



Residues of organochlorine pesticides (OCPs) in upper reach of the Huaihe River, East China

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ABSTRACT

Residues of HCHs and DDTs in surface water and suspended particulate matter (SPM) from upper reach of the Huaihe River, East China, were investigated. Levels of total HCHs (\sum HCH) and total DDTs (\sum DDT) in water detected by GC-ECD ranged from 0.85 to 12.77 ng L⁻¹ and from 3.54 to 33.59 ng L⁻¹, respectively. According to European and America water quality guidelines, HCHs were within safe levels while DDT would pose adverse biological effects. Distribution of OCPs in water indicated that input of tributaries was important factor for the Huaihe River. For OCPs in SPM, concentrations varied from 1.01 to 25.22 ng g⁻¹ for \sum HCH and not detected to 4.74 ng g⁻¹ for \sum DDT. Compared with sediment quality guidelines, HCHs and DDTs might have an ecological risk. The main reason for OCPs residues in the Huaihe River was usage of lindane and technical DDT. Furthermore, composition of DDTs reflected fresh inputs of dicofol mixture in some sites.

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1. Introduction

Organochlorine pesticides (OCPs) such as hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethane (DDTs) have been of great global concern because of their toxicity and environmental persistence. Due to their deleterious effect on nontarget organisms and biological accumulation via the food chain (Willett et al., 1998; Nakata et al., 2002; Chau 2005), OCPs pose great threats to ecosystems and human health. 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 (Tanabe et al., 1994; Sarkar et al., 1997). 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 four million tons between 1952 and 1984 (Li et al., 2001). Moreover, 3200 t of lindane (almost pure γ -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 (Zhang et al., 2002; Qiu et al., 2004; Tao et al., 2005). Extensive and continuous use of OCPs in China has resulted in ubiquitous OCPs pollution in various environmental matrixes (Nakata et al., 2002; Chau, 2005; Qian et al., 2006; Xue and Xu, 2006; Wang et al., 2007; Chen et al., 2011).

OCPs could be transported into aquatic environment (e.g., rivers or lakes) through runoff from non-point sources, atmospheric deposition, industrial discharge and other means. Due to their low water solubilities and high hydrophobicities, OCPs have a capacity of strong affinity for suspended particulate matter. Under favorable conditions, these contaminants could be released from suspended particulate matter into water and then pass onto people through consumption of drinking water, fish and agriculture food. Moreover, potential adverse biological effects on ecosystems of the OCPs might occur even with low dose of OCPs in an aquatic environment (Crisp et al., 1998). Therefore, more investigations on the OCP residues in an aquatic environment, such as water and SPM, are imperative and necessary.

The Huaihe River, one of the most important rivers in East China, flows 1000 km from the Tongbai Mountain to the Yangtze River and drains a populous area of 30,000 km². The upper reach of the Huaihe River locates in Henan province and flows across extensive agricultural regions where OCPs have been used extensively. In addition to being used for agriculture, the Huaihe River

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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 pollutants (POPs), has drawn a great concern from the public and government. So far, little information is available for OCPs contamination in the upper reach of the Huaihe River. Investigation on OCPs levels in water and SPM from upper reach of the 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 water and SPM from upper reach of the 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. Sample collection

The sampling sites are shown in Fig. 1. Total of sixteen sampling sites along upper reach of the Huaihe River and its tributaries and lakes were selected as such to cover the whole aquatic system in this basin. Among these sites, seven sites were located in the main stream, seven sites were located in the tributaries and two sites were located in lakes. The concurrent sampling of surface water and SPM were collected during two axial surveys on March 2007 and August 2007. This paper revealed OCPs residues in March (dry season). Another paper (as prepared) reported OCPs levels in August (flood season).

Surface water samples, 0.5 m below air–water interface, were collected with pre-cleaned 25 L containers using cylinder samplers. All samples were placed in the icebox after sampling, transported to the laboratory immediately, and stored in the refrigerator at 4 °C before analysis. All containers in contact with samples were previously rinsed with deionized water, acetone, dichloromethane and river water in sequence to eliminate interference with organic materials. After returning to the laboratory, SPMs were collected by filtering water sample through glass fiber filters (GF/F, 150 mm diameter, nominal pore size 0.7 μm, Whatman International Ltd., Maidstone, England). Then the GF/F filters were wrapped with aluminum foil and stored in double-layered plastic bags at –20 °C until analysis. The filtered water was then passed through a mixture resin (XAD-4 and XAD-2 1:1 mixture) glass column (400 mm × 25 mm i.d.) to retain dissolved organics.

