

Contents lists available at ScienceDirect

# Journal of Hazardous Materials



journal homepage: www.elsevier.com/locate/jhazmat

# Distribution and sources of organochlorine pesticides (OCPs) in sediments from upper reach of Huaihe River, East China

# Jianhui Sun<sup>a</sup>, Jinglan Feng<sup>a,\*</sup>, Qun Liu<sup>b</sup>, Qilu Li<sup>c</sup>

<sup>a</sup> College of Chemistry and Environmental Sciences, Henan Normal University, Henan Key Laboratory for Environmental Pollution Control, Xinxiang, Henan 453007, PR China <sup>b</sup> State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, PR China <sup>c</sup> Conserve and Institute of Constrainty, Chinas Anderson, Conserve Sciences, Conserve and Constrainty, Chinas

<sup>c</sup> Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China

#### ARTICLE INFO

Article history: Received 26 December 2009 Received in revised form 31 July 2010 Accepted 7 August 2010 Available online 14 August 2010

*Keywords:* Distribution Organochlorine pesticides Sediment Huaihe River

#### ABSTRACT

Residues of hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) and their environmental risks in surface sediments collected from upper reach of Huaihe River, East China, are investigated in this paper. Based on dry weight (dw), the concentrations of  $\Sigma$ HCH ( $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -HCH) and  $\Sigma$ DDT (p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD) in sediments ranged from 1.95 to 11.05 ng g<sup>-1</sup> dw (mean 4.53 ng g<sup>-1</sup> dw) and 4.07 to 23.89 ng g<sup>-1</sup> dw (average 11.07 ng g<sup>-1</sup> dw), respectively. Compared with some published guideline values of organochlorine pesticides (OCPs) in sediments, the concentrations of HCHs were at safe levels while the residues of DDTs would pose adverse biological effects in this studied area. The distribution of OCPs in sediments were influenced by total organic carbon contents of sediments. The present study suggested that historical usage of lindane and technical DDT was the main reason for OCP residues in the sediments from both rivers and lakes. Furthermore, the composition of DDTs reflected fresh inputs of dicofol mixture in this region.

© 2010 Elsevier B.V. All rights reserved.

# 1. Introduction

Organochlorine pesticides (OCPs) such as hexachlorocyclohexanes (HCHs) and dichlorodiphenvltrichloroethane (DDTs) are known for their global concerns and environmental persistence. Due to their impact on nontarget organisms and biological accumulation via the food chain [1–3], OCPs pose great risks to ecosystems and human health. With low-water solubilities and high hydrophobicities, OCPs are readily sorbed onto suspended particulate matter and subsequently deposit into river and marine sediments [4]. Sediments, one of important repositories of OCPs, can be resuspended and released bound-OCPs from particles into water under favorable conditions, which result in second contamination of water [3]. Through interaction between sediment and water, the transfer of OCPs from sediments to organisms is now regarded as a major route of exposure for many species [5]. Consequently, the residues of OCPs in sediments can serve as a useful index of pollution and potential environmental risks.

Although the application of OCPs has been banned in many developed countries, some developing countries are still producing and consuming these persistent pesticides because of their low cost and versatility in controlling various insects [6,7]. China is a large producer and user of OCPs in the world. In the previous decades, large amounts of OCPs have been used to obtain high yield to sustain overpopulation in China. HCHs and DDTs were heavily consumed in China from 1952 to 1983. The total production of technical HCHs is around 4 million tons between 1952 and 1984 [8]. Moreover, 3200 tons of lindane (almost pure  $\gamma$ -HCH) was still in use between 1991 and 2000. And DDTs production also continued due to export demand and dicofol production after the restriction of technical HCHs and DDTs in 1983 [9–11]. Extensive and continuous use of OCPs in China has resulted in ubiquitous OCPs pollution in various environmental media, especially in sediments [2,3,12–15]. Recently levels and distributions of OCPs in sediments have frequently been detected [4,12,16,17]. All these studies indicated that further research is essential to reveal the sources and assess the risk of OCPs residues in sediments.

Huaihe River, one of the most important rivers in East China, flows 1000 km from the Tongbai Mountain to Yangtze River and drains a populous area of 30,000 km<sup>2</sup>. The upper reach of Huaihe River Basin locates in Henan province and flows across extensive agricultural regions where OCPs have been used extensively. In addition to being used for agriculture, Huaihe River is main source of drinking water and industrial water in this basin. And with the rapid growth of economy and urbanization, more and more wastes are discharged into the river. Recently, organic pollutants contamination of large rivers in China, especially persistent organic

<sup>\*</sup> Corresponding author. Tel.: +86 373 3325971; fax: +86 373 3326336. *E-mail addresses*: sunjh\_hj@yahoo.com.cn (J. Sun), fengjl23@yahoo.com.cn, fengjinglan@gmail.com (J. Feng), ldqun@yahoo.com.cn (Q. Liu).

