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# Residues of HCHs and DDTs in Soils and Sediments of Preconstructing Urban Wetland

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**Abstract** Residues of hexachlorohexanes isomers (HCHs) and dichlorodiphenyltrichloroethane and metabolites (DDTs) in the soils and sediments of Dayanghan Wetland in Wuhu, China were investigated. The concentrations of ΣHCH in soils and sediments averaged 1.35 and 3.77 μg/kg with the predominance of $\beta$-HCH and $\delta$-HCH, respectively. The concentrations of ΣDDT in soils and sediments averaged of 7.80 and 2.80 μg/kg, respectively, with the dominance of *o, p′*-DDT. The concentrations of HCHs in the soils and sediments and DDTs in the sediments were categorized as no pollution, but the level of DDTs in the soils was classified as low pollution.

**Keywords** HCHs · DDTs · Soils and sediments · Dayanghan Wetland

Organochlorine pesticides (OCPs) such as hexachlorocyclohexane (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) have drawn great concern from environmental scientists and the public as a result of their large production and usage, chronic toxicity, persistence, bioaccumulation, endocrine disrupting effects and long-range transport toxicity (Willett et al. 1998). They were widely used as insecticides around the world before the 1970s because of their low cost and high insecticidal efficacy. Although the production and usage of most of HCHs and DDTs were officially banned and their residue levels in the environment have considerably declined in the past years, some HCHs and DDTs are currently used in developing countries or are present as residues of previous usage, which is still a major global pollution problem (Wu et al. 1999). Soil and sediment are important reservoirs of HCHs and DDTs and more than 70 % of DDTs in the environment is partitioned into the soil compartment (Wania and Mackay 1995), which result in high levels of these pesticides in soils and sediments (Mai et al. 2002; Meijer et al. 2003; Chen et al. 2005; Gao et al. 2008). Soils and sediments play an important role in the global fate and distribution of HCHs and DDTs and have been identified as a sink for these toxic chemicals, from which they can be released into water or air (Meijer et al. 2003). A full understanding of the fate of HCHs and DDTs requires knowledge of their concentrations and distributions in the soils and sediments of all major ecological zones.

Urban wetlands, a complex social–economic–natural ecosystem, are known to play an important role in the habitat of numerous species, environmental management and public recreation (Jia et al. 2011). Most of urban wetlands are changed from natural wetlands, which are usually used as agricultural land, and thereby large amount of HCHs and DDTs may have been intensively used in history and resided in the soils and sediments of urban wetlands. Consequently, it is necessary to investigate the remained levels of HCHs and DDTs in soils and sediments of urban wetland before construction and assess their potential environmental risk. Nonetheless, so far no research had focus on the residues of organochlorine pesticides in the soils and sediments of urban wetland before construction. Therefore, Dayanghan Wetland was selected as a case study on the concentrations, compositions and distributions of HCHs and DDTs remained in the soils and sediments of preconstructing urban wetland in the this study. Also, the environmental risk of HCHs and DDTs in the soils and sediments of Dayanghan Wetland was assessed.

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## Materials and Methods

Dayanghan Wetland is located the Yangtze River Delta, (31°22′209″N, 118°25′145″E), with an area of 10.8 $km^2$, and is the largest wetland in the suburbs of Wuhu city, China. It is mainly comprised of pound, river, bottomland and reclaimed rice paddy, vegetable land and woodland and is an important production base for foodstuff. With the rapid urbanization and industrialization, it has been planned to construct an urban wetland park. Samples were collected from the soils and sediments of Dayanghan Wetland in March, 2011. The sampling sites are shown in Fig. 1. In total, 30 surface samples (top 0–20 cm) including 10 sediment samples and 20 soil samples from different types of land use patters such as woodland, vegetable land, farmland and bottomland were collected and each sample consisted of 5 sub-samples. After sampling, the soil samples were kept at −18°C in dark and a portion was freeze-dried for further analysis. A globe position system (GPS) was used to locate the sampling positions.

