Bull Environ Contam Toxicol (2011) 87:561–566
DOI 10.1007/s00128-011-0368-y

Organochlorine Pesticides in Soils from a Typical Alluvial Plain of the Yangtze River Delta Region, China

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Received: 15 April 2011 / Accepted: 15 July 2011 / Published online: 22 July 2011

Abstract Residues of organochlorine pesticides (OCPs), dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH), their risks and affecting factors in 544 representative soils collected from a typical alluvial plain of the Yangtze River Delta region, China, were investigated. Mean concentrations of ΣDDT and ΣHCH in soils were 88.8 and 99 ng/g, respectively. Historical application of DDT and HCH were the major sources of their residues in soils. Concentrations of DDT in soils had relative greater levels of contamination, while concentrations of HCH were almost at safe levels. Residues of DDT and HCH in soils were affected by soil types as well as soil textures.

Keywords Organochlorine pesticides · Soil contamination · Sources · Affecting factors

Organochlorine pesticides (OCPs) such as dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) are of significant concern and have been studied extensively in the last several decades due to high toxicity, long environmental half-lives and long scale transportation ability. These compounds can be transferred into food chains, and can enter aquatic environments through effluent release, atmospheric deposition, runoff and other means (Bakan and Ariman 2004; Zhou et al. 2008). Dichlorodiphenyltrichloroethane was listed on the Stockholm Convention as one of 12 persistent organic pollutants (POPs) in 2004, and α-HCH, β-HCH and γ-HCH (lindane) were added to the list in 2009. As one of the largest agricultural production countries, China has been a major producer and consumer of OCPs, until its ban on production and agricultural use was enforced in 1983. From 1950 to 1983, an estimated total of 0.46 million tons of DDT and more than 4 million tons HCH were produced in China with most of the production applied in agriculture in China (Tao et al. 2008). Although production of technical DDT and HCH were officially banned by China for nearly 30 years, they were still detected at considerable levels in some soils in China (Feng et al. 2003; Hu et al. 2009). Soils can play an important role in the global fate and distribution of pollutants since they have been identified as a sink from which they can be released into water or air (Shegunova et al. 2007). Several earlier studies focused on how OCPs were distributed in the soils, but only a few studies discussed the factors influencing the residue levels and patterns (Hu et al. 2010).

The Yangtze River Delta (YRD) region lies in the east of China, holding the highest density of population and fastest economic developing provinces in China. Agriculture in this region is intensive and highly productive, thus large amount of DDT and HCH pesticides have been intensively used historically as an insecticide on croplands, such as cotton and paddy fields, to increase agricultural production (Li et al. 2008; Li et al. 1999; Zhang et al. 2009). Previous study in the YRD region showed that large applications of dicofol in agricultural practice especially in cotton cultivation have resulted in serious DDT pollution (Yang et al. 2008). Thus, protection of the soils surrounding the Yangtze River Delta is of great importance for safeguarding the aquatic environment and food quality

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produced in this region. Organochlorine pesticide residues have been studied in different environment media of the YRD region (Feng et al. 2003; Li et al. 2008; Tang et al. 2007; Yang et al. 2005; Zhang et al. 2009), but these reports focused on limited sites and may not reflect the general situation of soil pollution in the alluvial plain of the YRD region. The objectives of the paper were to determine the residue characteristics, sources and environmental risks of DDT and HCH in soils from a typical alluvial plain of the YRD region, China, and also to explore how the environmental factors affect DDT and HCH residues in soils.

Materials and Methods

This study focused on a typical flat alluvial plain in the YRD region of China (31°43′-32°01′N, 120°22′-120°49′E), Zhangjiagang County, where covers a total terrestrial area of 799 km^2 with an arable land area of 409 km^2. From the 1960s to the 1980s, large amount of pesticides, including DDT and HCH, were applied in the croplands of Zhangjiagang County, especially for the cotton and paddy fields. Five hundred forty four topsoil samples were collected in 2004 throughout the county based on soil types, land uses, and spatial homogeneity (Fig. 1). The main soil types in the study area can be divided into two soil orders, Anthrosols (Paddy soils) and Cambosols (Fluvo-aquic soils), according to Chinese Soil Taxonomy (CRGCST 2001). Each sample was made from a mixture of five subsamples collected from five spots of an area of about 5 m^2. All soil subsamples were collected at a depth of 0–20 cm using a stainless steel shovel. Fresh soil samples (about 1 kg) were transported to the laboratory in polyethylene zip-lock bags, lyophilized, sieved through a 2-mm mesh, and stored at 4°C in pre-cleaned glass jars until analysis.