<sup>0304-3894/\$ -</sup> see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2010.08.016



Fig. 1. Map of sampling sites. M, mainstream of Huaihe River; T, tributaries in upper reach of Huaihe River; L, Lakes in upper reach of Huaihe River.

pollutants (POPs), has drawn great concern from the public and government. So far, little information is available for OCPs contamination in the upper reach of Huaihe River. Investigation on OCPs levels in sediments from upper reach of Huaihe River is essential in order to better understand the contribution of that to the middle and lower reaches' pollution.

The aims of this research are to survey the levels and distributions of OCPs in surface sediments from upper reach of Huaihe River and to assess their environmental risks in this basin. Furthermore, the contamination profiles and possible sources of HCHs and DDTs were also discussed for the purpose of future strategic environmental management.

# 2. Materials and methods

# 2.1. Sampling and pretreatment

The sampling sites are shown in Fig. 1. Total of 16 sampling sites along upper reach of Huaihe River and its tributaries, lakes were selected as such to cover the whole aquatic system in this area. Sediment samples were collected using grab sampler in March 2007, and then put in stainless steel containers. All sediment samples were freeze-dried and then ground, homogenized and stored in pre-cleaned dark glass bottles at -18 °C prior to analysis.

#### 2.2. Chemical reagents

Eight individual standards of OCPs including  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -HCH and *p*,*p*'-DDT, *o*,*p*'-DDT, *p*,*p*'-DDE, *p*,*p*'-DDD were purchased from National Research Center for Certified Reference Materials of China. The standard OCPs including  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -HCH, p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD, aldrin, hepta-chlor, endosulfan I, endosulfan II, methoxychlor, dieldrin, endrin, endosulfan sulfate, endrin aldehyde, and hepta-chlor expoxide and internal standards (pentachloronitrobenzene) were purchased from Accustandard (USA). The working standard solutions were prepared by diluting appropriate volumes of the standard solutions. All solvents used for sample processing and analysis (dichloromethane, acetone, hexane and methanol), purchased from Dikma Co. (USA), were analytical grade and re-distilled in a full-glass distilling appliance. Anhydrous sodium sulfate (analytical grade, Guangzhou Chemicals Inc., Guangzhou, China), neutral silica gel (80-100 mesh) and alumina (100-200 mesh) (Wushi Chemicals Inc., Shanghai, China) were baked in a furnace oven at 650 °C for 6 h, kept in a sealed desiccator prior to use. NaCl and Cu were obtained from Damao Chemicals Co. (Tianjin, China). Deionized water was produced by a Milli-Q system (Millipore Co., USA).

#### 2.3. Samples analysis

The pretreatment procedure of OCPs in sediments was a modification of the method described previously [18,19]. 15g of freeze-dried, homogenized sediment was soxhlet-extracted for 48 h with 120 mL of dichloromethane. 2g of activated Cu was added for desulphurization. The extracts were concentrated to 1–2 mL by a rotary evaporator and subject a solvent exchange to hexane. The concentrated extract was passed through a 1:2 alumina/silica gel glass column with 1 cm anhydrous sodium sulfate on the top for clean-up and fractionation. Elution was performed with 70 mL hexane/dichloromethane (7:3, v/v). Elutes were concentrated to 1–2 mL, subject to a solvent exchange to hexane, and then concentrated to 0.2 mL with a gentle steam of purified nitrogen. The internal standard (pentachloronitrobenzene) was added to the sample prior to GC-ECD analysis.

OCPs were analyzed using a Hewlett-Packard 6890 gas chromatography with a  $^{63}$ Ni electron capture detector (GC-ECD). Separation was carried out using a HP-5 capillary column (30 m × 0.25 mm × 0.25 µm). Instrumental conditions were as follows: the injector port and detector temperature were maintained at 250 °C and 315 °C, respectively. Column temperature was programmed at 60 °C (hold for 2 min) increasing at 6 °C/min to 200 °C, then increasing at 1 °C/min to 210 °C, 210–290 °C at a rate of 10 °C/min and hold for 10 min at 290 °C. Helium was the carrier gas at a flow of 1.0 mL/min under the constant flow mode. 1 µL of each sample was injected in the splitless mode. Concentration of individual OCPs was obtained by the internal standard peaks area method and 6-point calibration curve for individual components [18].