Sample extraction, separation and analysis of HCHs and DDTs were detailed elsewhere (Chen et al. 2005; Mai et al. 2002). Briefly, the frozen soil samples were smashed to small pieces and freeze-dried for 24 h, pulverized and sieved through a 100-meshed stainless steel mesh. 2, 4, 5, 6-tetrachloro-*m*-xylene (TMX) and decachlorobiphenyl (PCB 209) were added as surrogate standards and the spiked samples were Soxhlet-extracted for 72 h with redistilled dichloromethane. Then the extract was concentrated and solvent-exchanged to hexane and further reduced to approximately 1 mL under a gentle nitrogen stream. A 1:2 alumina/silica gel column was used to purify and fractionate the extract. An appropriate amount of pentachloronitrobenzene (PCNB) was added as an internal standard prior to instrument analysis. After extraction and separation, HCHs and DDTs were measured using a HP-6890 GC equipped with a $^{63}Ni$ electron capture detector (ECD) and a HP-5 (30 m × 0.32 mm i.d., 0.25 μm film thickness) fused silica capillary column. Nitrogen was used as carrier gas at 1.5 mL/min. The chromatographic temperature program was programmed initially at 80°C, holding for 0.5 min, increasing to 180°C at 10°C/min, then to 280°C at 3°C/min, and then to 310°C at 10°C/min and holding for 15 min. Injector and detector temperature was maintained at 280 and 315°C, respectively. Identification of HCHs and DDTs was confirmed using GC-MSD system on SIM mode with GC conditions identical to those used for GC-ECD analysis.

Quantification for both HCHs and DDTs was performed using the internal calibration method based on five-point calibration curve for individual component. A DDT degradation check solution was analyzed daily to examine the extent of degradation of DDT, which had to be less than 15 % before sample analysis could be initiated. Method blanks (solvent), duplicate samples and spiked blanks (standards spiked into solvent) were analyzed. No HCHs and DDTs were detected in method blank samples. The relative standard deviations (RSDs) were less than 10 % after 10 replicate analysis of a standard mixture. The

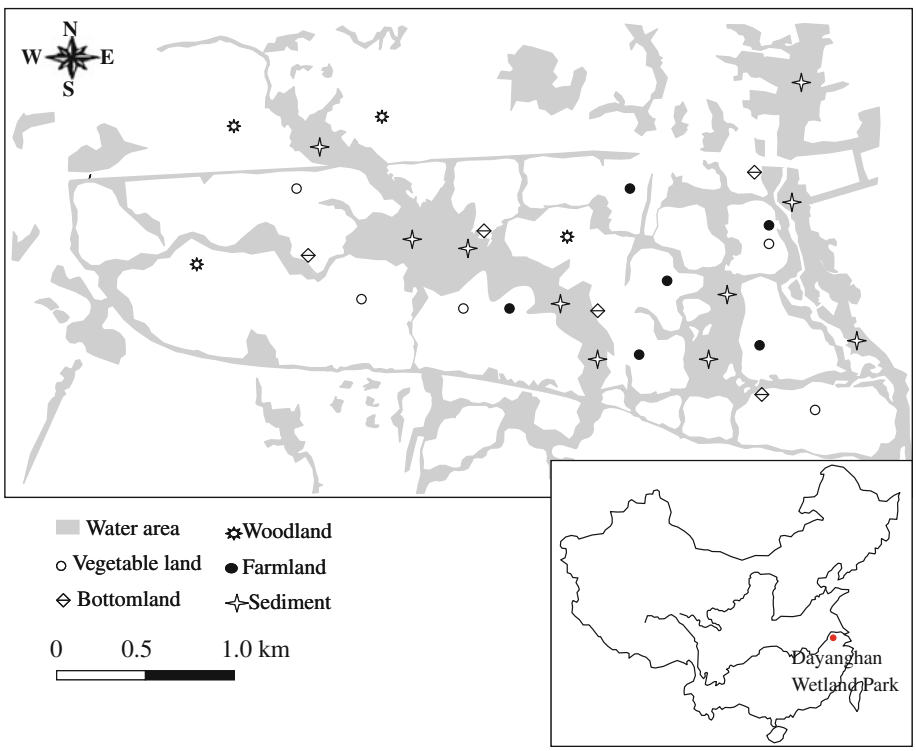


**Fig. 1** The map of sampling sites of Dayanghan Wetland

recovery for HCH and DDT standards were between 67 % and 112 % and the recovery ratios for the surrogates in the samples ranged from 74 % to 118 %. The concentrations of HCHs and DDTs were corrected for the recovery ratios for the surrogates. The method detection limits (MDL) defined as three times the noise level ranges from 0.01 to 0.15 μg/kg for HCHs and DDTs.