2.2. Chemical reagents

Eight individual standards of OCPs including α -, β -, γ -, δ -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 α -, β -, γ -, δ -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 epoxide 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 of 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). Amberlite XAD resins (Supelco, Rohm and Haas Co., Spring House, PA, USA) were Soxhlet extracted sequentially using dichloromethane and methanol, and then stored in methanol. Glass fiber filter (GF/F, 150 mm diameter, nominal pore size 0.7 μm, Whatman, England) used to collect SPMs was pre-combusted at 450 °C for 4 h before using. Deionized water was produced by a Milli-Q system (Millipore Co., USA).

2.3. Extraction procedure

The procedure for eluting dissolved OCPs from XAD resins were as follows: Each of XAD resin column containing OCPs from water samples was eluted with 50 mL methanol followed by 50 mL dichloromethane. Afterwards, XAD resin was transferred into a glass flask and extracted with dichloromethane/methanol (v/v, 2:1) in an ultrasonic bath (3 × 100 mL). The extracts were combined and then liquid–liquid extracted three times with 50 mL saturated NaCl solution and 50 mL dichloromethane for removal residual methanol. After that, the dichloromethane fraction was extracted with deionized water to remove residual methanol and drained through a glass column containing 15 g of anhydrous sodium sulfate Na₂SO₄ to remove any residual water. Finally, the dichloromethane fraction was concentrated to 1–2 mL using a rotary evaporator, and subject to a solvent exchange to hexane.

The SPM-loaded glass fiber filters were Soxhlet-extracted for 48 h with 120 mL dichloromethane in a water bath maintained at 60 °C. Activated Cu was added for desulphurization. The extract for each sample was concentrated using a rotary evaporator and solvent-exchanged to hexane, and further reduced to approximately 1–2 mL by a gentle nitrogen stream.

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 35 mL hexane/dichloromethane (1:1, 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.

2.4. Instrumental analysis

OCPs was analyzed using a Hewlett–Packard 6890 gas chromatography with a ⁶³Ni 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

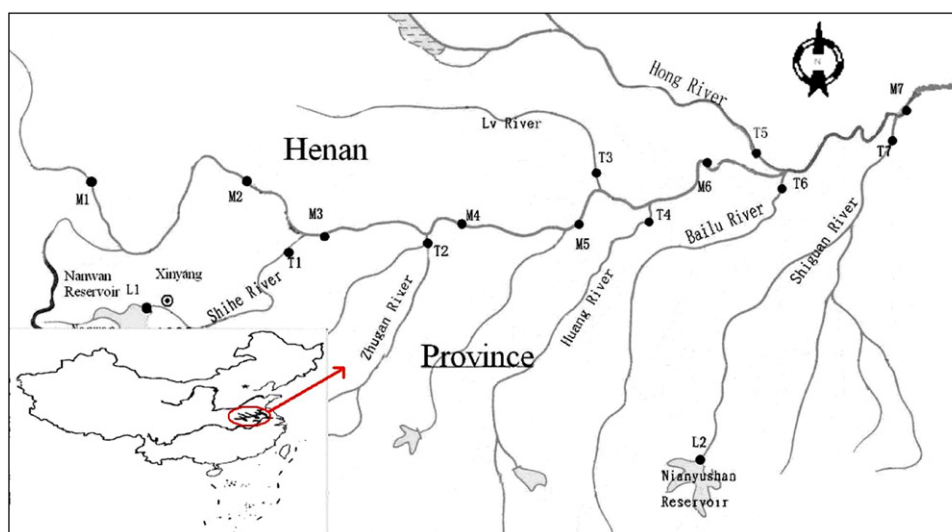


Fig. 1. Map of sampling sites. M—mainstream of the Huaihe River; T—tributaries in upper reach of the Huaihe River; L—Lakes in upper reach of the Huaihe River.

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–200 °C, then increasing at 1 °C/min–210 °C, 210 °C–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.

2.5. 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), average spiked recoveries and relative standard deviation (RSD) are listed in Table 1. The spiked recoveries of HCHs and DDTs in water and SPM were set in a range of 75.1–103.9 percent and 69.7–107.4 percent, respectively. The MDLs ranged from 0.03 to 0.05 ng L⁻¹ in water and from 0.01 to 0.03 ng g⁻¹ for SPM.

3. Results

3.1. Levels of OCPs in water

Residues of HCHs and DDTs were detected in surface water from upper reach of the Huaihe River, East China. Table 2 illustrated analysis results of water sample. The Kolmogorov–Smirnov (K–S)

Table 1
Mean recoveries, method detection limits (MDLs) and relative standard deviation (RSD) of OCPs in water and suspended particulate matter (SPM).