## 2.4. Analytical quality controls

All analytical operations were conducted under strict quality control guidelines. Procedural blanks and spiked samples with standard were used to monitor procedural performance and matrix effects. All experiments were carried out in duplicate. The method detection limits (MDLs) of  $\alpha$ -,  $\beta$ -,  $\gamma$ -and  $\delta$ -HCH were 0.02, 0.01, 0.02 and 0.03 ng g<sup>-1</sup> dw, and those of *p*,*p*'-DDT, *o*,*p*'-DDT, *p*,*p*'-DDD, *p*,*p*'-DDD were 0.02, 0.03 and 0.03 ng g<sup>-1</sup> dw, respectively. The spiked recoveries of  $\alpha$ -,  $\beta$ -,  $\gamma$ -and  $\delta$ -HCH were 105.4 ± 7.4%, 95.2 ± 9.3%, 107.4 ± 5.6% and 89.8 ± 4.7%, respectively.

#### Table 1

Levels of OCPs (ng g<sup>-1</sup> dw) and physicochemical characteristics of the sediments from Huaihe River (M) and its tributaries (T) and nearby lakes (L) in upper reach of Huaihe River.

	α-HCH	β-НСН	γ-ΗCΗ	δ-НСН	ΣΗCΗ	p,p'-DDE	p,p'-DDD	o,p'-DDT	p,p'-DDT	ΣDDT
M-1	1.05	0.57	1.75	0.12	3.49	0.07	0.34	1.74	5.72	7.87
M-2	1.22	0.66	2.17	0.14	4.19	0.08	0.40	2.02	6.65	9.15
M-3	0.70	0.30	0.89	0.06	1.95	0.00	0.18	0.91	2.98	4.07
M-4	1.10	0.16	4.62	0.35	6.23	5.72	2.40	5.33	3.59	17.04
M-5	1.43	0.60	2.08	0.12	4.23	0.07	1.33	1.82	5.97	9.19
M-6	1.36	0.52	1.77	0.11	3.76	0.06	0.81	1.59	5.22	7.68
M-7	1.22	0.66	1.97	0.14	3.99	0.08	0.40	2.01	6.61	9.10
Mean	1.15	0.50	2.18	0.15	3.98	0.87	0.84	2.20	5.25	9.16
T-1	0.95	0.38	1.12	0.08	2.53	0.00	0.96	1.17	3.83	5.96
T-2	2.59	2.46	2.89	0.10	8.04	2.62	7.93	4.15	2.48	17.18
T-3	1.19	0.65	3.62	0.14	5.60	0.08	4.07	1.97	8.06	14.18
T-4	1.29	4.94	4.69	0.13	11.05	2.67	8.64	2.14	2.21	15.66
T-5	1.07	0.58	2.25	0.12	4.02	0.07	1.65	1.78	7.54	11.04
T-6	1.36	0.57	1.67	0.12	3.72	0.07	1.67	1.73	7.01	10.48
T-7	1.19	0.65	1.83	0.14	3.81	0.08	1.18	1.97	6.47	9.70
Mean	1.38	1.46	2.58	0.12	5.54	0.80	3.73	2.13	5.37	12.03
L-1	0.66	0.36	1.00	0.08	2.10	0.00	0.22	1.09	3.60	4.91
L-2	1.39	0.50	1.77	0.11	3.77	0.06	7.94	3.71	12.18	23.89
Mean	1.02	0.43	1.38	0.10	2.94	0.03	4.08	2.40	7.89	14.40

and those of *p*,*p*'-DDT, *o*,*p*'-DDT, *p*,*p*'-DDE, *p*,*p*'-DDD were  $83.7 \pm 7.9\%$ ,  $103.2 \pm 6.5\%$ ,  $69.7 \pm 5.4\%$  and  $97.2 \pm 8.3\%$ , respectively.

# 2.5. Other analysis

Total organic carbon (TOC) contents of sediments were determined using a Liqui TOC (Elementar, Germany) analyzer. The dried and homogenized sediment samples were first acidified with 1.6%HCl to remove carbonates, then dried at 60  $^{\circ}$ C and analyzed for TOC.

#### 3. Results and discussion

#### 3.1. Levels and risks of OCPs

The contents of OCPs in sediments from upper reach of Huaihe River were presented in Table 1. It could be seen in Table 1 that residues of HCHs and DDTs were detected in all samples. In the present study,  $\Sigma$ HCH (equivalent sum of  $\alpha$ + $\beta$ ++ $\gamma$ -+ $\delta$ -HCH) ranged from 1.95 to 11.05 ng g<sup>-1</sup> dw (mean 4.53 ng g<sup>-1</sup> dw) and  $\Sigma$ DDT (equivalent sum of *p*,*p*'-DDE+*p*,*p*'-DDD+*o*,*p*'-DDT+*p*,*p*'-DDT) ranged from 4.07 to 23.89 ng g<sup>-1</sup> dw (average 11.07 ng g<sup>-1</sup> dw), respectively. The level of  $\Sigma$ DDT was higher than that of  $\Sigma$ HCH, consistent with previous studies on OCPs residues in freshwater sediments in China, because DDTs had low-water solubility, vapor pressure, biodegradability and high lipophilicity, particle affinity compared with HCHs [4,25]. The levels of OCPs in sediments in present study compared with those in other rivers were shown in Table 2. As seen in Table 2, OCPs levels in sediments from the mainstream of Huaihe River were rel-

### Table 2

Comparison of OCPs concentrations in sediments from the studied Chinese River.