## Results and Discussion

Analysis results showed that four HCH isomers and two DDT isomers and their four metabolites were found in samples. As shown in Table 1, four HCHs, o,*p*′-DDT, o,*p*′-DDE and *p*,*p*′-DDE were detected in all soil and sediment samples, but lower detection frequency was found for *p*,*p*′-DDT (20 %), o,*p*′-DDD (86.7 %) and *p*,*p*′-DDD (33.3 %). *β*-HCH was the most abundant HCH in soils and shared 43 % of total HCH, while *δ*-HCH predominated in the HCH isomers in sediments and had a share of 33 % of total HCH. Among DDT and its metabolites, *o, p*′-DDT dominated, accounting for 70.6 % and 44.6 % of the total DDT in soils and sediments, respectively.

The concentrations of ΣHCH in soils and sediments ranged from 0.66 to 3.71 μg/kg and from 2.22 to 6.60 μg/kg with means of 1.35 and 3.77 μg/kg, respectively, while the concentrations of ΣDDT ranged from 2.15 to 24.61 μg/kg and from 1.88 to 3.75 μg/kg with means of 7.80 and 2.80 μg/kg, respectively. Compared with earlier records in other area around the middle and lower reaches of Yangtze River, such as the survey results from the arable soils of Yangtze River Delta region, Shanghai, Taihu Lake region and Xixi Wetland Park during 2000s (Table 2), a sharp decline of HCH and DDT residues in soils has been

**Table 1** Concentrations of HCHs and DDTs in soils and sediments of Dayanghan Wetland

| OCPs | Detection frequency (%) | Concentrations (μg/kg) | | Reference values | |
|---|---|---|---|---|---|
| | | Soils | Sediments | Soils[a] | Sediments[b] |
| α-HCH | 100 | 0.32 (0.17–0.79) | 0.96 (0.69–1.66) | 2.5 | 6 |
| *β*-HCH | 100 | 0.58 (0.14–2.20) | 0.72 (0.12–1.57) | 1 | 5 |
| *γ*-HCH | 100 | 0.14 (0.02–0.31) | 0.82 (0.34–1.40) | 0.5 | 3 |
| *δ*-HCH | 100 | 0.31 (0.18–0.46) | 1.26 (0.53–1.98) | – | – |
| ΣHCH | 100 | 1.35 (0.66–3.71) | 3.77 (2.22–6.60) | 10 | – |
| *o*,*p*′-DDT | 100 | 5.80 (1.50–21.45) | 1.22 (0.70–1.47) | – | 8[c] |
| *p*,*p*′-DDT | 20 | 0.02 (n.d–0.25) | 0.12 (n.d–0.35) | – | |
| *o*,*p*′-DDE | 100 | 0.17 (0.04–0.50) | 0.21 (0.11–0.31) | – | – |
| *p*,*p*′-DDE | 100 | 1.69 (0.58–4.54) | 1.01 (0.55–1.59) | – | 5 |
| *o*,*p*′-DDD | 86.7 | 0.10 (n.d–0.31) | 0.24 (0.07–0.90) | – | |
| *p*,*p*′-DDD | 33.3 | 0.02 (n.d–0.11) | n.d | – | 8 |
| ΣDDT | 100 | 7.80 (2.15–24.61) | 2.80 (1.88–3.75) | 2.5 | 7 |

Concentration is presented as mean (min–max)

[a] The Netherlands soil contamination guidelines (Department of Soil Protection 1994)