Pesticides	Surface water (n=6)			SPM (n=6)		
	Recovery (percent)	RSD (percent)	MDLs (ng L ⁻¹)	Recovery (percent)	RSD (percent)	MDLs (ng g ⁻¹)
α-HCH	100.2	8.2	0.04	105.4	7.4	0.02
β-HCH	92.3	6.9	0.05	95.2	9.3	0.01
γ-HCH	103.9	7.7	0.04	107.4	5.6	0.02
δ-HCH	93.1	5.6	0.03	89.8	4.7	0.03
p,p'-DDT	87.5	6.4	0.04	83.7	7.9	0.02
o,p'-DDT	99.8	8.3	0.04	103.2	6.5	0.02
p,p'-DDE	75.1	4.9	0.05	69.7	5.4	0.03
p,p'-DDD	98.5	7.6	0.05	97.2	8.3	0.03

Table 2
Levels of HCHs and DDTs (ng L⁻¹) in water from upper reach of the Huaihe River (M) and its tributaries (T) and nearby lakes (L) detected by GC-ECD.

Sampling	α-HCH	β-HCH	γ-HCH	δ-HCH	∑HCH	p,p'-DDE	p,p'-DDD	o,p'-DDT	p,p'-DDT	∑DDT
M-1	1.79	n.d.	1.84	0.42	4.05	0.68	0.97	0.77	2.64	5.06
M-2	1.04	n.d.	1.59	0.60	3.23	1.40	3.06	1.56	3.7	9.72
M-3	1.56	n.d.	3.77	0.80	6.13	2.32	1.99	9.94	19.34	33.59
M-4	1.26	0.15	2.00	0.60	4.01	1.37	0.79	0.59	2.72	5.47
M-5	0.24	n.d.	0.23	n.d.	0.47	0.45	1.32	0.62	2.05	4.44
M-6	1.16	0.07	1.56	0.48	3.27	1.09	2.66	0.68	2.59	7.02
M-7	2.09	0.15	1.75	0.46	4.45	3.86	3.62	1.13	10.41	19.02
Mean										
T-1	3.96	0.54	4.57	0.86	9.93	3.55	3.43	4.61	21.63	33.22
T-2	1.91	0.29	3.90	0.84	6.94	3.02	5.41	1.33	4.94	14.7
T-3	1.10	0.17	1.72	n.d.	2.99	6.18	1.25	1.17	7.86	16.46
T-4	0.72	n.d.	1.48	0.75	2.95	1.11	0.65	1.41	2.35	5.52
T-5	3.38	3.41	5.98	n.d.	12.77	7.95	3.33	4.76	6.98	23.02
T-6	0.79	0.07	1.25	0.48	2.59	1.69	1.51	1.25	2.32	6.77
T-7	0.40	n.d.	0.45	n.d.	0.85	0.55	1.46	0.81	2.67	5.49
Mean	1.75	0.64	2.76	0.42	5.57	3.44	2.43	2.19	6.96	15.02
L-1	0.40	n.d.	0.47	n.d.	0.87	0.33	0.62	0.56	2.03	3.54
L-2	1.08	n.d.	1.88	n.d.	2.96	1.06	1.19	0.87	3.74	6.86
Mean	0.74	n.d.	1.18	n.d.	1.92	0.70	0.90	0.72	2.88	5.20

Note: n.d., levels lower than detection limits; mean, reported as arithmetic means.

test was carried out to test the frequency distribution of OCPs data. The results indicated that all variables achieved a normal distribution with $P > 0.05$. Thus, arithmetic means are reported in Table 2. It can be seen from Table 2 that concentration of total HCHs (∑HCH, equivalent sum of α-+β-+γ-+δ-HCH) ranged from 0.85 to 12.77 ng L⁻¹, with the mean concentration of 4.29 ng L⁻¹. The highest ∑HCH level was detected at the site T5, located at the Hong River, a tributary of the Huaihe River. Residues of total DDTs (∑DDT, equivalent sum of p,p'-DDE+p,p'-DDD+o,p'-DDT+p,p'-DDT) in water varied from 3.54 to 33.59 ng L⁻¹ (average 12.49 ng L⁻¹). The highest ∑DDT concentration was observed at the mainstream of the Huaihe River, site M3. The results indicated that DDTs were the predominant contaminant in surface water from upper reach of the Huaihe River. As for HCHs residues, relatively low levels were observed compared to DDTs in water. The level of ∑DDT was higher than that of ∑HCH, consistent with previous studies on OCPs residues in water from the Huaihe River at the Jiangsu section (Wang et al., 2009).