Yangtze River (W) 0.10-11.72 1.55-15.63 Tang et al. [14]   Yangtze River (N) 0.18-1.41 0.21-4.50 Xu et al. [20]   Daliao watershed 1.86-21.48 0.5-2.81 Wang et al. [15]   Haihe River 1.88-18.76 0.32-80.18 Yang et al. [25]   Qiantang River 8.22-152.1 1.14-100.2 Zhou et al. [17]   TonghuiRiver 0.06-0.38 0.11-3.78 Zhang et al. [16]	Rivers	ΣΗCΗ	ΣDDT	References
Pearl River 5.0-91.0 1.2-17.0 Mai et al. [18] Huzibe River (11) 1.95-6.23 4.07-17.04 This study	Yangtze River (W) Yangtze River (N) Daliao watershed Haihe River Qiantang River TonghuiRiver Pearl River Huaibe River (II)	0.10-11.72 0.18-1.41 1.86-21.48 1.88-18.76 8.22-152.1 0.06-0.38 5.0-91.0 1.95-6.23	1.55-15.63 0.21-4.50 0.5-2.81 0.32-80.18 1.14-100.2 0.11-3.78 1.2-17.0 4.07-17.04	Tang et al. [14] Xu et al. [20] Wang et al. [25] Yang et al. [25] Zhou et al. [17] Zhang et al. [16] Mai et al. [18] This study

atively low  $(1.95-6.23 \text{ ng g}^{-1} \text{ dw for } \Sigma$ HCH,  $4.07-17.04 \text{ ng g}^{-1} \text{ dw}$  for  $\Sigma$ DDT) and similar to those in sediments from Nanjing section of Yangtze River and Tonghui River [4.14–18.20].

Few environmental standards of OCPs have been set up for freshwater sediments in China. Therefore, potential environmental risk of OCPs residues was evaluated against some published sediment quality guidelines (SQGs) [21–24]. The comparison between OCPs concentrations in sediments from upper reach of Huaihe River and SQGs was listed in Table 3. It could be concluded in Table 3 that concentrations of  $\alpha$ -HCH were lower than the lowest effect level (LEL) in all samples. In the case of  $\gamma$ -HCH, a few sites (M4, T2, T4) had slightly higher levels than the consensus-based threshold effect concentration (CB-TEC; below which adverse effects are not expected to occur). This suggested that sediments from upper reach of Huaihe River were not heavily polluted with HCHs. As for DDT, average concentrations of  $\Sigma$ DDT in this study exceeded the effect range low (ERL; below which adverse biological effects are rarely observed) at all sampling sites, but were all below the effect

#### Table 3

Comparison between OCP levels in this study and sediment concentrations as guideline values ( $ng g^{-1} dw$ ).

Chemicals	TECs				PECs				OCPs in sediments <sup>a</sup>			
	TEL	LEL	ERL	CB-TEC	PEL	SEL	ERM	CB-PEC	Huaihe River	Tributaries	Lakes	
<i>p,p′</i> -DDD	3.54	8	2	4.88	8.51	60	20	28.0	0.18-8.12 (1.71)	0.96-10.55 (4.53)	0.22-8.00 (4.11)	
p,p'-DDE	1.42	5	2.2	3.16	6.75	190	27	31.3	n.d. to 5.72 (0.87)	n.d. to 2.62 (0.80)	n.d. to 0.06 (0.03)	
p,p'-DDT and o,p'-DDT	-	-	1	4.16	-	710	7	62.9	3.89-8.92 (7.45)	4.35-10.03 (7.50)	4.69-15.89 (10.29)	
ΣDDT	3.89	7	1.58	5.28	51.7	120	46.1	572	4.07-17.04 (9.16)	5.96-17.18 (12.03)	4.91-23.89 (14.40)	
ү-НСН	0.94	3	-	2.37	1.38	10	-	4.99	0.89-4.62 (2.18)	1.12-4.69 (2.58)	1.00-1.77 (1.39)	
α-HCH	-	6	-	-	-	-	-	-	0.70-1.43 (1.15)	0.95-2.59 (1.38)	0.66-1.39 (1.03)	

Note. TECs, threshold effect concentrations; PECs, probable effect concentrations; TEL, threshold effect level; PEL, probable effect level [23]; LEL, lowest effect level; SEL, severe effect [22]; ERL, effect range low; ERM, effect range median [21]; CB-TEC, concensus-based TEC; CB-PEC, concensus-based PEC [24].

