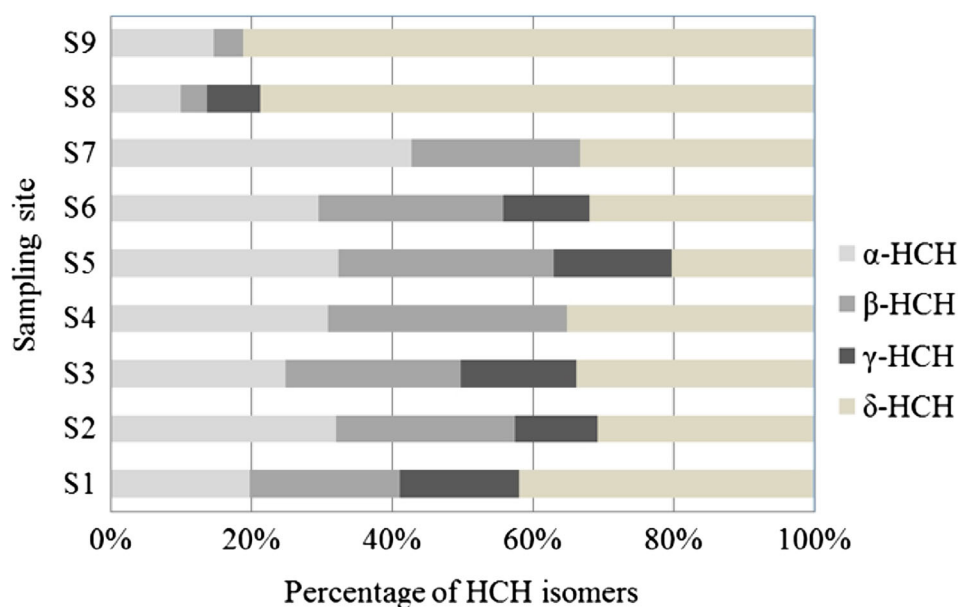
#### Composition and Identification of HCHs and DDTs in Water

**HCHs:** Fig. 2 shows compositions of HCH isomers in all water samples of nine water sources from south China. Tech-

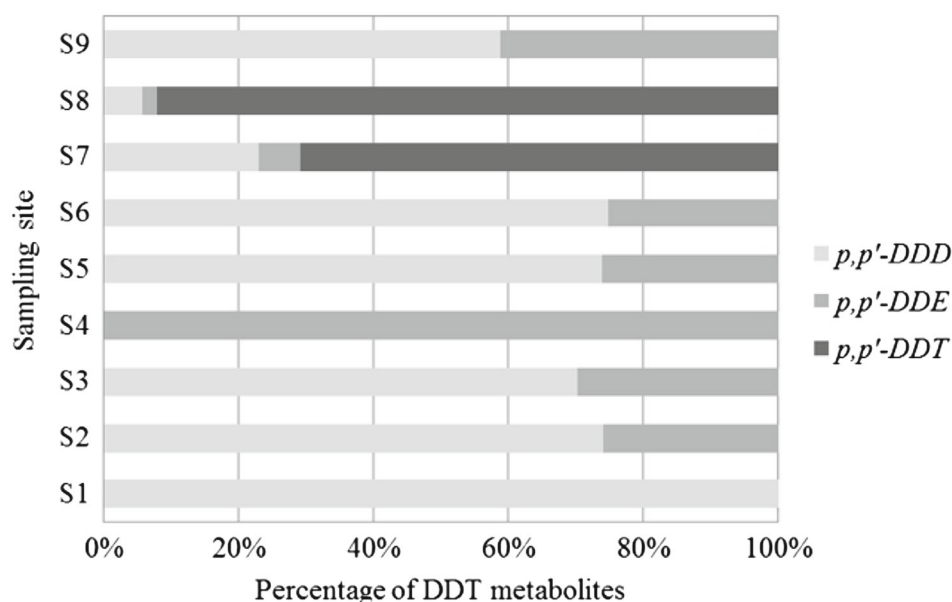
nical HCH was used as a broad spectrum insecticide for agricultural activity, forestry and public health purpose during 1950s to 1980s in China (Hua and Shan 1996). The typical technical HCHs contain 60–70 % of α-HCH, 5–12 % of β-HCH, 10–15 % of γ-HCH and 6–10 % of δ-HCH, while γ-HCH is above 99 % in lindane (Walker et al. 1999). The ratio of α-HCH/γ-HCH approximately 4–7 indicates that the input of HCHs was technical HCHs, when the ratio was close to 0, it indicates that the input of HCHs was lindane. Thus, the ratio of α-HCH/γ-HCH can be used to identify the source of the HCHs and to indicate the history use of HCH (Sheryl et al. 2001). In this study, δ-HCH was the predominant isomer in sampling sites 9 and 8, while the concentrations of α-HCH, β-HCH and γ-HCH were low. The composition percentages of different HCH isomers were similar in seven of the nine sampling sites. The ratios of α-HCH/γ-HCH of the sampling sites S8, S6, S5, S3, S2 and S1 ranged from 1.17 to 2.70, indicating that the input of HCHs was a mixture of technical HCH and fresh lindane. No γ-HCH has been detected in the sampling sites S9, S7 and S4, this may be explained by higher transportability of α-HCH than γ-HCH or γ-HCH has been removed in these sites due to photochemical transformation and biodegradation of γ-HCH to α-HCH in the environment (Strandberg et al. 1998).