For extraction of pesticides from the soil, n-hexane and dichloromethane (J.T. Baker, HPLC) were used. Anhydrous sodium sulfate (analytical grade) and silica gel (60 mesh, for column chromatograph) were activated at 180°C for 24 h. Solid phase extraction (SPE, 6 ml, Supelco, Bellefonte, PA, USA) cartridges containing 1 g of florisil was washed with 10 mL of n-hexane before using. A mixture of standard solution containing α-, β-, γ-, δ- HCH isomers, *p, p′*-DDE, *p, p′*-DDD, *o, p′*-DDT, and *p, p′*-DDT at 1 mg/g per compound was obtained from the National Research Center for Certified Reference Materials of China. The amount of substance in the extracts was quantified using the internal standard (2, 4, 5, 6-tetrachloro-m-xylene or TCMX) supplied by Supelco (Supelco, Bellefonte, PA, USA). Agilent 6890 gas chromatograph (GC) equipped a ^{63}Ni electron capture detector (μECD) (Agilent Technologies, Wilmington, DE, USA) was used for the analysis. The column used was HP-5 silica capillary column with 30 m × 0.32 mm i.d × 0.25 μm film thickness.

Soil sample (5.0 g dry weight) was mixed with 1 g anhydrous sodium sulfate. One milliliter of 2, 4, 5, 6-tetrachloro-m-xylene at the concentration of 0.08 μg/mL was added. The mixture was extracted twice with 35 mL of hexane/dichloromethane (1:1, v/v) by ultrasonication for 60 min and then centrifuged. Extracts were concentrated to about 2 mL by rotary evaporation, and further purified with SPE cartridges loaded with 1 g silica gel and 1 g anhydrous sodium sulfate. The elution was subsequently carried out using 20 mL of hexane/dichloromethane (7:3, v/v).

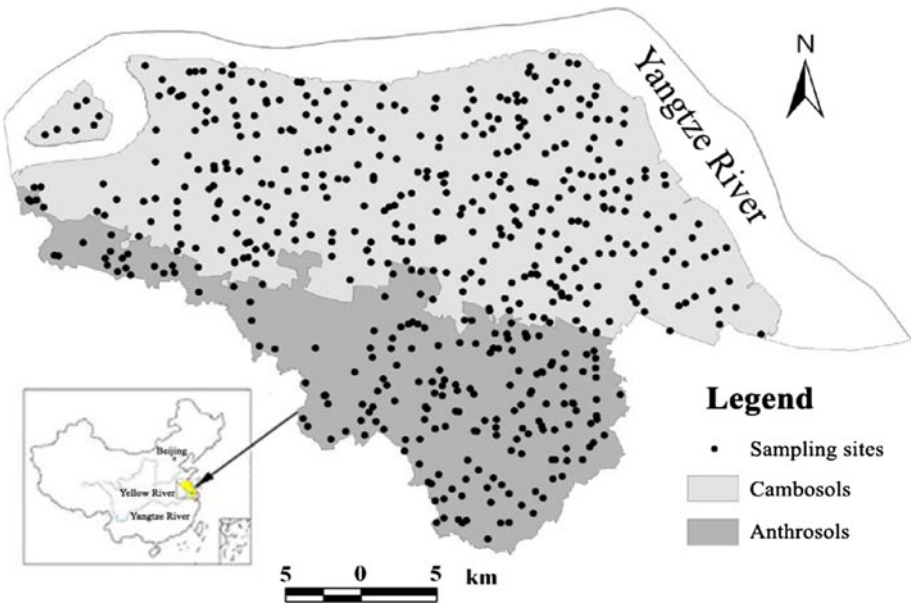

Fig. 1 Study area and sampling sites of the typical alluvial plain of the Yangtze River Delta region

The eluant was concentrated to a final volume of 1 ml for GC analysis. Reagent blanks were also analyzed simultaneously with the experimental samples. The purified extract was analyzed using GC-μECD under splitless injection mode with ultrapure 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 four DDT homologues (*p, p′*-DDE, *p, p′*-DDD, *o, p′*-DDT, and *p, p′*-DDT) and four HCH isomers (α, β, γ, δ) were identified by retention time matched to standards and were quantified based on peak area. Concentrations of ∑DDT and ∑HCH were calculated by summing the four DDT metabolites and four HCH isomers, respectively and reported on a dry soil basis.