[b] Guidelines for the protection and management of aquatic sediment quality in Ontario (Persaud et al. 1993) and Interim sediment criteria values for nonpolar hydrophobic organic contaminants (U. S. Environmental Protection Agency 1988)

[c] Sum of *o*,*p*′-DDT, *p*,*p*′-DDT, *o*,*p*′-DDD, *p*,*p*′-DDD, *o*,*p*′-DDE and *p*,*p*′-DDE

n.d, not detected

**Table 2** Comparison of ΣHCH and ΣDDT contents (μg/kg) in soils of Dayanghan Wetland with the reported contents of other regions

| Region | Sampling year | ΣHCH | | ΣDDT | | Ref. |
|---|---|---|---|---|---|---|
| | | Mean | Range | Mean | Range | |
| Yangtze River Delta Region | 2003 | 3.23 | 0.28–17.93 | 28.87 | 0.46–484.24 | Zhang et al. (2009) |
| Shanghai | 2007 | 2.41 | n.d–10.38 | 21.41 | 0.44–247.45 | Jiang et al. (2009) |
| Xixi Wetland Park | 2006 | 18.44 | 14.56–29.43 | 20.80 | 12.82–47.36 | Shao et al. (2008) |
| Dayanghan Wetland | 2011 | 1.35 | 0.66–3.71 | 7.80 | 2.15–24.61 | This paper |

n.d, not detected

occurring. Average concentrations of HCHs and DDTs in the topsoil have decreased to 6.7 % and 13.7 % of the maximal average concentrations recorded in the past decade, respectively. In addition, the residue levels of ΣHCH or individual HCH except $\beta$-HCH in four types of soils were significantly ($p < 0.05$) lower than those in sediments, while it is opposite in terms of ΣDDT and two major DDTs ($o,p'$-DDT and $p,p'$-DDE) (Fig. 2). For $\beta$-HCH, its highest concentration was found in the soil of vegetable land, but its mean concentration in soils was still

