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Organochlorine pesticides in soils under different land usage in the Taihu Lake region, China

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Abstract

A field study was conducted in the Taihu Lake region, China in 2004 to reveal the organochlorine pesticide concentrations in soils after the ban of these substances in the year 1983. Thirteen organochlorine pesticides (OCPs) were analyzed in soils from paddy field, tree land and fallow land. Total organochlorine pesticide residues were higher in agricultural soils than in uncultivated fallow land soils. Among all the pesticides, ∑DDX (DDD, DDE and DDT) had the highest concentration for all the soil samples, ranging from 3.10 ng/g to 166.55 ng/g with a mean value of 57.04 ng/g and followed by ∑HCH, ranging from 0.73 ng/g to 60.97 ng/g with a mean value of 24.06 ng/g. Dieldrin, endrin, HCB and α-endosulfan were also found in soils with less than 15 ng/g. Ratios of *p*,*p*′-(DDD+DDE)/DDT in soils under three land usages were: paddy field > tree land > fallow land, indicating that land usage inlfuenced the degradation of DDT in soils. Ratios of *p*,*p*′-(DDD+DDE)/DDT >1, showing aged residues of DDTs in soils of the Taihu Lake region. The results were discussed with data from a former study that showed very low actual concentrations of HCH and DDT in soils in the Taihu Lake region, but according to the chemical half-lives and their concentrations in soils in 1980s, the concentration of DDT in soils seemed to be underestimated. In any case our data show that the ban on the use of HCH and DDT resulted in a tremendous reduction of these pesticide residues in soils, but there are still high amounts of pesticide residues in soils, which need more remediation processes.

Key words: DDT; HCH; land-use; pesticide residue; degradation

Introduction

Organochlorine pesticides (OCPs), including DDT, HCH, HCB, dieldrin and endrin, have a long history of use in the world for control of agricultural pests. They are typical persistent organic pollutants (POPs). Their ability to persist in the environment and accumulate in food chain and their potential to elicit toxic effects led to the cancellation of their production in many countries during the 1970s and 1990s (Li *et al*., 1999, 2001). However, OCPs are still routinely found in soil, water, air and even foodstuff in many countries (Aigner *et al*., 1998; Falandysz *et al*., 2001; Ribes and Grimalt, 2002; Miglioranza *et al*., 2003; Gong *et al*., 2004; Barriada-Pereira *et al*., 2005; Concha-Graña *et al*., 2006).

China had produced and consumed a large amount of HCH and DDT between the 1950s and 1983s, e.g., total 4.5×10^6 t of HCH and 0.27×10^6 t of DDT (Li *et al*., 1999, 2001). Even after the ban of technical HCH and DDT in 1983, lindane (3200 t totally) was further used in forest management until the year 2000 and DDT was produced for export and for further producing dicofol (another kind of pesticides which is still in use in China) (Li *et al*., 2001). Endosulfan is one of the few OCPs that are still in use but right now there are no exact data on its consumption in China.

The Taihu Lake region is located in the Yangtze River Delta, southeast of China. It is one of the most important rice production areas and also one of the areas where OCPs were most extensively used from the 1950s to 1980s (Li *et al*., 2001; Qiu *et al*., 2004; Wang *et al*., 2005). Concentrations of these compounds in soils increased due to this intensive application of organochlorine chemicals in the past. Zhang *et al*. (1983) has found that the concentration of ∑HCH residues in paddy soils varied between 21–1960 ng/g. In 1983, concentrations of OCPs in paddy soils ranged from 35–3669 ng/g for ∑HCH and from 13–5747 ng/g for ∑DDT (Ma *et al*., 1986). After the ban of HCH and DDT in 1983, their conentrations were decreased. The reported maximum concentrations for two OCPs were 3.4 ng/g and 5.3 ng/g, respectively, in 2000 (Feng *et al*., 2003). According to the half-life of DDT in agricultural soils (4–35 years, average 10–10.5 years) (Dimond and

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Owen, 1996; Harner *et al*., 1999), the DDT concentrations seemed to be very low in a former study (Feng *et al*., 2003). Thus, there was a need of better understanding their residue levels and the distribution characteristics in soils since the ban of OCPs was more than 20 years ago. In this studty, a field survey was conducted in 2004 to reveal the distribution characteristics of OCPs in soils from different land usage systems in the Taihu Lake region.