For quality assurance and quality control, procedural blanks and matrixes spiked with the standard solution were analyzed. None of the target compounds were detected in the procedural blanks. All solvents used were distilled in glass (PR grade) and were checked for interferences or contamination prior to use. Extraction efficiency, as indicated by recovery of the surrogate standards (TCMX), was 85 ± 10%. The limits of detection (LOD) were described as three times of signal-to-noise ratio (S/N). The detection limit ranged from 0.05 ng/g, dw to 0.2 ng/g, dw. A standard solution containing *p, p′*-DDE, *p, p′*-DDD, *o, p′*-DDT, and *p, p′*-DDT, α-, β-, γ-, δ- HCH isomers at 1 mg/g of each compound was obtained from the National Research Center for Certified Reference Materials (CRM) of China. The recovery of CRM spiked to soil ranged from 73.1% to 109.3%. Gas chromatograph analysis was repeated twice for each replicate sample and the relative standard deviation (RSD) of replicate analyses were between 5% and 18%.

Soil texture was measured by analyzing the proportion of sand, silt, and clay particles present in a soil, then using these percentages to determine the soil texture by consulting the soil texture triangle (Smith 1996). Soil pH (<2-mm) was measured in a 1:2.5 soil to water paste mixture using a glass electrode pH meter (PHS-3C, Shanghai, China). Soil organic matter (SOM) was determined using the Walkley and Black method and soil samples with <0.149 mm particle size (Nelson and Sommers 1996).

Concentrations of DDT and HCH in soils were described by minimum, maximum, difference between mean, standard deviation and coefficient of variation (CV). The SPSS 13.0 for windows was employed for statistical analysis. T-test was used to identify the differences of DDT and HCH concentrations between Anthrosols and Cambosols.

Results and Discussion

Concentrations of DDT and HCH in soils are presented in Table 1. The mean concentrations of ΣDDT and ΣHCH were 88.8 and 3.2 ng/g, dw, ranging from <LOD to 600 ng/g, dw and <LOD to 99 ng/g, dw, respectively. On the whole, the concentrations of ΣDDT in soils were much greater than those of ΣHCH. This result was consistent with the previous measurements of concentrations of ΣDDT and ΣHCH in the soils of the Haihe Plain, China (Tao et al. 2008), the soils in the vicinity of watersheds of Beijing Reservoirs, China (Hu et al. 2009) and the agricultural soils of central Germany (Cai et al. 2008). The

Table 1 Concentrations (ng/g, dw) of DDT and HCH in soils from the typical alluvial plain of the Yangtze River Delta region of China

OCPs	Mean	Standard deviation	Minimum	Maximum	CV[b] (%)	Detection rate (%)
p, p′-DDE	49.0	61.7	<LOD	344.3	126	96
p, p′-DDD	9.9	11.6	<LOD	86.8	118	94
o, p′-DDT	4.9	8.4	<LOD	61.2	170	54
p, p′-DDT	25.0	37.2	<LOD	384.7	149	88
ΣDDT[a]	88.8	96.5	<LOD	600.0	109	96
α-HCH	0.1	0.5	<LOD	5.3	455	6
β-HCH	0.3	1.1	<LOD	12.8	332	17
γ-HCH	0.8	2.4	<LOD	18.0	308	21
δ-HCH	2.0	8.2	<LOD	91.5	407	16
ΣHCH[a]	3.2	10.3	<LOD	99.0	320	22

[a] ΣDDT = *p, p′*-DDE + *p, p′*-DDD + *o, p′*-DDT + *p, p′*-DDT, ΣHCH = α-HCH + β-HCH + γ-HCH + δ-HCH

