

# Perfluorinated compounds and organochlorine pesticides in soils around Huaihe River: a heavily contaminated watershed in Central China

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**Abstract** Perfluorinated compounds (PFCs) and organochlorine pesticides (OCPs) were analyzed in surface soils along the Huaihe River. Sixteen target PFCs and nine OCPs were quantified in soils from a region of intensive industrial and agricultural development. Concentrations of PFCs and OCPs ranged from less than the limit of detection (LOD) to 1.22 ng/g and 3.63 to 227 ng/g, respectively. Contamination by OCPs was more serious than that of PFCs, which was consistent with the fact that OCPs were widely used in agriculture of the district while there was no known production or application of PFCs in the study area. The predominant PFCs in soils were PFOA and PFOS with concentrations that ranged from <LOD to 0.20 ng/g and <LOD to 0.21 ng/g, respectively. Among the three groups of OCPs, average concentrations of HCHs, DDTs, and HCB were 4.7, 23.7, and 1.4 ng/g, respectively. Results of principal component analysis revealed relatively weak associations between concentrations of PFCs and those of OCPs, while concentrations of OCPs exhibited similar patterns of distributions. Among the mainstream and five tributaries, the highest concentrations of PFCs were observed along the Pihe River, while the highest concentrations of OCPs occurred along the Xifeihe River. In general, concentrations of PFCs were evenly

distributed, while those of OCPs exhibited relatively greater spatial differences.

**Keywords** PFCs · OCPs · Soil · Land use · Watershed · Huaihe River

## Introduction

Two classes of persistent organic pollutants (POPs), current-use perfluorinated compounds (PFCs) and past-use organochlorine pesticides (OCPs), have received great attention due to their bioaccumulation, persistence, toxicity, and potential for long-range transport. PFCs have been widely used as processing additives during the production of fluoro-polymers and as surfactants in consumer applications, such as surface coatings for carpets, furniture, and paper products (Giesy and Kannan 2001). China began large-scale production of perfluorooctane sulfonate (PFOS) since 2003. Before 2004, the total production of PFOS in China was less than 50 tons, whereas in 2006, 15 Chinese enterprises produced a total of more than 200 tons of perfluorooctane sulfonylfluoride, of which 100 tons were exported (Bao et al. 2009). PFCs, regarded as emerging contaminants, should receive long-term and continuous monitoring and assessment so as to better manage such POPs.

OCPs were widely used to control pests and thus improve crop yields until the official ban in 1983. From the 1950s to 1980s, productions of hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) in China were over 4.9 million tons and 0.4 million tons, accounting for 33 and 20 % of the total world production, respectively (Wang et al. 2007). Furthermore, OCPs (such as HCH and DDT) accounted for about 80 % of the total pesticides produced (Wei et al. 2007). Although the application of OCPs has been forbidden for decades, residues continue to affect the environment.

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PFCs and OCPs in soil can transport through volatilization, diffusion, leaching, and mass flow transfer to atmosphere, surface water, and groundwater. They can go through the biological concentration and accumulate through the food chain to cause adverse effects on wildlife and humans. After years of their ban, residues of POPs are still emitting from soil, which results in soil switching from a major sink to a secondary emission source (Aigner et al. 1998; Finizio et al. 1998; Cai et al. 2008). Therefore, the issue of adverse impacts on ecosystem and human health as well as secondary release of PFCs and OCPs from soil is still of long-term public concerns.

The Huaihe River, located between the Yellow River and Yangtze River in Central China, flows through a populous area of 270,000 km<sup>2</sup>. With the rapid development of township industry, the watershed has become more and more vulnerable to organic pollutants. There have been many serious pollution accidents along the Huaihe River since 1975, causing severe losses on nearby industry, agriculture, and fishery (Huang et al. 2008). A series of reports on cancer villages around the Huaihe River have led the state to study the relationship between environmental pollution and human health, including the contamination by POPs. Recently, attention from the government and researchers has focused primarily on OCPs in surface water and sediment around the Huaihe River (Huang et al. 2006; Wang et al. 2009a; Sun et al. 2010; Feng et al. 2011). Little attention has been given to PFCs in this area to date. In addition to the agricultural nonpoint sources, the papermaking, chemical, leather, and other heavy-pollution industries are still the leading industries throughout this area. As the middle segment of the Huaihe River, the Anhui reach receives pollutants from local industrial and agricultural activities, as well as inflows from upstream. However, little information is available for PFC and OCP contamination in the Anhui reach of the Huaihe River so far.

The objectives of this study were to determine the concentrations and distribution of PFCs and OCPs in soils, thereby to identify potential sources and provide information for future management and soil remediation. Very few studies have reported PFCs in soil (Kannan 2011), and this is one of those very few studies. This study presented the first investigation on the spatial distribution and sources analysis of PFCs and OCPs in soils around the Huaihe River.

## Materials and methods

### Sample collection

The Anhui reach of the Huaihe River flows through six streams, with a catchment area of 66,900 km<sup>2</sup>. Geographically from west to east, tributaries flowing into Huaihe River are Yinghe River, Pihe River, Xifeihe River, Dongfeihe River,

and Wohe River. Among the five tributaries, the Yinghe River is the longest with a catchment area of 36,700 km<sup>2</sup>. The major crops grown in this region are rice, wheat, corn, soybean, rape, and cotton. Textile, household appliances, steel, cement, and fertilizer are the major industries distributed along the Huaihe River (Anhui Bureau of Statistics 2010). The soil in the Huaihe watershed is of mortar black soil and mainly composes of clay (Anhui Agricultural College 1980). This type of soil contains about 1 % organic matter, which slows the degradation of POPs. Eighteen soil samples were collected along the rivers in October 2008 (Fig. 1).