<sup>a</sup> Level of OCPs in sediments expressed as range (average). n.d., levels lower than detection limit.



Fig. 2. Distribution of OCPs in sediments from upper reach of Huaihe River.

range median (ERM; above this level adverse biological effects are frequently observed) (Table 3). Mean concentrations of p,p'-DDD above ERL was found not only in mainstream but also in tributaries and lakes. Of the sites above ERL of p,p'-DDE, one located in the mainstream of Huaihe River, the others were all from the tributaries. Moreover, sum DDT levels (p,p'-DDT and o,p'-DDT) above ERM were found in 13 sampling sites, including M1, M2, M4, M5, M6, M7, T2, T3, T4, T5, T6, T7, and L2. Based on these results, it was concluded that DDTs were the chemical of most concern and adverse biological effects were possible in this studied area.

#### 3.2. Distribution of OCPs

Table 4

Spatial differences of OCPs residues were investigated in this area. In the tributaries, the concentrations of  $\Sigma$ HCH were high at sites T4 (11.05 ng  $g^{-1}$ ) in the Huang River, followed T2 (8.04 ng  $g^{-1}$ ) in the Zhugan River. These two tributaries, major rivers in the studied area, flowed across not only an extensive agricultural region where large amounts of technical HCHs had been used but also areas of intensive industrial activities, including pharmaceutical, chemical, papermaking factories. Therefore, relatively high HCHs residues may originate from not only agricultural usage but also industrial waste discharges. Relatively low-HCHs concentrations were monitored at sites Shihe River (T1), Bailu River (T6) and Shiguan River (T7) despite these rivers flowing across an extensive agricultural region. Apart from the ban or restricted use of OCPs, this may be due to the large flow and rapid current velocity in these rivers.  $\Sigma$ DDT had a different distribution patterns in comparison to HCHs residues. The concentration statistic in Table 1 showed that Zhugan River (T2), Huang River (T4) and Lv River (T3) were relatively heavily polluted with DDTs, while Shihe River (T1) was much less polluted. This implied that different usage of technical DDT or various new inputs occurred in these tributaries.

Correlation matrix of OCPs and TOC of sediment from upper reach of Huaihe River (n = 16).

Huaihe River. It could be seen in Fig. 2 that  $\Sigma$ DDT and  $\Sigma$ HCH had similar distribution pattern. There was no significant fluctuation in the loading of  $\Sigma$ DDT and  $\Sigma$ HCH in sediments along Huaihe River apart from M3 and M4 (Fig. 2). The maximum concentrations of both  $\Sigma$ HCH and  $\Sigma$ DDT were loaded at site M4, downstream of the confluence of Huaihe River and Zhugan River (Fig. 2). This may be attributed mainly to OCP inputs from Zhugan River by abundant water and sediments. In addition, particles adsorbing OCPs tended to deposit since water flow turned slow due to the afflux of Zhugan River. Site M3 (downstream of the confluence of Huaihe River and Shihe River) was loaded with much less OCPs (Fig. 2). This may be due to flux dilution effect of Shihe River which loaded relatively low level of OCPs. The distribution of OCPs in sediments influenced by physic-

Fig. 2 illustrated the fluctuations of OCPs in the mainstream of

The distribution of OCPs in sediments influenced by physicochemical properties of sediments was observed in this study. Correlations between OCPs and sediment geochemical property were listed in Table 4. Hydrophobic organic substances were mainly sorbed onto particles, which were often correlated with the contents of TOC in sediments [14,25]. This study showed that there was a significant positive correlation between TOC contents and concentrations of  $\Sigma$ DDT (p < 0.01) but no  $\Sigma$ HCH, which was possibly explained by the less lipophilic and more volatile nature of HCHs than the DDTs [4]. The result corresponded with the previous findings of OCPs in sediments in other regions [4,14,26].

### 3.3. Composition and sources

Composition differences of HCH isomers or DDT congeners in the environment could reveal different pollution sources [17,27]. Typical technical HCH contains 60–70%  $\alpha$ -HCH, 5–12%  $\beta$ -HCH, 10–15%  $\gamma$ -HCH and 6–10%  $\delta$ -HCH, respectively.  $\gamma$ -HCH is above 99% in lindane. These HCH isomers have different physicochemical properties.  $\alpha$ -HCH and  $\gamma$ -HCH can be easily broken away from sediments because of high Henry's Law constant value while B-HCH, low-water solubility and vapor pressure, is the most stable and relatively resistant to microbial degradation [26]. Also it should be noted that  $\alpha$ -HCH and  $\gamma$ -HCH could be converted to  $\beta$ -HCH in the environment [28]. Therefore,  $\beta$ -HCH would be predominant in most of sediments if no fresh inputs of technical HCH while the predominant of  $\gamma$ -HCH in some environmental samples reflects the recent use of lindane. Compositions of HCH isomers in this study are plotted in Fig. 3. The average percentage of HCH isomers measured in the sediment samples are  $\alpha$ -HCH: 29.9%,  $\beta$ -HCH: 17.1%,  $\gamma$ -HCH: 49.9%,  $\delta$ -HCH: 3.1%. As seen in Fig. 3, a high percentage of  $\gamma$ -HCH, ranging from 35.9 to 74.2%, is recorded in sampling sites. On the other hand, the ratio of  $\alpha$ -HCH/ $\gamma$ -HCH ranged from 3 to 7 for technical HCH [29]. The low  $\alpha$ -HCH/ $\gamma$ -HCH ratio in the sediment samples implies the usage of lindane formulation [30]. In the present study, the ratio of  $\alpha$ -HCH/ $\gamma$ -HCH varies from 0.24 to 0.90 (mean 0.62) in the sediments. Li et al. [8] reported that about