1 Materials and methods

1.1 Studying area and land usage in the Taihu Lake region

The Taihu Lake region, located between the Yangtz River and the Taihu Lake, is characterized by northern subtropical monsoon with 1100–1400 mm of annual precipitation, annual mean temperatures around 16°C and a growing season of 290 d, 230 of which are frost-free (Ellis and Wang, 1997). There are two basic land-use types in the Taihu Lake region agroecosystems: paddy and dryland (including tree land and fallow land), interlaced with a network of canals and ditches for irrigation (Ellis and Wang, 1997). About 70%–90% of cropped land was paddy fields and the dryland only accounted for 5%–30% of the total farm area. Paddy fields were sometimes converted to dryland and planted to wheat, barley, grain legumes, rapeseed or vegetables. Tree lands were often intercropped with vegetables, wheat, barley and grain legumes in a form of agroforestry. Both paddy and tree lands were small but numerous (less than 0.15 hm^2 each), and occupied around 90% of the total farm area. Less than 10% of total area was fallow land, located close to common buildings, along canals and on graves within the cropped areas (Ellis and Wang, 1997).

1.2 Soil sampling

The location of sampling sites in the Taihu Lake region is shown in Fig.1 and the grid reference of each sampling site is given in Table 1. Seven sampling sites were selected at each location. All soil samples were collected from surface (0–20 cm) and subsurface (20–40 cm) layers, except that only surface soils were sampled in the tree land in Shuangqiao (SQ) and fallow land in Industrypark (IP) and Yuanhe (YH). The collected soil samples (about 5 kg for each location) were combined and transferred to laboratory. Soil samples were air dried at 20°C, sieved (≤2 mm sieve) and stored at 4°C until analysis.

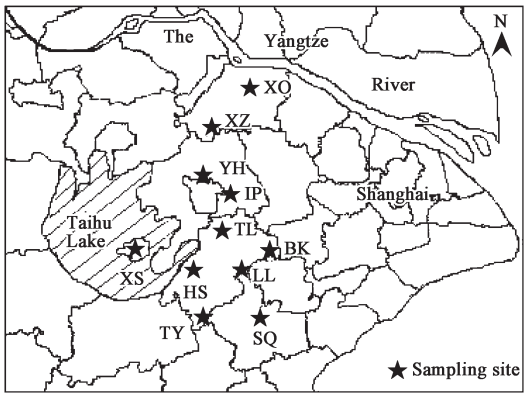

Fig. 1 Soil sampling stations in the Taihu Lake Region in China. SQ: Shuangqiao; TY: Taoyuan; LL: Lili; BK: Beiku; HS: Hengshan; TL: Tongli; IP: Industrypark; YH: Yuanhe; XZ: Xingzhuang; XQ: Xieqiao; XS: Xishan.

1.3 Soil pH and total organic carbon analysis

Soil pH and total organic carbon (TOC) analysis were conducted by conventional standard procedures (Lu, 2000): soil pH was determined at a soil to water ratio of 1:2.5 by a potentiometric glass electrode; TOC was measured by digestion of soil samples with $K_2Cr_2O_7$ and subsequently titration with H_2SO_4.

1.4 Soil OCPs analysis and quality control

Aliquots (2 g) of soil samples were homogenized with 20 ml acetone/petroleum ether (1/5, v/v) with a vortical mixer for 1 min. The mixture was extracted for 1.5 h in an ultrasonic bath and centrifuged at 3000 r/m for 15 min. The supernatant was removed and the soil sample was re-extracted twice with the same procedure. The extracts were combined and concentrated to about 1 ml by rotary evaporator.

For cleanup of the extracts, 1 ml concentrated extract was loaded onto the top of a solid-phase extraction column containing 1 g Na_2SO_4 and 1 g celite, which was prewashed with 4 ml petroleum ether. The analytes were eluted with 10 ml dichloromethane/petroleum ether (1/10, v/v), concentrated to 1 ml by a rotary evaporator using a gentle nitrogen stream for GC-μECD analysis.