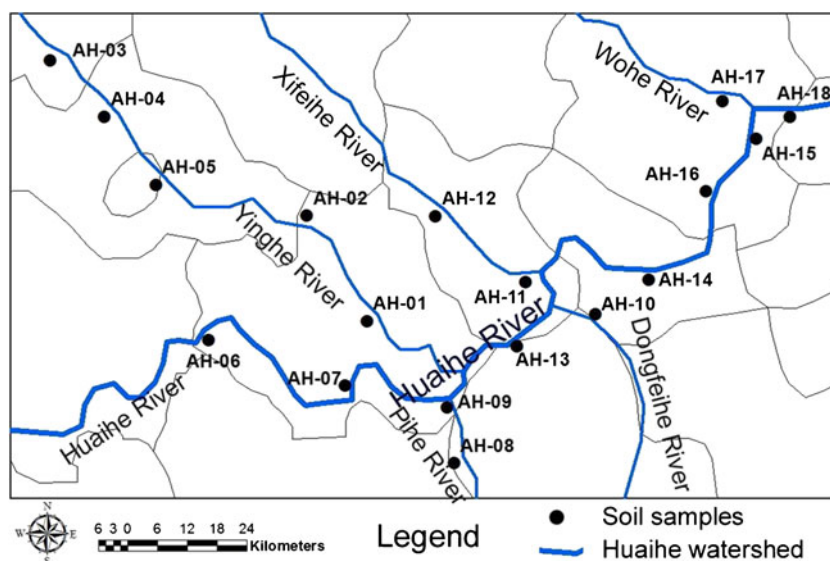
Surface (top 1–10 cm) soils were collected using a clean methanol rinsed stainless steel trowel. Every representative sample was prepared by mixing five sub-samples from the area of about 5 × 5 m<sup>2</sup>. Wet soil samples were transported to the laboratory in polyethylene zip-lock bags, air-dried, sieved through a 2-mm mesh, and stored at 4 °C in pre-cleaned glass jars until further analysis.

### PFCs analysis

Extraction of PFCs was accomplished using a method similar to previously described method (Higgins et al. 2005). Briefly, 2.5 g of sample was transferred to a 50-mL PP tube, and then moistened by 2 mL Milli-Q water with vortexing. One milliliter of 0.5 M tetrabutylammonium hydrogensulfate, 2 mL of 25 mM sodium acetate, and 100 µL of 100 ng/mL internal standards were added for extraction by vortexing. Subsequently, 5 mL of methyl tert-butyl ether (MTBE) was added and shaken for 20 min. After centrifuging for 20 min at 3,500 rpm, the supernatant MTBE was collected. This process was repeated twice resulting in a final volume of 15 mL MTBE wash. The solution was evaporated to 0.5 mL under a gentle flow of high-purity nitrogen, then filtered through a 0.2-µm nylon filter, and transferred into a 1.5-mL PP snap top vial with polyethylene cap.

A HP 1200 high-performance liquid chromatography system by Agilent Technologies was used for separating of all target analytes. An aliquant of 2 mM ammonium acetate was used as an ionization aid and methanol as mobile phase. The temperature of the column was kept constant at 35 °C. Mass spectra were collected using an Applied Biosystems SCIEX 3000 (Foster City, CA) tandem mass spectrometer, fitted with an electrospray ionization source, operated in negative ionization mode. Chromatograms were recorded using a multiple reaction monitoring mode with a dwell time of 40 ms. The following instrument parameters were used: desolvation temperature (450 °C), desolvation (curtain) gas 6.0 arbitrary units (AU); nebulizer gas flow 5 AU; ion spray voltage 3500 V; and collision gas 12 AU. The optimal settings for collision energies and declustering potential were determined for the transitions of each analyte.

**Fig. 1** Soil sampling area and sites in the Huaihe watershed, China



### OCPs analysis

Soils were extracted based upon the method that was employed by Wang et al. (2009b). Each sample weighing 5.0 g was mixed with 1 g anhydrous sodium sulfate, and spiked with 1 mL of 2,4,5,6-tetrachloro-*m*-xylene. The mixture was extracted twice with 35 mL of hexane/dichloromethane (1:1, *v/v*), followed by ultrasonication and centrifugation. The supernatant was concentrated to approximately 2 mL by rotary evaporation, and further purified with solid phase extraction (6 mL, Supelco) cartridges loaded with 1 g silica gel and 1 g anhydrous sodium sulfate. Elution was performed with 20 mL of hexane/dichloromethane (7:3, *v/v*) and concentrated to a final volume of 1 mL for quantification of OCPs.

An Agilent 6890 gas chromatography equipped a  $^{63}\text{Ni}$  electron capture detector (Agilent Technology Co., Santa Clara, CA) was used for analysis. The purified extract was analyzed under splitless injection mode with ultra-pure nitrogen as the carrier gas and the make-up gas. The injector and detector temperatures were 220 and 300 °C, respectively. The oven temperature was initially set at 100 °C with a 2-min hold, ramped at 10 °C/min to 160 °C with a 2-min hold, 4 °C/min to 230 °C with a 5-min hold, 10 °C/min to 270 °C with a 2-min hold. The OCPs were identified by retention time matched to standards and were quantified based on peak area.