	α-HCH	β-НСН	γ-ΗCΗ	δ-HCH	$\Sigma$ HCH	p,p'-DDE	p,p'-DDD	o,p'-DDT	p,p'-DDT	ΣDDT	TOC
α-HCH	1	0.415	0.308	0.009	0.553*	0.287	0.610	0.534*	-0.024	0.541*	0.513*
β-НСН		1	$0.576^{*}$	-0.084	0.878**	0.363	0.712**	0.131	-0.408	0.344	0.408
γ-HCH			1	0.686**	0.872**	0.784**	0.571*	0.625**	-0.187	$0.610^{*}$	0.272
δ-НСН				1	0.329	0.783**	0.037	0.722**	-0.035	0.402	-0.010
ΣHCH					1	0.653**	0.766**	$0.499^{*}$	-0.310	0.594	0.441
p,p'-DDE						1	0.414	0.802**	-0.459	0.495	0.219
p,p'-DDD							1	$0.550^{*}$	0.062	0.845**	0.871**
o,p'-DDT								1	0.057	0.807**	$0.562^{*}$
p,p'-DDT									1	0.393	0.367
ΣDDT										1	0.863**

\* Correlation is significant at the 0.05 level.

\*\* Correlation is significant at the 0.01 level.



Fig. 3. Compositions of HCH isomers in different sediments from upper reach of Huaihe River.



Fig. 4. Compositions of DDT congeners in different sediments from upper reach of Huaihe River.

 $3.2 \times 10^3$  tons of lindane was used in China between 1991 and 2000. Therefore, it can be concluded that lindane may be used recently in upper reach of Huaihe River.

The compositions of DDTs in the studied sediments are plotted in Fig. 4. As shown in Fig. 4, the average composition of DDT congeners detected in the sediment samples are  $p_{,p'}$ -DDT (58%) > o,p'-DDT (20%) > p,p'-DDD (18%) > p,p'-DDE (4%) with the dominance of *p*,*p*′-DDT. Technical DDT generally contains 80–85% p,p'-DDT and 15-20% o,p'-DDT [31]. If there was no new technical DDT input, the compositional percentage of *p*,*p*'-DDT would decrease and the metabolites DDE+DDD would increase. Therefore, the ratio of p,p'-DDT/ $\Sigma$ DDT can be used as an indicator to identify a recent input of technical DDT [26]. High ratios suggest a recent input of technical DDT while low ratios indicate no recent input [26]. In the present study, relatively high ratios of  $p_{,p'}$ -DDT/ $\Sigma$ DDT, ranging from 0.14 to 0.73 (mean 0.58) as illustrated in Fig. 4, indicate that there is a recent input of technical DDT. Furthermore, DDT can be biodegraded to DDD under anaerobic conditions and DDE under aerobic conditions, it is expected that DDD is much higher than DDE in sediment samples. This is the case as illustrated in Fig. 4 since the sediment samples are anaerobic. On the other hand, the content of p,p'-DDT is much higher than that of o,p'-DDT in technical DDT [31]. However, levels of *o*,*p*'-DDT above *p*,*p*'-DDT are measured in some sediment samples (sites M4, T2), which are much different from the composition of technical DDT. In China, dicofol has been widely used in agriculture since DDT usage was banned in 1983 [32]. This pesticide contains on average 11.4% o,p'-DDT and 1.7% p,p'-DDT [32]. Therefore, the high ratio of o,p'-DDT in sites M4, T2 could be traced to the agricultural use of dicofol in this area.