**DDTs:** The composition difference of DDT and its metabolites can provide useful information on the pollution source. DDT can be degraded into DDD under anaerobic conditions and into DDE in aerobic conditions. Hence, aerobic metabolism of DDT is indicated when a DDD/

**Fig. 2** Compositions of HCH isomers in all water samples from nine water sources in south China



**Fig. 3** Compositions of DDT metabolites in all water samples from nine water sources in south China



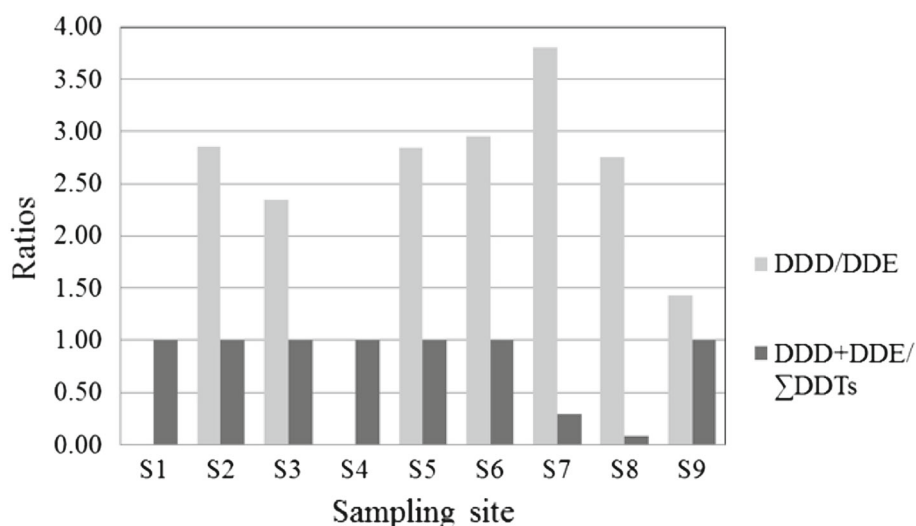
DDE ratio is less than 1.0, whereas anaerobic metabolism of DDT is indicated when the ratio is greater than 1.0 (Sun et al. 2005). Moreover, a ratio of (DDE+DDD)/ $\sum$ DDTs being > 0.5 indicates long-term weathering (Hites and Day 1992; Schmitt et al. 1990).