To understand the status of HCHs and DDTs in the studied area, concentration variations of them were compared with other rivers in China as well as other rivers in the world. The levels of OCPs in water in the present study in comparison to those in other rivers around the world are shown in Table 3. As shown by Table 3, amongst the Chinese large rivers, the level of ∑HCH in water (0.47–6.13 ng L⁻¹) from upper reach of the Huaihe River ranked the lowest, with which only that from the Huaihe River at the Jiangsu section could be comparable (Wang et al., 2009). When compared with other rivers over the world, concentration of ∑HCH in water from upper reach of the Huaihe River was similar to that of Ebro River, Spain and less than that of other rivers (Fernández et al., 1999; Gollinopoulos et al., 2003; Singh et al., 2005; Turgut, 2003; Kaushik et al., 2008). As for DDT, residue of ∑DDT in water from upper reach of the Huaihe River was at a medium level among Chinese studied rivers, which was higher than that of the Yangtze River (Tang et al., 2008), the Pearl River (Yang et al., 2004), the Liaohe River (Gawlik et al., 2000) and the Huangpu River (Xia et al., 2006) but lower than that of the Haihe River (Wang et al., 2007), the Qiantang River (Zhou et al., 2008), the Minjiang River (Zhang et al., 2003), the Jiulong River (Zhang et al., 2001) and the Peacock River (Chen et al., 2011). In comparison with those reported for other rivers around the world, concentration of ∑DDT were at relatively low levels in water from

Table 3
Concentrations of HCHs and DDTs in surface water from rivers over the world.

Rivers	Sampling time	\sum HCH (ng L ⁻¹)	\sum DDT (ng L ⁻¹)	References
Yangtze River(W)	2005	0.55–28.07	n.d.~16.71 ^a	Tang et al. (2008)
Yangtze River(N)	1998	9.27–10.51	1.57–1.79	Jiang et al. (2000)
Yangtze River (headstream to estuary)	2007	0.11–13.68	n.d.~21.31	Liu et al. (2011)
Pearl River	2001	5.80–99.70	0.52–9.53	Yang et al. (2004)
Haihe River	2004	300–1070	n.d.~156 ^a	Wang et al.(2007)
Qiantang River	2005–2006	0.74–543.1	n.d.~204.1	Zhou et al. (2008)
Mingjiang River, China	1999	52.09–515	40.61–233.5	Zhang et al. (2003)
Tonghui River, Beijing, China	2002	70.12–992.60	18.79–663.70	Zhang et al. (2004)
Jiulong River, China	1999	31.95–129.9	19.24–96.64	Zhang et al. (2001)
Liaohe River, China	1998–1999	6.19–35.19	n.d.~5.24 ^a	Gawlik et al. (2000)
Peacock River, Xinjiang, China	2006	n.d.~19 ^a	n.d.~176 ^a	Chen et al. (2011)
Huangpu River, China	2003–2004	42.13–75.47	3.83–20.90	Xia et al. (2006)
The Huaihe River (Jiangsu section), China	2002–2003	1.10–7.50	4.45–78.87	Wang et al. (2009)
The Huaihe River(U)	2007	0.47–6.13	4.44–33.59	This study
Ebro River, Spain	1995–1996	3.38 ^b	3.40 ^b	Fernández et al. (1999)
Nestos River, Greek	1996–1998	n.d.~68.00 ^a	n.d.~64.00 ^a	Golfinoopoulos et al. (2003)
Giomti River, India	1996–1999	0.02–4846.00	0.20–4578.00	Singh et al. (2005)
Kucuk Menderes River, Turkey	2002–2003	187.00–337.00	72.00–120.00	Turgut (2003)
Yamuna River, India	1999	12.76–593.49	66.17–722.94	Kaushik et al. (2008)

^a n.d., levels lower than detection limits.

^b Mean values.

Table 4
Concentrations of HCHs and DDTs (ng g⁻¹) in suspended particulate matter from upper reach of the Huaihe River (M) and its tributaries (T) and nearby lakes (L) detected by GC-ECD.

Sampling	α -HCH	β -HCH	γ -HCH	δ -HCH	\sum HCH	<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	\sum DDT
M-1	1.57	n.d.	1.95	n.d.	3.52	0.07	0.1	n.d.	0.24	0.41
M-2	1.57	n.d.	1.94	n.d.	3.51	0.10	0.07	0.1	0.38	0.65
M-3	11.42	n.d.	13.80	n.d.	25.22	0.86	1.25	0.61	2.02	4.74
M-4	0.36	0.19	0.46	n.d.	1.01	n.d.	n.d.	n.d.	n.d.	n.d.
M-5	7.78	n.d.	9.53	n.d.	17.31	0.34	0.51	0.33	0.93	2.11
M-6	9.29	n.d.	13.35	n.d.	22.64	1.06	1.12	0.7	1.8	4.68
M-7	0.89	n.d.	1.12	n.d.	2.01	n.d.	n.d.	n.d.	n.d.	n.d.

Note: n.d., levels lower than detection limits.

upper reach of the Huaihe River (Fernández et al., 1999; Golfinoopoulos et al., 2003; Singh et al., 2005; Turgut, 2003; Kaushik et al., 2008).