[b] CV (%) coefficient of variation

high standard deviations and large coefficients of variation (CV) (>100%) of DDT and HCH concentrations indicated intense spatial heterogeneity of DDT and HCH in the study area (Hu et al. 2010). This type of patchy distribution is often observed for concentrations of organic residues in soils and leads to non-normal frequency distributions. In fact, the log-normal or positively skewed distribution is common and for this distribution the mean often equals the standard deviation, which results in a CV of 100%. The ranking of relative concentrations of DDT metabolites were found to be in the order *p, p′*-DDE (52.2%) > *p, p′*-DDT (28.1%) > *p, p′*-DDD (11.1%) > *o, p′*-DDT (5.6%), with the *p, p′*-DDE accounting for the greatest proportion of ΣDDT. The greatest proportion of DDE found in the soils indicated that DDT in soils was mainly from aged residues. Technical DDT and dicofol were the main sources of DDT pollution in China (Yang et al. 2008). The relative proportions of α-, *β*-, *γ*-, and *δ*-HCH were 3.3%, 10.0%, 24.4% and 62.2%, respectively. These relative proportions of isomers were different from the originally manufactured technical mixture. Among the HCH isomers, α-HCH is more likely to partition to the air and transport for a long distance (Willett et al. 1998). The greatest proportion of *δ*-HCH and *γ*-HCH in the soils manifested that HCH was a mixture of historical technical HCH and lindane sources and had been in the environment for a relatively long period of time, not currently entering the environment.

To understand the contamination status of DDT and HCH in soils of the typical alluvial plain of the YRD region, China, concentrations of ΣDDT and ΣHCH in soils from different areas were compared. Concentrations of ΣDDT in the study area were significantly greater than those in soils in the mountain Andean Lakes (range: 0.10–1.10) (Borghini et al. 2005) and James Ross Island (range: 0.51–3.68) (Klanova et al. 2008), and were also greater than those of the Pearl River Delta, China (range: 0.52–414, median: 20.1) (Hu et al. 2009), the YRD region (range: 0.46–484.24, mean: 28.87) (Zhang et al. 2009), Nanjing, China (range: 6.3–1050.7, mean: 64.1) (Cai et al. 2008), the Haihe Plain, China (range: 0.40–2350, mean: 63.6) (Tao et al. 2008), central Germany (range: 23.7–173, mean: 72.0) (Cai et al. 2008) and Romania (range: 9–187.4, mean: 62.5) (Cai et al. 2008). In comparison with ΣHCH concentrations in soils from other areas, the mean concentrations were slightly greater than the residual levels reported for soils from the Pearl River Delta, China (range: 0.05–24.1, median: 2.94) (Hu et al. 2009) and James Ross Island (range: 0.49–1.34) (Klanova et al. 2008), similar to concentrations reported for soils from the YRD region (0.28–17.93, mean: 3.23) (Zhang et al. 2009), but were less than those from Nanjing, China (range: 2.7–130.6, mean: 13.6) (Cai et al. 2008), the Haihe Plain, China (range: 0.02–349, mean: 3.90) (Tao et al. 2008), central Germany (range: 4.60–11.5, mean: 7.52) (Cai et al. 2008) and Romania (range: 2.8–89.5, mean: 26.1) (Cai et al. 2008). In general, concentrations of ΣDDT in soils from the studied area were greater than those from other areas, while concentrations of ΣHCH were generally found to be moderate to low.

Multiple factors can affect residue levels of DDT and HCH in soils. In this study, soil types and soil textures were analyzed to examine the possible relationship with DDT and HCH residues. Concentrations of DDT and HCH in Anthrosols and Cambosols were compared (Table 2). In Anthrosols, mean concentrations of ΣDDT and ΣHCH were found to be 40.5 and 7.2 ng/g dw, respectively. In Cambosols, the ΣDDT and ΣHCH were detected as mean of 114.5 and 1.1 ng/g dw, respectively. Concentrations of *p, p′*-DDE, *o, p′*-DDT and ΣDDT in Cambosols were significantly ($p < 0.01$) higher than those of Anthrosols, which indicated that the Cambosols were more contaminated than were the Anthrosols. Cambosols occupy the northern part of the county along the Yangtze River and were developed from neo-alluvium parent materials with light-medium loamy texture. In the Cambosols, before the 1980s, the rotation of cotton as summer crop and wheat as winter crop was dominant, although, after the 1980s most of the cotton was increasingly substituted with rice. Areas with higher DDT concentrations were mainly located in the northern part of the county along the Yangtze River where fluvo-aquic soils (Cambosols) were the dominated soil types and historically heavy applications of DDT pesticides for cottons were identified according to our investigation. Concentrations of *β*-HCH, *γ*-HCH, *δ*-HCH and ΣHCH in