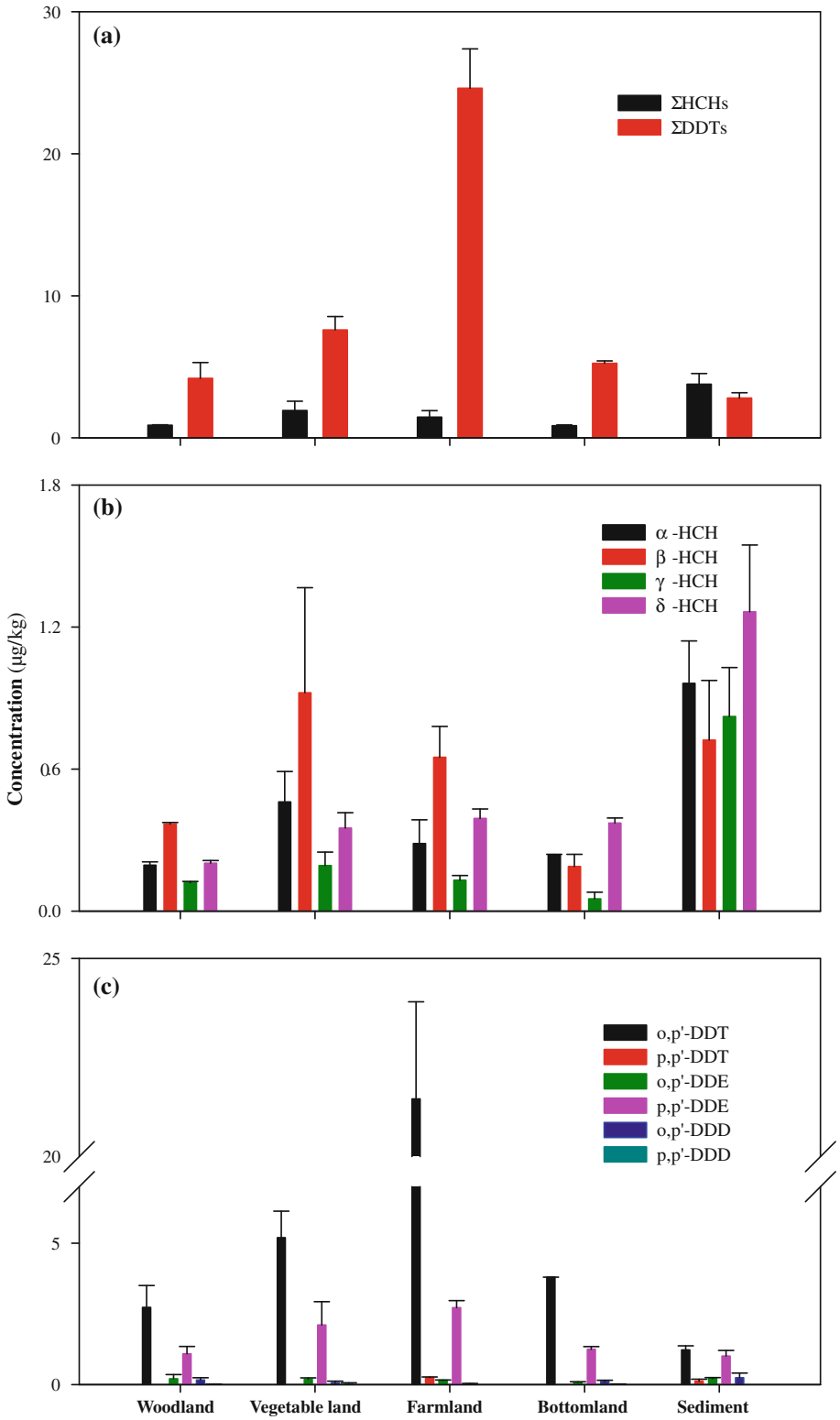


**Fig. 2** HCH and DDT residues in soils and sediments of Dayanghan Wetland

lower than that in sediments. Also, the ΣHCH concentration was lower than ΣDDT concentration in soils, while the ΣHCH content was higher than ΣDDT content in sediments (Table 1). The results may attributed to the fact that HCHs have higher solubility in water (S) and soil–water distribution coefficients of organic compounds ($K_{oc}$) than DDTs, and thus are easier transferred into water body with surface runoff and adsorbed in sediments. Quiet similar, Zhou et al. (2006) found the levels of ΣHCH were higher than those of ΣDDT in sediments from Qiantang River in East China. Moreover, the total concentrations of HCHs in soils of the four types of land use varied only slightly (Fig. 2a), which may be explained by the fact that the higher vapor pressure of HCHs cause HCHs much easier to volatilize from soil to atmosphere and return to soil through dry or wet deposition after atmospheric transportation, and thus more homogeneous distribution than DDTs in soils (Zheng et al. 2009). Meanwhile, the total concentrations of DDTs in farmland soils were significantly ($p < 0.05$) higher than those in the other three types of soils (Fig. 2a), in accordance with its large agricultural application rate from 1950s to 1980s (Li et al. 1999).

According to the soil protection guideline of the Netherlands (Table 1), the concentrations of ΣHCH and HCH isomers in soil samples collected in this study were significantly lower than the target value for unpolluted soil except one soil sample of woodland, in which $\beta$-HCH content (2.20 μg/kg) was slightly higher than the target value (1 μg/kg) for unpolluted soil. Nevertheless, the concentrations of ΣDDT in 19 of 20 soil samples in the present study were higher than the value for unpolluted soil (below 2.5 μg/kg). In comparison with soil quality standards of the Netherlands, HCH pollution in the soil of Dayanghan Wetland may be categorized as nonexistence, but the level of DDTs was classified as low pollution. For HCHs and DDTs in the sediments of Dayanghan Wetland, their concentrations were preliminary compared with the corresponding target values used in the aquatic sediment quality guides of US and Canada (Table 1), the concentrations of HCH isomers and DDT metabolites in sediments were significantly lower than the reference values for low environmental risk. The results implied that no remediation measures were required with respect to HCHs and DDTs in sediments of Dayanghan Wetland. In spite of this, the ecological and health effects of these endocrine disruptive pollutants through food chain should deserve concern in light of their possible biological magnifications in higher trophic organisms including human beings.

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