3.2. Pollutions of OCPs in SPM

Levels of HCHs and DDTs in SPM from upper reach of the Huaihe River are summarized in Table 4. As shown by Table 4, the residues of HCHs and DDTs in SPM ranged from 1.01 to 25.22 ng g⁻¹ dw (mean 10.74 ng g⁻¹ dw) and from lower than detection limit to 4.74 ng g⁻¹ dw (mean 1.80 ng g⁻¹ dw), respectively. The highest concentrations of HCHs and DDTs in SPM were both found in site M3, which agreed with the concentration distribution in surface water. Other higher OCPs concentrations occurred in sites M5 and M6.

4. Discussion

4.1. Spatial distributions of OCPs in water

Spatial differences of OCPs residues in water from upper reach of the Huaihe River were investigated. Furthermore, a repeated measures one-way ANOVA procedure was performed to test the significant differences of OCPs levels among the mainstream, tributaries and lakes of the Huaihe River. The results indicated that there were no significant differences among these samples (at the significant level of 0.05).

Amongst these tributaries, the highest content of \sum HCH was recorded at site T5 (12.77 ng L⁻¹) located in the Hong River, followed by site T1 (9.93 ng L⁻¹) in the Shihe River. These two tributaries, the major rivers in the studied basin, flowed across regions of extensive agricultural activities where HCHs related pesticides had been once broad used (Wu et al., 1997). Due to their environmental persistence, OCPs could be still existing years after the ban or control over their usages in agricultural activities (Wu et al., 1999). Residues of OCPs would be washed away from soils due to soil eroding and variations of land use in the upstream of a watershed (Munn and Gruber, 1997). Therefore, relatively high levels of \sum HCH in these two tributaries might be mainly attributed for their wide applications over the past decades in this catchment. \sum DDT had a different distribution pattern in comparison to HCHs residues. The concentration listed in Table 1 showed that the Shihe River (T1), the Hong River (T5) and the Lv River (T3) were relatively heavily polluted with DDTs while the Huang River (T4) and the Shiguan River (T7) were much less polluted. This implied that different usage of technical DDT or various new inputs occurred in these tributaries.

Fig. 2 delineated the fluctuations of OCPs in the mainstream of the Huaihe River. As shown by Fig. 2, \sum DDT and \sum HCH have a similar distribution pattern. The highest concentrations of both \sum HCH and \sum DDT were observed at site M3, downstream of the confluence of the Huaihe River and the Shihe River (Fig. 2). This results indicated that the inputs of OCPs from Shihe River should be emphasized due to relatively high levels of \sum HCH and \sum DDT recorded at the Shihe River. In addition, another peak residues of \sum HCH and \sum DDT were found at M7, which was in agreement

with water quality of inflowing tributaries, i.e. the Hong River. Therefore, these results suggested that important reason for OCP residues in the mainstream of the Huaihe River could be the inputs of its tributaries.

4.2. Compositions and sources of OCPs in water

Composition differences of HCH isomers and DDT congeners in the environment could indicate varied sources of OCPs (Doong et al., 2002). In China, usage of technical HCH in agriculture has been officially restricted; however, it may probably be used in some region without interference of government. In addition, lindane has been used in agriculture, since 1990 (Li et al., 2001). Typical technical HCH contains 60–70 percent of α -HCH, 5–12 percent of β -HCH, 10–12 percent of γ -HCH and 6–10 percent of δ -HCH (Willett et al., 1998). Lindane consists of almost pure γ -HCH (> 99 percent). Amongst the isomers of HCHs, β -HCH is the most stable and relatively resistant to microbial

degradation due to low water solubility and vapor pressure (Lee et al., 2001). Also it should be noted that α -HCH and γ -HCH could be converted to β -HCH in the environment (Walker et al., 1999). Therefore, predominance of β -HCH could be observed in the environment if no fresh inputs of technical HCH while high percentage of γ -HCH recorded in some environmental samples reflected the recent use of lindane. Details of the HCH isomers in this study are plotted in Fig. 3. The average percentage of HCH isomers measured in water samples are α -HCH: 36.4 percent, β -HCH: 3.4 percent, γ -HCH: 51.1 percent, δ -HCH: 9.21 percent. Herein low percentage of β -HCH in water indicated that usage of HCHs could be continuous in this area. As seen from Fig. 3, a high percentage of γ -HCH, ranged from 39.3 percent to 63.5 percent, was recorded in sampling sites, which indicated that lindane may be used recently in upper reach of the Huaihe River. On the other hand, the ratio of α -HCH/ γ -HCH ranged from three to seven for technical HCH while low α -HCH/ γ -HCH ratio in samples implied the usage of lindane formulation (Li et al., 1998; Pandit et al., 2006). In the present study, low ratios of α -HCH/ γ -HCH (from 0.41 to 1.19, mean, 0.73) in sampling sites were detected. Therefore, the results suggested that there could be possible discharging sources of lindane at these sections.