The determination of analytes was carried out with a gas chromatography system (Agilent 6890 GC, USA) equipped with a ^{63}Ni microcell electron capture detector (μECD) and a tower 100 position 7683 autosampler under the splitless mode. The separation occurred on a 30 m×0.32 mm i.d. HP-5 capillary column with a film thickness of 0.25 μm and at a pressure of 50 kPa. Nitrogen was used as carrier gas at a flow rate of 1.5 ml/min. The column temperature was programmed from 60°C (1 min) to 140°C at 20°C/min and then to 280°C (5 min) at 8°C/min. The injector and detector temperature were 220°C and 280°C, respectively. A sample of 1 μl was injected with a syringe and concentrations of individual organochlorines were quantified according to the peak height of the respective external standards following calibration with authentic standards purchased from Dr. Ehrenstofer (Germany).

To estimate the recovery of OCPs residue in soils, a recovery study was carried out by spiking 10 ng of each compound in a mixture to 2 g soil. The results showed that the average recoveries ranged from (92.15±3.52)% to (109.56±7.36)%. All soil samples were analyzed in triplicates. All OCP concentrations were expressed on an air-dried weight basis and means were expressed in arithmetic value. The detection limits for analytes were as follows: HCB 0.03 ng/g; endrin 0.15 ng/g; *p*,*p*′-DDD, *o*,*p*′-DDT, *p*,*p*′-DDT 0.2 ng/g and 0.05 ng/g for the other compounds. All the data were analyzed by a software

Table 1 Soil sampling stations, soil pH, total organic carbon (TOC) and total organochlorine pesticide (∑OCP) concentrations in the soils from each sampling area

Sampling stations (abbreviation)	Land usage	Grid reference	Soil depth (cm)	pH (H_2O) value	TOC (g/kg)	∑OCP (ng/g)
Shuangqiao (SQ)	Paddy	30°50′44″N, 120°42′52″E	0–20	5.99	19.24	104.98±12.40
			20–40	7.16	13.75	116.49±10.36
	Tree land	30°50′44″N, 120°42′52″E	0–20	6.18	18.23	139.64±45.25
Taoyuan (TY)	Paddy	30°47′33″N, 120°28′46″E	0–20	5.45	22.82	139.31±44.48
			20–40	6.49	14.57	159.04±20.16
	Tree land	30°47′36″N, 120°28′49″E	0–20	5.64	22.17	127.71±8.39
			20–40	6.81	14.71	162.85±42.25
Lili (LL)	Paddy	31°0′18″N, 120°43′7″E	0–20	5.38	20.63	54.05±5.22
			20–40	6.55	10.93	46.23±18.37
	Fallow land	30°59′33″N, 120°43′11″E	0–20	5.63	18.19	105.85±6.80
			20–40	6.65	9.75	10.66±0.80
Beiku (BK)	Paddy	31°0′51″N, 120°45′42″E	0–20	5.81	18.96	70.40±4.70
			20–40	6.72	12.47	43.22±5.49
	Tree land	31°0′51″N, 120°45′42″E	0–20	5.42	16.52	66.18±1.92
			20–40	5.85	12.97	89.69±10.29
Hengshan (HS)	Paddy	31°0′11″N, 120°30′32″E	0–20	5.31	17.70	35.55±1.15
			20–40	6.31	11.83	121.11±10.01
	Paddy[a]	31°0′59″N, 120°30′32″E	0–20	5.21	13.35	40.53±1.35
			20–40	5.08	7.19	33.70±2.29
	Fallow land	31°0′24″N, 120°34′29″E	0–20	4.33	14.50	29.62±15.64
			20–40	6.62	18.91	45.94±13.68
Tongli (TL)	Paddy rape	31°9′12″N, 120°46′25″E	0–20	5.21	18.20	99.79±28.27
			20–40	6.76	7.16	53.44±3.85
	Tree land	31°9′12″N, 120°46′25″E	0–20	5.38	18.28	74.92±32.81
			20–40	6.70	13.95	105.07±29.33
Industrypark (IP)	Fallow land	31°19′41″N, 120°39′18″E	0–20	7.29	7.96	33.23±0.75
Yuanhe (YH)	Fallow land	31°22′27″N, 120°37°43″E	0–20	7.86	2.58	9.56±0.17
Xingzhuang (XZ)	Paddy wheat	31°32′57″N, 120°41′43″E	0–20	7.33	23.52	128.17±2.72
			20–40	8.06	13.71	102.44±4.76
Xieqiao (XQ)	Paddy wheat	31°42′54″N, 20°43′58″E	0–20	6.39	12.60	69.05±10.49
			20–40	7.61	5.89	30.21±7.66
Xishan (XS)	Asparagus[b, c]	31°7′43″N, 120°18′31″E	0–20	5.91	23.93	150.41±11.46
			20–40	5.45	20.06	159.23±14.27
	Tree land[b]	31°6′38″N, 120°17′27″E	0–20	4.88	11.73	218.84±37.56
			20–40	5.25	6.03	156.87±20.21

[a] Paddy irrigated with sewage; [b] green food base; [c] asparagus field was classified as paddy field.

package SPSS 12.0 for the purpose of statistics and the significance level was $p<0.05$.