To estimate the possible sources of OCPs in the catchment, the contamination pattern was further studied. There was a significant positive correlation between the levels of  $\beta$ -HCH and  $\gamma$ -HCH (p < 0.01) in the sediments (see Table 4), suggesting that they had a

common source. This result indicated that lindane was more widely used than technical HCHs in the studied area. In this study, the significant correlation between o,p'-DDT and p,p'-DDE (p < 0.01), o,p'-DDT and p,p'-DDD (p < 0.05) indicated that p,p'-DDE and p,p'-DDD originated mainly from the degradation of o,p'-DDT. However, the positive correlation between p,p'-DDT and o,p'-DDT was weak, suggesting that p,p'-DDT and o,p'-DDT were derived from different sources. Additionally, positive correlation between  $\alpha$ -HCH,  $\gamma$ -HCH and o,p'-DDT might provide insight to the common sources from historical usage of technical OCPs.

#### 4. Conclusions

This work provided the first systemic data on the contamination status of OCPs in sediments from upper reach of Huaihe River, East China. Due to previous excessive agriculture application, industrial pollutant discharge and difficulty of degradation, there still exists a variety of OCPs residues in sediments in East China. The results indicate a wide occurrence of HCHs and DDTs in this area. The predominant species is  $\gamma$ -HCH among HCHs, p,p'-DDT among DDTs in sediments. The dominance of  $\gamma$ -HCH in the most sediments samples reflects the recent use of lindane. The high concentration of *p*,*p*′-DDT depicts that there is a recent input of technical DDT. In addition, the composition of DDTs in sediments reflects that there are fresh inputs of dicofol mixture in this region. The OCP distribution is influenced considerably by the characteristics of surface sediments from upper reach of Huaihe River. In comparison to published guidelines and previous studies, HCH levels are at relatively safe levels, while the residue of DDTs would pose an adverse biological effect in this catchment. The results also indicate that there exist certain potential health risks to drinking water consumers and organism in Huaihe River basin. Further work is needed to determine the bioaccumulation of POPs in the food web and the associated risks to the ecosystems and human health.

#### Acknowledgements

The research was supported by Key Scientific and Technological Project of Henan province, People's Republic of China (Grant No. 082102350023) and Basic and Front-line Technological Research Project of Henan province, People's Republic of China (Grant No. 102300410196).

#### References

- K.L. Willett, E.M. Ulrich, R.A. Hites, Differential toxicity and environmental fates of hexachlorocyclohexane isomers, Environ. Sci. Technol. 32 (1998) 2197–2207.
- [2] H. Nakata, M. Kawazoe, K. Arizono, S. Abe, T. Kitano, H. Shimada, W. Li, X. Ding, Organochlorine pesticides and polychlorinated biphenyl residues in foodstuffs and human tissues from China: status of contamination, historical trend, and human dietary exposure, Arch. Environ. Contam. Toxicol. 43 (2002) 473–480.
- [3] K.W. Chau, Characterization of transboundary POP contamination in aquatic ecosystems of Pearl River delta, Mar. Pollut. Bull. 51 (2005) 960–965.
- [4] R.Q. Yang, A.H. Lv, J.B. Shi, G.B. Jiang, The levels and distribution of organochlorine pesticides (OCPs) in sediments from the Haihe River, China, Chemosphere 61 (2005) 347–354.
- [5] T. Zoumis, A. Schmidt, L. Grigorova, W. Calmano, Contaminants in sediments: remobilisation and demobilization, Sci. Total Environ. 266 (2001) 195–202.
- [6] S. Tanabe, H. Iwata, R. Tatsukawa, Global contamination by persistent organochlorine and their ecotoxiological impact on marine mammals, Sci. Total Environ. 154 (1994) 163–177.
- [7] A. Sarkar, R. Nagarajan, S. Chaphadkar, S. Pal, S.Y.S. Singbal, Contamination of oraganochlorine pesticides in sediments from the Arabian Sea along the west coast of India, Water Res. 31 (1997) 195–200.
- [8] Y.F. Li, D.J. Cai, Z.J. Shan, L.Z. Zhu, Gridded usage inventories of technical hexachlorocyclohexane and lindane for China with 1/6° latitude by 1/4° longitude resolution, Arch. Environ. Contam. Toxicol. 41 (2001) 261–266.
- [9] G. Zhang, P. Andrew, H. Alan, B.X. Mai, Sendimentary records of DDT and HCH in
- the Pearl River Delta, South China, Environ. Sci. Technol. 36 (2002) 3671–3677. [10] X.H. Qiu, T. Zhu, J. Li, H.S. Pan, Organochlorine pesticides in the air around the
- Taihu Lake, China, Environ. Sci. Technol. 38 (2004) 1368-1374.
- [11] S. Tao, F.L. Xu, J. Wang, W.X. Liu, Z.M. Gong, J.Y. Fang, L.Z. Zhu, Y.M. Luo, Organochlorine pesticides in agriculture soil and vegetables from Tianjin, China, Environ. Sci. Technol. 39 (2005) 2494–2499.
- [12] Y. Qian, M. Zheng, B. Zhang, L. Gao, W. Liu, Determination and assessment of HCHs and DDTs residues in sediments from Lake Dongting, China, Environ. Monit. Assess. 116 (2006) 157–167.
- [13] N. Xue, X. Xu, Composition, distribution, and characterization of suspected endocrine-disrupting pesticides in Beijing Guan Ting Reservoir (GTR), Arch. Environ. Contam. Toxicol. 50 (2006) 463–473.
- [14] Z.W. Tang, Z.F. Yang, Z.Y. Shen, J.F. Niu, R.F. Liao, Distribution and sources of organochlorine pesticides in sediments from typical catchment of the Yangtze River, China, Arch. Environ. Contam. Toxicol. 53 (2007) 303–312.
- [15] H.Z. Wang, M.C. He, C.Y. Lin, X.C. Quan, W. Guo, Z.F. Yang, Monitoring and assessment of persistent organochlorine residues in sediments from the Daliaohe