The compositions of DDTs in water from upper reach of the Huaihe River were plotted in Fig. 4. As shown by Fig. 4, the average composition of DDT congeners detected in samples were *p,p'*-DDT (47 percent) > *p,p'*-DDD (20 percent) > *p,p'*-DDE (eighteen percent) > *o,p'*-DDT (fifteen percent) with the dominance of *p,p'*-DDT. Technical DDT generally contains 80–85 percent *p,p'*-DDT and 15–20 percent *o,p'*-DDT (Metcalf, 1973). If there was no new technical DDT input, the compositional percentage of DDT would decrease and that of the metabolites DDE+DDD would increase. Therefore, the ratio of (DDE+DDD)/ Σ DDT could be used as an indicator to identify if there was a recent input of technical DDT (Lee et al., 2001). High ratios of (DDE+DDD)/ Σ DDT (> 0.5)

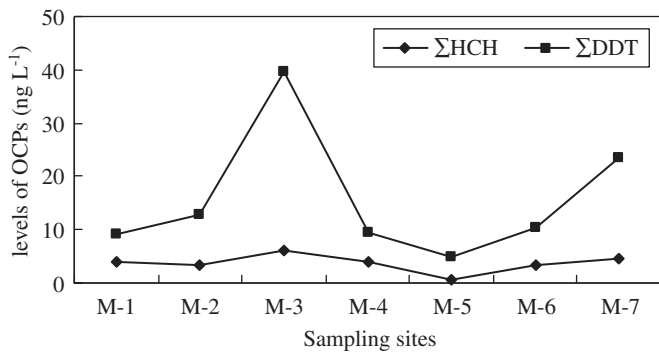


Fig. 2. Distribution of OCPs in water from upper reach of the Huaihe River.

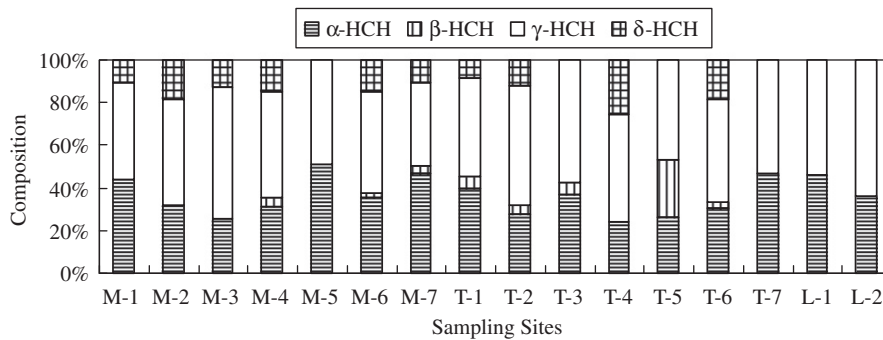


Fig. 3. Compositions of HCH isomers in water from upper reach of the Huaihe River.

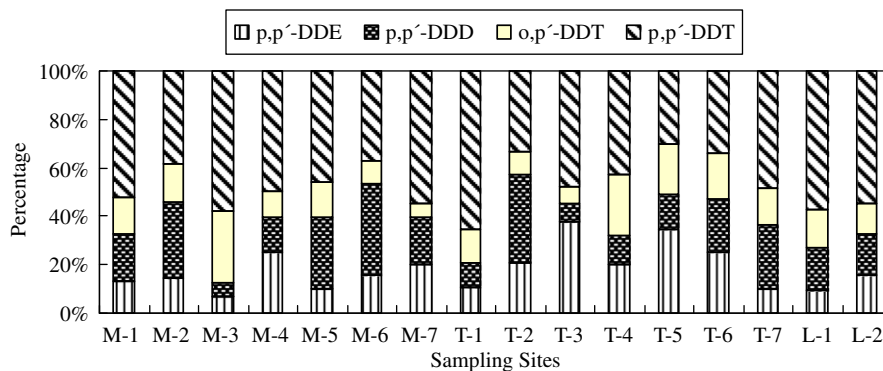


Fig. 4. Compositions of DDT congeners in water from upper reach of the Huaihe River.