2 Results and discussion

2.1 Total organochlorine pesticide residues in soils

The total organochlorine pesticide (∑OCP, as a sum of all single organochlorine pesticide) concentrations in surface and subsurface soil samples of investigated sampling stations are shown in Table 1. ∑OCP concentrations in most soil samples were in the range 100–200 ng/g. The highest ∑OCP concentration (218.84 ng/g) was in the surface soil at tree land in Xishan. Low ∑OCP concentrations were found (<50 ng/g) in paddy soils from Lili and Beiku, and in fallow land soils from Hengshan, Industrypark and Yuanhe. The total contaminant levels throughout the soil profile showed different distribution patterns among samples. For the soil samples from fallow land in Lili, from paddy fields in Beiku, Tongli, Xingzhaung and Xieqiao and from tree land in Xishan, higher ∑OCP concentrations were detected in the surface soil. However, lower ∑OCP concentrations were detected in the surface soils from paddy fields in Shuangqiao, Taoyuan and Hengshan and from tree land in Beiku. The results showed that although organic matter was known to be the most important OCPs' sorbent in soil surface horizons, additional factors such as particle-size characteristics and organic matter composition and physicochemical characteristics of OCPs were involved in pesticide retention (Manz *et al*., 2001; Gong *et al*., 2004).

With the development of the Chinese economy, Chinese government designed some regions as "green food bases" to produce safe, pollution-free, high-quality and nutritious food for Chinese as well as for export by meeting strict international requirements of developed countries (e.g. The Netherlands) for pesticide residues in food. Xishan (XS), located inside of the Taihu Lake region in China, is such a "green food base" (Fig.1). But the ∑OCP concentrations in soils from Xishan were identical or even higher than most of the fields at other locations. It showed that close attention should be paid to OCPs residues in soils when "green food bases" will be designed since OCPs residues from soils can be accumulated by plants and can menace the human health (Lee *et al*., 2003; Barriada-Pereira *et al*., 2005).

Table 2 Average concentrations of organochlorine pesticides in soils under three land usages [a]

OCPs	Average concentration (ng/g)						Target values	
	Tree land		Paddy field		Fallow land			
	0–20 cm	20–40 cm	0–20 cm	20–40 cm	0–20 cm	20–40 cm	C[b]	N[c]
α-HCH	4.34±2.84	6.73±1.79	5.91±2.70	5.38±2.41	2.21±2.73	1.33±1.84	-	2.5
β-HCH	8.89±7.74	20.27±13.68	14.00±6.57	8.75±5.37	6.09±9.11	2.27±1.04	-	1
γ-HCH	3.55±2.63	6.24±1.78	5.69±2.07	4.32±1.92	3.09±2.31	1.21±1.67	-	0.05
δ-HCH	4.17±3.53	5.53±3.70	2.95±3.52	1.78±2.49	2.14±3.51	1.42±0.64	-	-
∑HCH	20.94±12.4	38.84±18.45	28.53±10.77	20.22±8.21	13.53±17.01	6.24±5.19	500	10
o,p′-DDE	8.63±6.83	9.16±6.44	4.74±4.24	4.77±5.84	3.34±4.54	1.39±1.92	-	-
p,p′-DDE	27.90±16.50	22.64±9.08	22.78±13.38	18.54±13.85	7.51±4.17	8.15±2.19	-	-
p,p′-DDD	19.02±13.21	17.82±5.12	11.5±7.39	19.05±20.58	3.78±4.02	3.20±2.99	-	-
o,p′-DDT	6.92±12.08	4.74±6.98	2.64±3.51	4.77±5.84	2.67±3.29	nd	-	-
p,p′-DDT	27.78±22.67	19.32±6.90	8.55±6.32	12.49±8.53	7.96±5.23	6.31±8.72	-	-
∑DDX	90.25±53.17	74.04±29.71	50.23±28.70	57.75±42.87	25.26±19.04	19.13±15.82	500	2.5
HCB	5.13±3.49	4.72±1.73	3.76±2.27	2.74±2.54	1.86±1.21	1.21±1.69	-	2.5
α-Endosulfan	3.20±2.07	3.78±3.08	2.04±3.03	1.74±2.10	1.60±2.97	nd	-	-
Dieldrin	4.44±2.77	5.11±3.50	3.01±3.17	2.25±2.45	2.00±3.42	1.61±2.25	-	-
Endrin	1.50±2.36	2.56±3.18	1.64±2.33	4.06±4.44	0.32±0.51	nd	-	1
Drins	5.94±4.42	7.67±6.12	4.66±4.74	8.54±8.87	2.33±3.93	1.68±2.25	-	-
∑OCP	125.45±61.23	128.62±36.69	89.22±41.34	86.51±51.04	44.57±42.16	28.30±24.94	-	-