River Watershed, Northeast of China, Environ. Monit. Assess. 133 (2007) 231-242.

- [16] Z.L. Zhang, J. Huang, G. Yu, H.S. Hong, Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China, Environ. Pollut. 130 (2004) 249–261.
- [17] R.B. Zhou, L.Z. Zhu, K. Yang, Y.Y. Chen, Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China, J. Hazard. Mater. 137 (2006) 68–75.
- [18] B.X. Mai, J.M. Fu, G.Y. Sheng, Y.H. Kang, L. Zheng, G. Zhang, Y.S. Min, E.Y. Zeng, Chlorinated and polycyclic aromatic hydrocarbons in riverine and esturine sediments from Pearl River Delta, China, Environ. Pollut. 117 (2002) 457– 474.
- [19] L.G. Chen, Y. Ran, B.S. Xing, B.X. Mai, J.H. He, X.G. Wei, J.M. Fu, G.Y. Sheng, Contents and sources of polycyclic aromatic hydrocarbons and organochlorine pesticides in vegetable soils of Guangzhou, China, Chemosphere 60 (2005) 879–890.
- [20] S. Xu, X. Jiang, Y. Dong, C. Sun, J. Feng, L. Wang, D. Martens, B.M. Gawlik, Polychlorinated organic compounds in Yangtse River sediments, Chemosphere 41 (2000) 1897–1903.
- [21] E.R. Long, L.G. Morgan, The potential for biological effects of sedimentsorbed contaminants tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52, National Oceanic and Atmospheric Administration, Seattle, WA, 1991, p. 175.
- [22] D. Persaud, R. Jaagumagi, A. Hayton, Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario, Water Resources Branch, Ontario Ministry of the Environment, Toronto, 1993, p. 27.
- [23] S.L. Smith, D.D. MacDonald, K.A. Keenleyside, C.G. Ingersoll, J. Field, A preliminary evaluation of sediment quality assessment values for freshwater ecosystems, J. Great Lakes Res. 22 (1996) 624–638.
- [24] D.D. MacDonald, C.G. Ingersoll, T.A. Berger, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems, Arch. Environ. Contam. Toxicol. 39 (2000) 20–31.
- [25] R. Yang, G. Jiang, Q. Zhou, C. Yuan, J. Shi, Occurrence and distribution of organochlorine pesticides (HCH and DDT) in sediments collected from East China Sea, Environ. Int. 31 (2005) 799–804.
- [26] K.T. Lee, S. Tanabe, C.H. Koh, Distribution of organochlorine pesticides in sediments from Kyeonggi Bay and nearby areas, Korea, Environ. Pollut. 114 (2001) 207–213.
- [27] R.A. Doong, C.K. Peng, Y.C. Sun, P.L. Liao, Composition and distribution of organochlorine pesticide residues in surface sediments from the Wu-Shi River estuary, Taiwan, Mar. Pollut, Bull. 45 (2002) 246–253.
- [28] K. Walker, D.A. Vallero, R.G. Lewis, Factors influencing the distribution of lindane and other hexachlorocyclohexanes in the environment, Environ. Sci. Technol. 33 (1999) 4373–4378.
- [29] Y.F. Li, D.J. Cai, A. Singh, Technical hexachlorocyclohexane use trends in China and their impact on the environment, Arch. Environ. Contam. Toxicol. 35 (1998) 688–697.
- [30] G.G. Pandit, S.K. Sahu, S. Sharma, V.D. Puranik, Distribution and fate of persistent organochlorine pesticides in coastal marine environment of Mumbai, Environ. Int, 32 (2006) 240–243.
- [31] R.L. Metcalf, A century of DDT, J. Agric. Food Chem. 21 (1973) 511-520.
- [32] X. Qiu, T. Zhu, B. Yao, J.X. Hu, S.W. Hu, Contribution of dicofol to the current DDT pollution in China, Environ. Sci. Technol. 39 (2005) 4385–4390.