The compositions of DDT metabolites are shown in Fig. 3, the ratios of DDD/DDE and (DDD+DDE)/ $\sum$ DDTs are shown in Fig. 4. *p,p'*-DDE and *p,p'*-DDD were the predominant isomers in seven of the nine sites (S1–S6, and S9) (Fig. 3). The concentrations of *p,p'*-DDT were low at the sampling sites 9, 6, 5, 4, 3, 2, and 1. It is interesting that *p,p'*-DDT was the predominant isomer for the sampling sites 8 and 7, while *p,p'*-DDE and *p,p'*-DDD were low. It is also interesting that the samples from sites 1 and 4 were detected

*p,p'*-DDT and *p,p'*-DDE only, respectively. The ratio of DDD/DDE for all sampling sites ranged from 1.43 to 3.81, which were all greater than 1 (Fig. 4). This result indicated anaerobic metabolism of DDT in the studied region. The ratio of (DDE+DDD)/DDT ranged from 0.08 to 1.0, indicating that the DDT compounds may be mainly derived from DDT-treated aged and weathered agricultural soils.

Other OCPs. The trend of concentrations of 8 other OCPs in the water was as follows: endrin-aldehyde > methoxychlor > endrin > heptachlor > aldrin > heptachlor-epoxide >  $\alpha$ -endosulfan >  $\beta$ -endosulfan. In the present study, the mean concentrations of endrin-aldehyde, methoxychlor, endrin, heptachlor and aldrin were 5.37, 3.05, 2.22, 1.9 and 1.81 ng L<sup>-1</sup>, respectively, which were higher than

**Fig. 4** Ratios of DDD/DDE and  $(\text{DDD} + \text{DDE})/\sum\text{DDTs}$  in all water samples from nine water sources in south China



**Table 4** Non-carcinogenic risk of DDTs and HCHs pesticides in all water samples from nine water sources in south China

Sites	<i>p, p'</i> -DDT		DDTs		$\gamma$ -HCH		HCHs		HI <sub>1</sub>	HI <sub>2</sub>
	HI <sub>1</sub>	HI <sub>2</sub>	HI <sub>1</sub>	HI <sub>2</sub>	HI <sub>1</sub>	HI <sub>2</sub>	HI <sub>1</sub>	HI <sub>2</sub>		
S1	nd	nd	1.6	0.7	1.1	0.5	3.7	1.6	6.4	2.8
S2	nd	nd	0.9	0.4	1.0	0.4	5.7	2.5	7.6	3.3
S3	nd	nd	0.4	0.2	0.8	0.3	3.1	1.4	4.3	1.9
S4	nd	nd	0.2	0.1	nd	nd	3.0	1.3	3.1	1.4
S5	nd	nd	1.4	0.6	1.4	0.6	6.7	2.9	9.4	4.1
S6	nd	nd	1.7	0.7	1.3	0.6	7.4	3.2	11	4.6
S7	2.1	0.9	3.0	1.3	nd	nd	3.2	1.4	8.3	3.6
S8	1.2	0.5	1.3	0.6	0.6	0.3	1.6	0.7	4.6	2.0
S9	nd	nd	0.1	0.1	nd	nd	1.1	0.5	1.2	0.5

HI<sub>1</sub>: Non-carcinogenic risk for drinking, one per ten thousand ( $10^{-4}$ );

HI<sub>2</sub>: Non-carcinogenic risk for bathing, one per billion ( $10^{-9}$ );

nd not detected

DDTs (mean  $1.76 \text{ ng L}^{-1}$ ). In particular, the concentrations of endrin-aldehyde and methoxychlor ranged from  $0.45$  to  $11.75 \text{ ng L}^{-1}$  and from not detected to  $9.23 \text{ ng L}^{-1}$ , respectively. However, in many other studies HCHs and DDTs were predominant and these compounds (endrin-aldehyde, methoxychlor, endrin, heptachlor, and aldrin) were in lower concentrations (Chen et al. 2008; Sun et al. 2009; Tang et al. 2008; Xia et al. 2006; Yang et al. 2004a, b, 2013). This may be due to endrin-aldehyde, methoxychlor, endrin, heptachlor, and aldrin were still using for agricultural and public health purposes because of the low cost and versatility in controlling various insects in some areas of China, and also presumably as a result of long-range atmospheric transport from other regions (e.g., India).

