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

Jinglan Feng[a], Mengxiao Zhai[a], Qun Liu[b], Jianhui Sun[a,*], Jiajia Guo[a]

[a] *College of Chemistry and Environmental Sciences, Henan Normal University, Key Laboratory of Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Key Laboratory for Environmental Pollution Control, Xinxiang, Henan 453007, PR China*

[b] *State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, PR 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.

## 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 km$^2$. 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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[*] Corresponding author. Fax: +86 373 3326336.
*E-mail addresses:* fengjl1123@yahoo.com.cn (J. Feng), zhaimengxiao@126.com (M. Zhai), ldqun@yahoo.com.cn (Q. Liu), sunjh_hj@yahoo.com.cn (J. Sun).

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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 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 of analytical grade and redistilled 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 $Na_2SO_4$ 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 $^{63}$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

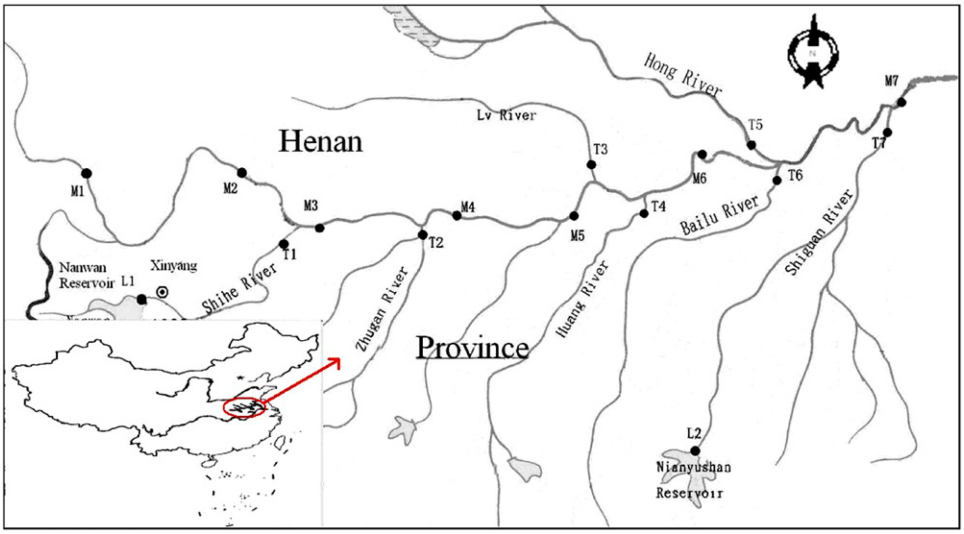

**Fig. 1.** Map of sampling sites. M—mainstream of the Huaihe River; T—tributaries in upper reach of the Huaihe River; L—Lakes in upper reach of the Huaihe River.