### Quality control and quality assurance

For quality assurance and quality control, procedural blanks and matrixes spiked with the standard solution were analyzed. Concentrations of all target PFCs and OCPs in all field and laboratory blanks were lower than the limit of detection (LOD), where the LOD was defined as three times

of signal-to-noise ratio. Recoveries of PFCs were determined in the range from  $75 \pm 8$  to  $107 \pm 12$  %, and LOD was from 0.03 to 0.30 ng/g. For OCPs, the recoveries ranged from  $78.1 \pm 5.6$  to  $93.0 \pm 4.9$  %, and LOD was from 0.05 to 0.24 ng/g (Table 1).

## Results and discussion

### Concentrations of PFCs and OCPs

Concentrations of PFCs were generally less than their respective LODs. Although 16 PFCs were investigated, only 11 PFCs were detected. The concentrations of perfluorocarboxylates (PFCAs) ranged from n.d. to 0.64 ng/g, and the concentrations of perfluorosulfonates (PFASAs) ranged from n.d. to 0.74 ng/g (Table 2). Among the precursors of PFASAs, only N-EtFOSE (0.32 ng/g) in AH-15 was detected. Rates of detection of PFPeA (27.8 %), PFOA (55.6 %), PFNA (33.3 %), and PFOS (33.3 %) were relatively large, which might be due to the relatively wide distribution. Although the LODs of PFBA (0.21 ng/g), PFHpA (0.24 ng/g), and PFHxS (0.3 ng/g) were larger, these PFCs could be detected with maximum concentrations of 0.47, 0.40, and 0.55 ng/g, respectively. The fact that LODs of PFDA (0.09 ng/g) and PFBS (0.09 ng/g) and their detection rates were lower indicated that the region was less polluted by PFDA and PFBS. The results obtained in the present study were compared with those of previous studies conducted in other areas (Table 3) (Li et al. 2010; Pan et al. 2011; Wang et al. 2011a; Wang et al. 2011b; Wang et al. 2012a). Concentrations measured in this study were lower than those observed in other areas, especially Shanghai. This might be due to different levels of industrialization. Guanting Reservoir, Tianjin, and North Bohai Sea are located in the Bohai

**Table 1** The detection limit and recovery of PFCs and OCPs

|  | LOD (ng/g) | Recovery (%) | Detection rate <sup>a</sup> (%) |
|--|------------|--------------|---------------------------------|
| Perfluorobutanoic acid (C4, PFBA)                          | 0.21       | 76±7         | 3 (16.7)                        |
| Perfluoropentanoic acid (C5, PFPeA)                        | 0.03       | 94±11        | 5 (27.8)                        |
| Perfluorohexanoic acid (C6, PFHxA)                         | 0.09       | 83±5         | 0 (0)                           |
| Perfluoroheptanoic acid (C7, PFHpA)                        | 0.24       | 96±10        | 1 (5.6)                         |
| Perfluorooctanoic acid (C8, PFOA)                          | 0.11       | 89±3         | 10 (55.6)                       |
| Perfluorononanoic acid (C9, PFNA)                          | 0.09       | 92±5         | 6 (33.3)                        |
| Perfluorodecanoic acid (C10, PFDA)                         | 0.09       | 86±4         | 2 (11.1)                        |
| Perfluoroundecanoic acid (C11, PFUDA)                      | 0.15       | 88±8         | 0 (0)                           |
| Perfluorododecanoic acid (C12, PFDoA)                      | 0.09       | 92±7         | 0 (0)                           |
| Perfluorobutane sulfonate (C4, PFBS)                       | 0.09       | 76±9         | 3 (16.7)                        |
| Perfluorohexane sulfonate (C6, PFHxS)                      | 0.30       | 94±8         | 2 (11.1)                        |
| Perfluorooctane sulfonate (C8, PFOS)                       | 0.09       | 97±9         | 6 (33.3)                        |
| Perfluorodecane sulfonate (C10, PFDS)                      | 0.21       | 95±11        | 2 (11.1)                        |
| 2-N-ethylperfluoro-1-octanesulfonamido-ethanol (N-EtFOSE)  | 0.24       | 85±6         | 1 (5.6)                         |
| 2-N-methylperfluoro-1-octanesulfonamido-ethanol (N-MeFOSE) | 0.27       | 75±8         | 0 (0)                           |
| Perfluoro-1-octanesulfonamide (FOSAA)                      | 0.10       | 107±12       | 0 (0)                           |
| α-HCH  | 0.15       | 82.2±7.0     | 4 (22.2)                        |
| β-HCH  | 0.20       | 81.4±9.2     | 18 (100)                        |
| γ-HCH  | 0.05       | 83.9±5.3     | 7 (38.9)                        |
| δ-HCH  | 0.05       | 89.8±5.7     | 1 (5.6)                         |
| <i>p,p'</i> -DDE   | 0.10       | 93.0±4.9     | 11 (6.1)                        |
| <i>p,p'</i> -DDD   | 0.20       | 87.1±9.2     | 5 (27.8)                        |
| <i>o,p'</i> -DDT   | 0.10       | 89.7±1.3     | 1 (5.6)                         |
| <i>p,p'</i> -DDT   | 0.10       | 91.9±2.8     | 11 (61.1)                       |
| HCB  | 0.24       | 78.1±5.6     | 18 (100)                        |

<sup>a</sup> number of samples detected and % - occurrence in parenthesis given

economic circle, and Shanghai is one of the most economically developed regions. The Anhui reach of the Huaihe River is less developed than other regions cited in the present study. The observed results are similar to previously reported results (Wang et al. 2012b), which showed the relationship between concentrations of PFCs and the level of industrialization.