#### Human Health Risk of DDTs and HCHs in the Water

Tables 4 and 5 illustrate the non-carcinogenic and carcinogenic risk of DDTs and HCHs pesticides in water samples of

nine water source from south China for drinking or bathing. According to USEPA (USEPA 1989), the acceptable non-carcinogenic hazard index (HI) was 1.0 and the acceptable carcinogenic risk of chemical pollutants ranged from  $10^{-7}$  to  $10^{-4}$ , which means the water is considered to be safe for use when non-carcinogenic hazard indices are less than 1.0 and carcinogenic risks are below  $10^{-7}$ . In this study, the non-carcinogenic risk of DDTs and HCHs were much less than 1.0, the carcinogenic risk of DDTs and HCHs for bathing ranged from  $1.1 \times 10^{-12}$  to  $5.4 \times 10^{-12}$ . It can be found that the levels of DDT and its metabolic products detected in water samples from south China did not pose carcinogenic risks. But the risks of  $\alpha$ -HCH and  $\beta$ -HCH for drinking, ranged from  $1.8 \times 10^{-7}$  to  $8.1 \times 10^{-7}$  and from  $0.2 \times 10^{-7}$  to  $2.1 \times 10^{-7}$ , respectively, were much greater than those of the other investigated compounds. This result indicated that the water of nine water sources in south China was safe for bathing and at acceptable level for drinking.

**Table 5** Carcinogenic risk of DDTs and HCHs pesticides in all water samples from nine water sources in south China

Sites	$\alpha$ -HCH		$\beta$ -HCH		$\gamma$ -HCH		HCHs		$p, p'$ -DDT		$p, p'$ -DDD		$p, p'$ -DDE		DDTs		R <sub>1</sub>	R <sub>2</sub>
	R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>		
S1	3.2	1.4	0.9	0.4	0.6	0.3	0.5	0.2	nd	nd	0.2	0.08	nd	nd	0.3	0.1	5.7	2.5
S2	6.7	2.9	1.5	0.7	0.5	0.2	0.8	0.3	nd	nd	0.1	0.04	0.04	0.01	0.2	0.07	9.8	4.2
S3	3.0	1.3	0.8	0.4	0.4	0.2	0.4	0.2	nd	nd	0.03	0.01	0.02	0.01	0.07	0.03	4.8	2.1
S4	3.6	1.6	1.1	0.5	nd	nd	0.4	0.2	nd	nd	nd	nd	0.03	0.01	0.03	0.01	5.2	2.3
S5	6.8	3.0	1.8	0.8	0.7	0.3	0.9	0.4	nd	nd	0.1	0.05	0.06	0.03	0.3	0.1	1.1	4.7
S6	8.1	3.5	2.1	0.9	0.7	0.3	1.0	0.5	nd	nd	0.2	0.07	0.07	0.03	0.3	0.1	12	5.4
S7	5.2	2.3	0.8	0.4	nd	nd	0.5	0.2	0.4	0.2	0.1	0.04	0.03	0.01	0.5	0.2	7.5	3.3
S8	1.8	0.8	0.2	0.1	0.3	0.1	0.2	0.1	0.2	0.1	0.01	0.01	0.01	0.01	0.2	0.1	3.0	1.3
S9	2.1	0.9	0.2	0.1	nd	nd	0.2	0.06	nd	nd	0.01	0.01	0.01	0.01	0.02	0.01	2.5	1.1

R<sub>1</sub>: carcinogenic risk for drinking, one per ten million ( $10^{-7}$ );

R<sub>2</sub>: carcinogenic risk for bathing, one per trillion ( $10^{-12}$ )

nd not detected

## Conclusions

The results suggested that most of the OCPs have been detected in almost all water samples from nine water sources in south China. The total concentrations of OCPs in water samples of nine water source from south China ranged from 12.89 to 42.99 ng L<sup>-1</sup>, the concentrations of DDTs in this study were much lower than that of other areas in the world and the concentrations of HCHs were at a low level when compared with other places of other countries. Notably, the studied OCPs originated from both current and historical use. The non-carcinogenic and carcinogenic risks of DDTs and HCHs indicated the water of nine water sources in south China was safe for bathing and at acceptable level for drinking.

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