could be thought to be subjected a long-term weathering while low ratios (< 0.5) suggest a recent input of technical DDT (Lee et al., 2001). In the present study, apart from M6 (0.53) and T2 (0.57), ratios of $(DDE+DDD)/\sum DDT$ were less than 0.5 in all sampling sites. The predominance of parent pollutants probably reflected a few potential ways of technical DDTs into water in the studied area. On the other hand, recently, o,p' -DDT/ p,p' -DDT was used to distinguish the DDTs pollution caused by technical DDTs from that by dicofol, which contained on average 11.4 percent o,p' -DDT and 1.7 percent p,p' -DDT (Qiu et al., 2005). Since, o,p' -DDT was more unstable than p,p' -DDT in the environment (Martijn et al., 1993), it was impossible that ratios of o,p' -DDT/ p,p' -DDT were higher than that of technical DDTs. However, the characteristic of “dicofol type DDTs contamination” was with a higher o,p' -DDT/ p,p' -DDT ratio than of technical DDTs. Generally, o,p' -DDT/ p,p' -DDT ranged from 0.2 to 0.3 in technical DDTs and from 1.3 to 9.3 or higher in dicofol (Qiu et al., 2005). In this study, ratios of o,p' -DDT/ p,p' -DDT ranged from 0.11 to 0.69. The value in nine samples with ratio < 0.3 showed that source of technical DDTs, and that in seven samples with the ratio between 1.3 and 0.3 indicated the mixed pollution source of technical DDT and dicofol. As a result, DDTs pollution in the surface water from upper reach of the Huaihe River not only came from the residue of technical DDT in the environment but also from the input of dicofol impurity.

4.3. Compositions and sources of OCPs in SPM

Compositions of HCHs isomers in SPM were plotted in Fig. 5. As seen from Fig. 5, a high percentage of γ -HCH, ranged from 45.5 percent to 59.0 percent, was recorded in sampling sites, which indicated that lindane may be used recently in the studied area. In addition, low ratios of α -HCH/ γ -HCH (from 0.70 to 0.83) in sampling sites were detected. Therefore, the results suggested that there could be possible discharging sources of lindane at these sections. Details of DDTs, as shown in Fig. 6, varied significantly with locations across this catchment. The ratio of DDD/DDE, above 1.0 for all SPM samples, reflected that biodegradation of DDTs was predominant under anaerobic condition. Ratios of $(DDE+DDD)/\sum DDTs$ varying from 0.26 to 0.47 (average is 0.40), suggested that a recent input of technical DDT. Moreover, ratios of o,p' -DDT/ p,p' -DDT ranged from 0.00 to 0.39 for SPM samples, which indicated the mixed pollution source of technical DDT and dicofol in some sites. Therefore, the results indicated that there probably existed new OCPs input of lindane, technical DDTs and dicofol into the river.

4.4. Potential ecosystem risk assessment

According to some water quality guidelines, the potential risk of HCHs and DDTs in water from upper reach of the Huaihe River was evaluated. Results from this study showed that the concentrations of HCHs and DDTs in water from all sampling sites were less than the environment quality standard for surface water (GB3838-2002), which was set up by State Environment Protection Agency of China (SEPA) ($< 1000 \text{ ng L}^{-1}$ for Lindane and $< 2000 \text{ ng L}^{-1}$ for $\sum DDT$) (SEPA (State Environment Protection Agency of China) 2002). Based on the guideline recommended by USEPA (2002), the Criteria Maximum Concentration (CMC) of γ -HCH in surface water should be 950 ng L^{-1} . Level of γ -HCH in all samples from upper reach of the Huaihe River was within the required range of the guideline. This revealed that HCHs residues in water at this basin could be considered within the safe levels. With 1.0 ng L^{-1} of p,p' -DDT as the Criterion Continuous Concentration (CCC) recommended by USEPA (2002), all sites loading p,p' -DDT above this guideline were investigated, which was considered to pose adverse effects on eco-systems and human health. With 20 ng L^{-1} of HCHs as the environmental quality standard applicable to surface water (2000/60/EC) set up by European Union, levels of HCHs in all samples were within the required range of the standard, while that of DDTs in some samples (M3 and T1) were slightly higher than the guideline (25 ng L^{-1}). Therefore, the results indicated that HCHs in water from upper reach of the Huaihe River were within safe levels but DDT residues might have an ecological risk.

Compared with some published sediment quality guidelines (SQGs) (Long and Morgan, 1991; Persaud et al., 1993; Smith et al., 1996; MacDonald et al., 2000), potential environmental risk of OCPs residues in SPM was evaluated. The comparison between OCPs concentrations in SPM from upper reach of the Huaihe River and SQGs was listed in Table 5. It could be concluded from Table 5 that concentrations of $\sum HCH$ exceeded the probable effect level (PEL; above which adverse effects are expected to occur frequently) in all samples. In the case of γ -HCH, a few sites (M3, M6) had higher levels than severe effect level (SEL; above which is anticipated to have significant adverse impacts on benthic resources). Therefore, there is a potential risk for human health and these sites should be paid close attention to. As for DDT, residues of $\sum DDT$ in this study exceeded the effect range low (ERL; below which adverse biological effects are rarely observed) at some sampling sites (M3, M5, M6) but were all below the effect range median (ERM; above this level adverse biological effects are frequently observed)(Table 3). Moreover, sum