HCHs (α+β+γ+δ-HCH), DDTs (*p,p'*-DDE + *p,p'*-DDD + *o,p'*-DDT + *p,p'*-DDT) and HCB are three groups of OCPs that were detected in this study. Results of OCPs in soils from the Anhui reach of the Huaihe River were summarized (Table 2). The mean concentrations of HCHs, DDTs, and HCB constituted 15.7, 79.8, and 4.5 % of the total OCPs contents in soil samples, respectively. Among the three classes OCPs, HCHs, and HCB were detected in all samples, and the detection rate of DDTs was 77.8 %. Concentrations of OCPs in soils observed in the present study were similar to those in other rivers (Table 4) (Zhang et al. 2005; Wang et al. 2007; Ma et al. 2008; Tao et al. 2008; Hu et al. 2011). Concentrations of HCHs in soils from the studied area were relatively high with a mean of 4.46 ng/g. This value was comparable to concentrations in soils from the Yangtze River Delta and Pearl River

Delta, which had a mean of 3.2g and 4.42 ng/g, respectively. Concentrations of DDTs observed in soils in the present study were relatively moderate, with a mean of 23.69 ng/g. Concentrations of HCHs and DDTs in soils from northern China were lower than those from southern China, which was probably caused by the types of crops in different regions (Li et al. 2001). In general, concentrations of DDTs were higher than those of HCHs in soils from the Chinese watersheds. This may be due to the differences in physicochemical and biochemical properties, wherein DDTs have lower water solubility, vapor pressure, and biodegradability, and greater affinity for lipids as compared to the HCHs (Nhan et al. 2001). DDTs tend to remain in the soils longer than HCHs.

#### Distribution of PFCs and OCPs

There was no significant difference among concentrations of PFCs along the Huaihe River and its tributaries (Fig 2). Mean concentrations of PFCs were 0.66 ng/g (Pihe River), 0.65 ng/g (Yinghe River), 0.62 ng/g (Wohe River), 0.43 ng/g (Huaihe River), 0.34 ng/g (Dongfeihe River), and 0.28 ng/g (Xifeihe River). Site AH-08 was the only site located along the Pihe

**Table 2** Concentrations of PFCs and OCPs

|                  | Minimum | Maximum | Mean | Median |
|------------------|---------|---------|------|--------|
| PFBA             | n.d.    | 0.47    | 0.07 | n.d.   |
| PFPeA            | n.d.    | 0.29    | 0.07 | n.d.   |
| PFHpA            | n.d.    | 0.40    | 0.02 | n.d.   |
| PFOA             | n.d.    | 0.20    | 0.08 | 0.12   |
| PFNA             | n.d.    | 0.17    | 0.04 | n.d.   |
| PFDA             | n.d.    | 0.13    | 0.01 | n.d.   |
| PFCAs            | n.d.    | 0.64    | 0.30 | 0.28   |
| PFBS             | n.d.    | 0.22    | 0.03 | n.d.   |
| PFHxS            | n.d.    | 0.55    | 0.06 | n.d.   |
| PFOS             | n.d.    | 0.21    | 0.05 | n.d.   |
| PFDS             | n.d.    | 0.51    | 0.05 | n.d.   |
| PFSAs            | n.d.    | 0.74    | 0.20 | 0.13   |
| N-EtFOSE         | n.d.    | 0.32    | 0.02 | n.d.   |
| PFCs             | n.d.    | 1.22    | 0.51 | 0.49   |
| $\alpha$ -HCH    | 0.43    | 1.74    | 0.20 | n.d.   |
| $\beta$ -HCH     | 1.51    | 11.4    | 4.04 | 3.32   |
| $\gamma$ -HCH    | n.d.    | 1.72    | 0.34 | n.d.   |
| $\delta$ -HCH    | n.d.    | 1.80    | 0.10 | n.d.   |
| HCHs             | 1.51    | 14.0    | 4.69 | 3.32   |
| <i>p,p'</i> -DDE | n.d.    | 126     | 11.1 | 0.66   |
| <i>p,p'</i> -DDD | n.d.    | 73.1    | 6.23 | n.d.   |
| <i>o,p'</i> -DDT | n.d.    | 7.46    | 0.41 | n.d.   |
| <i>p,p'</i> -DDT | n.d.    | 45.2    | 5.95 | 2.98   |
| DDTs             | n.d.    | 211     | 23.7 | 4.20   |
| HCB              | 0.34    | 4.40    | 1.35 | 0.98   |
| OCPs             | 3.63    | 227     | 29.7 | 8.40   |

River, where there was rubbish dump. Along the Yinghe River, PFCs in soils at site AH-01 (1.22 ng/g) were highest, which might be due to the chemical plants nearby. Meanwhile, due to the southeast flow of the Yinghe River and local southeast and northwest prevailing wind, the Yinghe River had higher PFC concentrations under the effect of atmospheric dry and wet deposition. Subject to the local industrial park, which operates packaging, textile, rubber, and fluorine materials, site AH-17 along the Wohe River and sites AH-15, 16, 18 along the Huaihe River had higher concentrations of PFCs.