Table 2 Mean concentrations (ng/g dw) and *t* test of DDT and HCH between Anthrosols and Cambosols

	p, p′-DDE	*p, p′*-DDD	*o, p′*-DDT	*p, p′*-DDT	∑DDT	α-HCH	*β*-HCH	*γ*-HCH	*δ*-HCH	∑HCH
Anthrosols (n = 189)	17.7	6.8	1.1	14.9	40.5	0.1	0.6	1.6	4.9	7.2
Cambosols (n = 355)	65.7	11.5	7.0	30.4	114.5	0.1	0.2	0.4	0.5	1.1
t	−9.3	−4.6	−8.3	−4.7	−9.2	0.5	4.1	6.0	6.3	6.9
p value	0.0**	0.1	0.0**	0.1	0.0**	0.3	0.0**	0.0**	0.0**	0.0**

Difference is significant ** at the 0.01 level

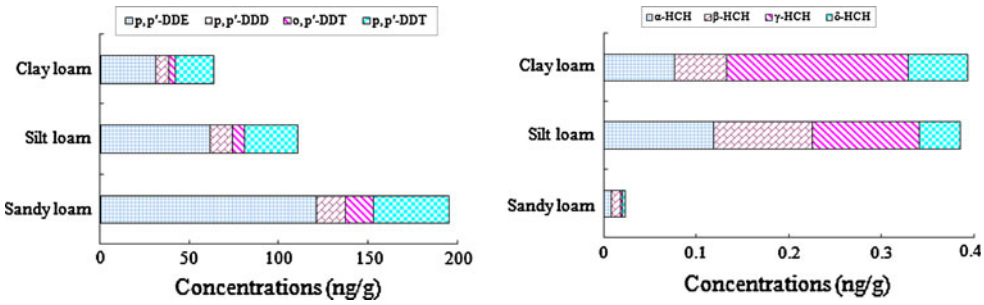

Fig. 2 Concentrations (ng/g dw) of DDT and HCH in soils with different soil textures

Anthrosols were significantly ($p < 0.01$) greater than those of Cambosols. Anthrosols are the dominant order on the plains of the southern part of the county, develop from lacustrine deposits on alluvium, with a loamy clay texture. In the Anthrosols, the rotation of rice and wheat has always been the dominant planting system. Areas with lower DDT but greater HCH concentrations were mainly distributed in southern part of the county where historically heavy applications of HCH pesticides for rice were identified.

In addition, soils collected from 3 types of soil textures as clay loam soil, silt loam soil and sandy loam soil were analyzed to delineate the influence of soil textures on DDT and HCH residues. The concentrations of DDT and HCH by different soil textures are given in Fig. 2. For DDT and its metabolites, the mean levels of ΣDDT decreased in the following order: sandy loam > silt loam > clay loam. The residues of DDT in sandy loam soils were significantly greater ($p < 0.05$) than those in clay and silt loam soils, which were different from the soils around watersheds of Beijing Reservoirs, north of China (Hu et al. 2010). Generally, compare to sandy loam soils, clay and silt loam soils can hold more plenty of moisture and organic materials, which have the effect of strengthening the ability of the soil particles to adsorb DDT, as well as the ability of decelerating the degradation and cleanup process of this pollutant. However, it's not the case in this research, suggesting that the influence of soil texture on the absorption of DDT is minor compared with the influence from historical usage. The levels of HCH and its isomers in soils with the 3 soil textures differed from those of DDT. The higher levels of ΣHCH were found in clay and silt loam soils, which may be explained because the clay and silt loam soils have the effect of strengthening the ability of the soil particles to adsorb HCH, together with intensive rice cropping and large amount of HCH pesticides application in the past.

Acknowledgments This study was supported by the funding from the National Natural Science Foundation of China (40773075, 41071299) and the Special Research Foundation of the Public Natural Resource Management Department from Ministry of Environmental Protection of China (201109018).

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