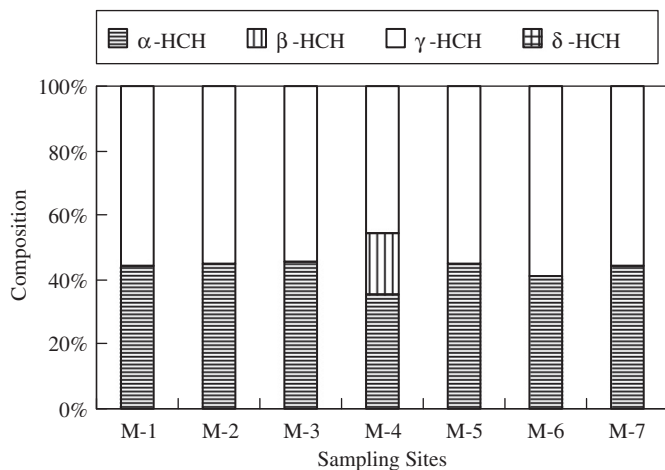


Fig. 5. Compositions of HCH isomers in suspended particulate matter from upper reach of the Huaihe River.

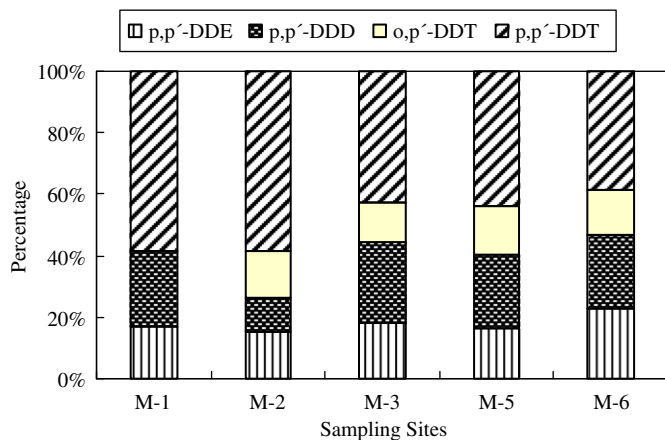


Fig. 6. Compositions of DDT congeners in suspended particulate matter from upper reach of the Huaihe River.

Table 5Comparison between OCP levels in this study and sediment concentrations as guideline values (ng g^{-1} dw).

Chemicals	OCPs in SPM	TECs				PECS			
		TEL	LEL	ERL	CB-TEC	PEL	SEL	ERM	CB-PEC
<i>p,p'</i> -DDD	n.d.~1.25	3.54	8	2	4.88	8.51	60	20	28.0
<i>p,p'</i> -DDE	n.d.~1.06	1.42	5	2.2	3.16	6.75	190	27	31.3
<i>p,p'</i> -DDT and <i>o,p'</i> -DDT	n.d.~2.63	–	–	1	4.16	–	710	7	62.9
Σ DDT	n.d.~4.74	3.89	7	1.58	5.28	51.7	120	46.1	572
γ -HCH	0.46–13.80	0.94	3	–	2.37	1.38	10	–	4.99
α -HCH	0.36–11.42	–	6	–	–	–	–	–	–
Σ HCH	1.01–25.22	0.32	–	–	–	0.99	–	–	–

Note. TECs, threshold effect concentrations; PECS, probable effect concentrations; TEL, threshold effect level; PEL, probable effect level (Smith et al., 1996); LEL, lowest effect level; SEL, severe effect level (Persaud et al., 1993); ERL, effect range low; ERM, effect range median (Long and Morgan, 1991); CB-TEC, consensus-based TEC; CB-PEC, consensus-based PEC (MacDonald et al., 2000) Level of OCPs in sediments expressed as range (average). n.d., levels lower than detection limit.

DDT levels (*p,p'*-DDT and *o,p'*-DDT) above ERL were also found in these sampling sites. Based on these results, it was concluded that DDTs in this studied area had adverse biological effects.

5. Conclusions

Comprehensive surveys and experimental analysis of organochlorine pesticides in surface water and suspended particulate matter (SPM) from upper reach of the Huaihe River were conducted in this study. Results showed that although residues of the OCP in water were lower than the corresponding concentration levels in China's related standards, adverse effects on human health and eco-systems should be concerned. In comparison to other rivers across China, the lowest level of HCHs and medium level of DDTs in water were observed at this typical section in the Huaihe River. Risk assessment and comparison with some published sediment quality guidelines indicated contamination of OCPs in SPM were not too severe in this area while some sites should be paid closer attention to because HCHs levels surpassed severe effect level (SEL) and DDTs residues were above effect range low (ERL). Ratios of HCHs isomers and DDTs in environmental matrix indicated there probably existed new OCPs input of lindane, technical DDTs and dicofol into the river in some sites. Meanwhile, inflows of its tributaries could be one of the important contributors to the existence of OCP residues in the upper reach of the Huaihe River. Further work is needed to determine the bioaccumulation of POPs in the food web and the associated risks to the ecosystems and human health.

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