**Table 3** Comparison of PFCs concentrations in soils from the studied areas in China

*n.d.* levels lower than the detection limits

| Location                | Sampling time | PFOS        | PFOA       | PFCs        | References        |
|-------------------------|---------------|-------------|------------|-------------|-------------------|
| Huaihe River            | 2008          | n.d.–0.21   | n.d.–0.20  | n.d.–1.22   | This study        |
| Guanting Reservoir      | 2008          | n.d.–0.86   | n.d.–2.8   | 0.13–8.5    | Wang et al. 2011a |
| North Bohai Sea         | 2008          | n.d.–0.702  | n.d.–0.473 | n.d.–1.72   | Wang et al. 2011b |
| Tianjin Binhai New Area | 2008          | n.d.–9.4    | n.d.–0.93  | 1.3–11      | Wang et al. 2012a |
| Tianjin                 | 2008          | 0.99 (mean) | n.d.–0.51  | 0.02–2.36   | Pan et al. 2011   |
| Shanghai                | 2007          | 8.58–10.4   | 3.28–47.5  | 14.41–63.62 | Li et al. 2010    |

There was no significant fluctuation in loading of OCPs in soils along the Huaihe River apart from the Yinghe River and Xifeihe River (Fig. 3). The primary contributors to the higher concentrations of OCPs along the Yinghe River and Xifeihe River were AH-03 and AH-11, respectively. AH-03 and AH-11 had similar characters, such as polluted river irrigation. Among the three groups of OCPs, at AH-03 and AH-11, concentrations of DDTs (211 and 146 ng/g, respectively) were the highest. A ratio of DDT/(DDE+DDD)<1 in AH-03 (0.3) and AH-11 (0.1) indicated that there were no new source of DDTs (Meijer et al. 2001). During our investigation, we learned that there was a pesticide factory in the past at AH-03, which led to the high residues nearby. Meanwhile, we found that there were high incidences of cancers among the local residents, mainly the esophagus and stomach cancers, which might be related to the high OCPs in this area as OCPs have been proved to be carcinogenic, teratogenic, and mutagenic. More detailed studies are essential to prove the relationship between high incidences of cancer and high residues of OCPs.

Compositions and sources of PFCs and OCPs

Patterns of relative concentrations of PFCs were distinct among locations (Fig. 2). Apart from site AH-02 and AH-12, other sites had different concentrations of PFCs. At these locations, compositions of PFCs were simple with at most four quantifiable PFCs at any location. Rates of detection were 55.6 % for PFOA and 33.3 % for PFOS, which were greater than those of other PFCs. The compositions of PFOA (11.6 to 47.7 %) and PFOS (13.6 to 52.3 %) at their detected locations revealed great differences in both absolute and relative concentrations among the locations. PFCs in soils partly come from the transformation of their precursors in air such as fluorotelomer alcohol and atmospherically oxidative products and perfluoroalkyl sulfonamide. Furthermore, some PFCs existing in house and street dust could also be absorbed by soil and contribute to their levels in soils (Li et al. 2010). In general, each PFC showed a relatively balanced distribution, which suggested their different sources.

Differences in isomeric composition of HCH or DDT could indicate different sources. Typical technical HCH contains 60–70 %  $\alpha$ -HCH, 5–12 %  $\beta$ -HCH, 10–15 %  $\gamma$ -HCH, and

**Table 4** Comparison of OCPs concentrations in soils from the studied Chinese watersheds

| Watersheds          | Sampling time | HCHs       | Mean  | DDTs        | Mean  | References        |
|---------------------|---------------|------------|-------|-------------|-------|-------------------|
| Huaihe River        | 2008          | 1.51–14    | 4.69  | n.d.–211    | 23.69 | This study        |
| Yangtze River Delta | 2004          | n.d.–99    | 3.2   | n.d.–600    | 88.8  | Hu et al. 2011    |
| Guanting Reservoir  | 2003          | n.d.–8.96  | 0.56  | n.d.–94.07  | 5.11  | Zhang et al. 2005 |
| Haihe River         | 2004          | 0.02–349   | 0.44  | 0.40–2,350  | 8.68  | Tao et al. 2008   |
| Taihu Lake          | 2004          | 0.73–60.97 | 24.06 | 3.10–166.55 | 57.04 | Wang et al. 2007  |
| Pearl River Delta   | 2005          | 0.19–42.3  | 4.42  | 3.58–831    | 82.1  | Ma et al. 2008    |

*n.d.* levels lower than the detection limits

6–10 %  $\delta$ -HCH, respectively (Sun et al. 2010). The predominance of  $\alpha$ -HCH in some soils is consistent with the recent use of technical HCH. In this study, mean compositions of HCHs in soils were  $\alpha$ -HCH, 4.3 %;  $\beta$ -HCH, 86.2 %;  $\gamma$ -HCH, 7.3 %; and  $\delta$ -HCH, 2.2 % (Fig. 4a). Concentrations of  $\beta$ -HCH were highest among HCHs in soils at all sites. Since  $\alpha$ -HCH and  $\gamma$ -HCH can be converted to  $\beta$ -HCH through aging (Lee et al. 2001), the present HCHs were thought to be a result of historical input or long-range transport. Alternatively, the ratio of  $\alpha$ -HCH/ $\gamma$ -HCH ranged from 3 to 7 for technical HCH, while the  $\gamma$ -HCH content in lindane is over 99 % (Walker et al. 1999). The lower ratio of  $\alpha$ -HCH/ $\gamma$ -HCH observed in soils during the present study ( $\alpha$ -HCH/ $\gamma$ -HCH in AH-04, 07, 08, 09, 12 was zero) implied the usage of lindane. It has been reported that  $3.2 \times 10^3$  tons of lindane were used in China between 1991 and 2000 and about 5 % used in Anhui (Li et al. 2001). Therefore, it could be concluded that lindane may be used recently in the Anhui reach of the Huaihe River.

Technical DDT generally contains 75 % *p,p'*-DDT, 15 % *o,p'*-DDT, 5 % *p,p'*-DDE, and <5 % *p,p'*-DDD (Pandit et al. 2006). The average composition of DDTs detected in soils are *p,p'*-DDE (46.9 %) > *p,p'*-DDD (26.3 %) > *p,p'*-DDT (25.1 %) > *o,p'*-DDT (1.7 %; Fig. 4b). However, *p,p'*-DDT was the predominant DDT in soils from most locations, which is due to the

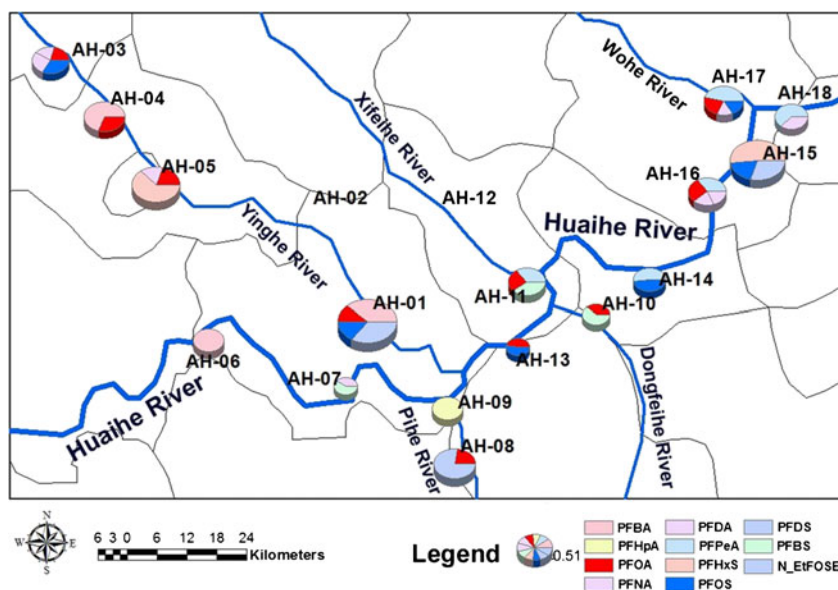
slow degradation of technical DDT. DDT can be biodegraded to DDE under aerobic conditions and to DDD under anaerobic conditions, while the ratio of DDT/(DDD+DDE) is indicative of possible sources (Bossi et al. 1992). The ratio of DDT/(DDD +DDE) > 1 in AH-01, 02, 12, 13, 14, 15, 16 suggested a recent input of technical DDTs or slow degradation.

Although production of HCB has ceased in most countries, it is still being inadvertently produced as a by-product and/or impurity in several chemical processes, such as the manufacture of chlorinated solvents, chlorinated aromatics, and pesticides. It is also released to the environment by incomplete combustion, and from old dumpsites (Barber et al. 2005). In this study, HCB was detected in soils at all sites, which suggested that HCB was derived from nonpoint sources, mainly incomplete combustion. The global mean background concentration of HCB in soil is 0.68 ng/g (Meijer et al. 2003), while the mean concentration of HCB in soils along the Huaihe River was twice at 1.35 ng/g.

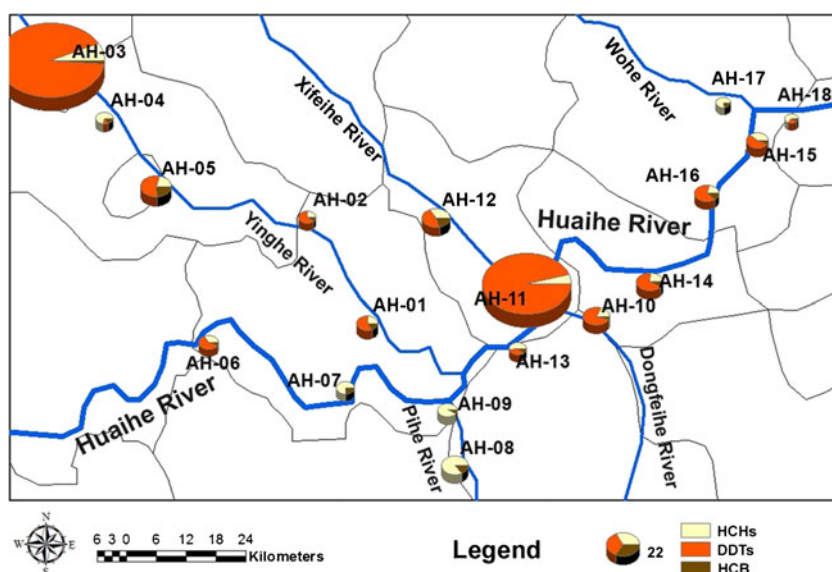
Relationship between contaminants and land use

Samples were grouped according to the soil cover into woodland (*n*=3), fallow (*n*=3), wheat land (*n*=8), and vegetable land (*n*=4; Fig. 5). The mean concentrations of HCHs and

**Fig. 2** Spatial distribution and relative contributions of individual PFCs in soils along the Huaihe River

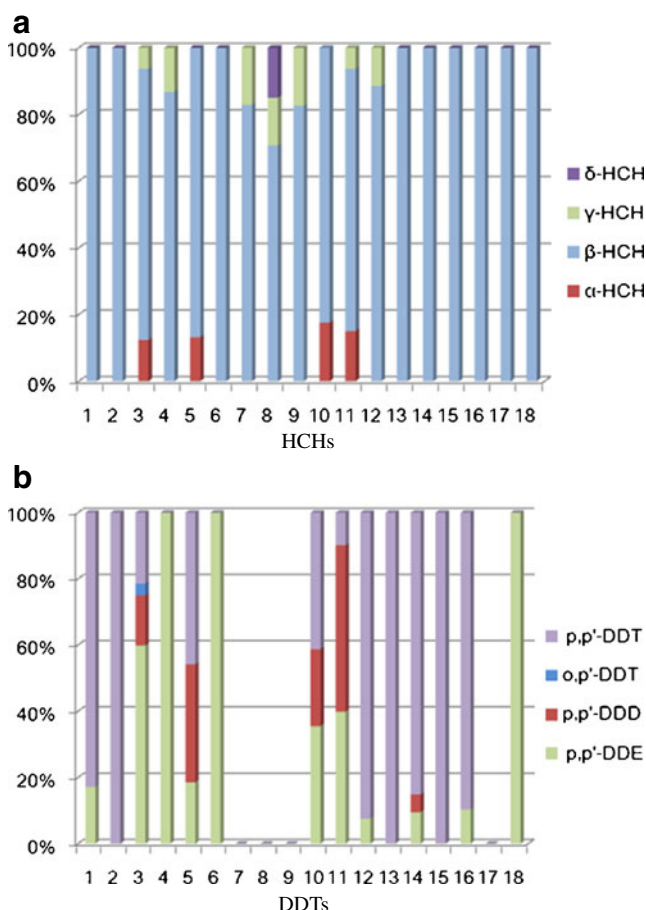


**Fig. 3** Spatial distribution and relative contributions of individual OCPs in the soils along the Huaihe River

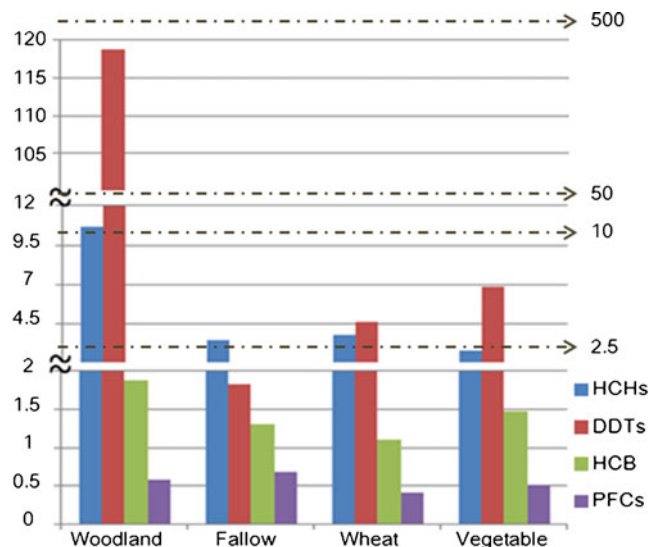


DDTs were generally greater than those of HCB or PFCs. Concentrations of HCB and PFCs were lower than 2 and 1 ng/g, respectively, which indicated a relatively uniform distribution of these residues. Concentrations of the OCPs

varied with different land uses as follows: woodland > vegetable land > wheat land > fallow. When compared with results of a study conducted in Hong Kong (Zhang et al. 2006), concentrations of OCPs in soils from farmland, which had a mean of 6.53 ng/g for HCHs and 1.85 ng/g for DDTs, were higher than those from woodland, where generally lower concentrations of OCPs were due to the local non-agricultural development, mainly industrial development. In the Tianjin Binhai New Area, concentrations of OCPs in farmland, mainly vegetable crops, were 65.6 ng/g for HCHs and 624 ng/g for DDTs, which were higher than those in woodland (Wang et al. 2009c). In the Taihu Lake region, concentrations of HCHs



**Fig. 4** Percentage composition of HCHs and DDTs in the soils along the Huaihe River



**Fig. 5** Concentrations of PFCs and OCPs in the soils under different land use types and comparison with the target value for OCPs set by China and Netherlands (2.5 ng/g: the value of DDTs and HCB for unpolluted soil, Netherlands; 10 ng/g: the value of HCHs for unpolluted soil, Netherlands; 50 ng/g: the first value of HCHs and DDTs, China; 500 ng/g: the second value of HCHs and DDTs, China)

in woodland (2.94 ng/g) were lower than those in paddy fields (28.53 ng/g), whereas concentrations of DDTs in woodland (90.25 ng/g) were greater than those in paddy fields (50.23 ng/g) (Wang et al. 2007). It could be concluded that the concentrations of DDTs and HCHs in woodland were generally lower than those in farmland among these studies, while the concentrations of DDTs and HCHs in woodland soils in the present study were higher than those in farmland soils, including those used to grow vegetables and wheat. The result suggested that OCPs were largely used to control the pests and disease. Although there were woodlands in these locations along the Huaihe River, these were very young shelter forests. Much of the land along Huaihe River is currently farmland, and it is not possible to determine whether this had been woodland in the past. Therefore, these lands possibly were used to grow crops and amounts of OCPs were used, or OCPs might also be used to prevent the woodland from pests before the banning. Moreover, woodland soils tended to remain stable and non-ploughed, while farmland was subject to plough and rotation, which could speed up the degradation of OCPs. Concentrations of HCB and PFCs were uniform, which is consistent with the conclusion that emissions of HCB and PFCs were not closely related to land use. It is due to the HCB source of incomplete combustion and industrial sources of HCB and PFCs.

According to national environmental quality standards for soil in China (Science and Technology Department of State Environmental Protection Administration 1995), concentrations of HCHs in all soil samples in the present study were lower than the first quality level, while concentrations of DDTs were generally lower than the first quality level except for the concentration in woodland soils, which was between the first and second level.

In terms of the soil protection guideline of Netherlands (Netherlands Ministry of Housing, NMX 2000), concentrations of HCHs were generally lower than the target value for unpolluted soil (<10 ng/g) except for the concentration of HCHs in woodland soils, which was 10.68 ng/g. Concentrations of DDTs were generally greater than the value for unpolluted soil (<2.5 ng/g) except for the concentration in fallow soils. Concentrations of HCB in all soils were lower than the target value of HCB (<2.5 ng/g) for unpolluted soil. It implied that further soil remediation is required at certain locations in order to improve soil quality with respect to the OCPs, especially DDTs. In addition, more detailed research, such as the analysis of soil profiles and intensive sampling around the target locations, is required to determine the depth and scale of remediation. Soil characteristics are also needed to identify the specific methods of remediation.

### Principal component analysis

PCA was applied to examine the distribution of OCPs and PFCs among sampling sites (Skrbic and Durisic-Mladenovic 2007). When the first two axes of the ordination function are plotted, data with similar characteristics lie close together,

while those with dissimilar characteristics fall far apart (Vanwijngaarden et al. 1995). A plot of all the chemical variables against their values for axes  $X$  and  $Y$  represents PC1 (accounting for 31.42 % of total variance) and PC2 (accounting for 14.15 % of total variance), respectively (Fig. 6). It can be seen that HCHs and DDTs dominated the  $X$ -axis, and PFCs were closer to the  $Y$ -axis. Along the  $X$ -axis,  $\beta$ -HCH and HCHs distributed closely above the  $Y$ -axis, while DDT congeners and OCPs surrounded together under the  $Y$ -axis. It implied that  $\beta$ -HCH contributed greatly to HCHs, while DDTs contributed greatly to OCPs. Along the  $Y$ -axis, there were mainly PFCs, loosely arranged. It is also noted that PFOS and PFOA were closely distributed, indicating their similar source.

### Conclusions

Soil samples were collected to analyze PFCs and OCPs along the Anhui reach of the Huaihe River. The study provided systematic data on the contamination status of PFCs and OCPs, and indicated that contamination by OCPs was more serious than that of PFCs. Among the 16 investigated PFCs, 11 PFCs were detected, predominantly PFOS and PFOA. Concentrations of PFCs ranged from <LOD to 1.22 ng/g, which were lower than other studied regions in China. PFCs were evenly distributed along the Huaihe mainstream and other five tributaries due to the non-point source of application.

OCPs were widely distributed with relatively higher concentrations than that of other studied watersheds in China. Average concentrations of OCPs were 29.7 ng/g, with 4.69 ng/g for HCHs, 23.7 ng/g for DDTs, and 1.35 ng/g for HCB, respectively. HCHs and DDTs mainly derived from past agricultural application, with little current emission. HCB showed different spatial distribution due to the non-point source. In terms of the different types of land use, concentrations of OCPs in woodland were highest, followed by farmland, including wheat and vegetable land. Compared

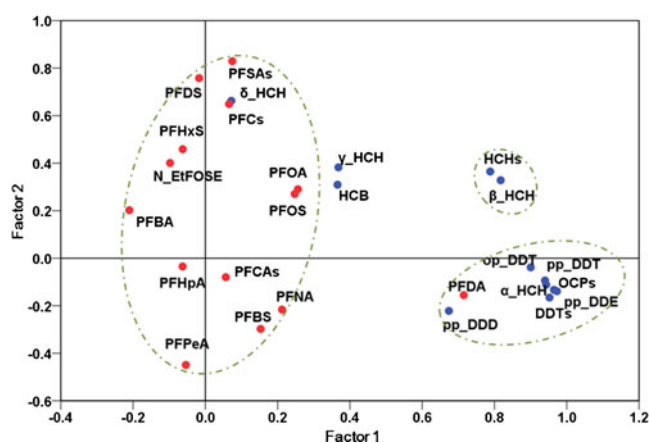


Fig. 6 Plot of principal component analysis for PFCs and OCPs



with soil environmental quality standards, concentrations of HCHs and DDTs at certain locations exceeded standard values, indicating a need for soil remediation. Further work is needed to determine the fate and risks of PFCs and OCPs in soils.

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