nd: Below the detection limit; ∑HCH: α-HCH + β-HCH + γ-HCH + δ-HCH; ∑DDX: *o,p′*-DDE + *p,p′*-DDE + *p,p′*-DDD + *o,p′*-DDT + *p,p′*-DDT; drins: dieldrin + endrin; ∑OCP: ∑HCH + ∑DDX + drins + HCB + α-endosulfan; [a] average concentration is presented as mean±standard deviation; [b]Chinese environmental quality standard for agricultural soils (GB15618-1995, China); [c] The Netherlands Soil Contamination Guidelines (1994).

2.2 OCPs residue in soils under three land usages

The average concentrations of organochlorine pesticides in soils under three land usages are presented in Table 2. Most of the OCPs were detected in soils from all land usages except *o,p′*-DDT, α-endosulfan and endrin in subsurface soils from the fallow land. Among all the pesticide concentrations, ∑DDX (DDD, DDE and DDT) had the highest concentration, followed by ∑HCH. Relative to ∑DDX and ∑HCH, lower concentrations of drins (dieldrin+endrin), HCB and α-endosulfan were found in soils, being less than 15 ng/g. The concentrations of pesticides in soil samples from different land usages were in the decreasing order of ∑DDX > ∑HCH > drins > HCB > α-endosulfan.

For OCP residues in soils under the three land usage systems, mean values were in the order of tree land ≈ paddy field > fallow land. The lower pesticide concentrations detected in soils from fallow land might mainly result from the drift of pesticides application and volatilization from agricultural soil, followed by atmospheric deposition on fallow land soils (Harner *et al*., 1999).

The concentrations of OCPs in these soils were compared with the corresponding target values used in China and in The Netherlands (Table 2). Although all the OCP concentrations in soils were much lower than the Chinese environmental quality standard for agricultural soils (GB15618-1995, China), the OCP concentrations, especially DDT, in soils were much higher than the values for unpolluted soils in the soil protection guideline of The Netherlands, an important vegetable exporting country. As it can be seen, further soil remediation is essential for improving soil quality to reach the international standard for producing and exporting agricultural products in this region.

2.3 OCP residues in soils in different years and estimation of their half-lives

As can be seen from Table 3, the average concentrations of ∑HCH and ∑DDT in this study were much lower than those reported in 1983, which indicated that degradation of these pesticides occurred in spite of a slow rate. Nevertheless, the OCP residues were still detectable in soil samples more than 20 years later the ban of these pesticides, showing that they are very persistent in the environment, which agree with the former reports (Dimond and Owen, 1996; Harner *et al*., 1999; Qiu *et al*., 2004).

Generally, half-lives of HCH are 20–50 d for γ-HCH and 20 weeks for α-HCH while half-life of DDT is 4–35 years (average 10–10.5 year) in agricultural soils (Dimond and Owen, 1996; Harner *et al*., 1999). According to the data given by Feng *et al*. (2003), half-lives of HCH and

Table 3 Concentrations and estimation of half-lives ($t_{1/2}$) of organochlorine pesticides in soils in the Taihu Lake region in different years[a]

Sampling year	Land usage	∑HCH			∑DDT			Reference
		Mean (ng/g)	Range (ng/g)	$t_{1/2}$(year)	Mean (ng/g)	Range (ng/g)	$t_{1/2}$ (year)	
1980			169–1065					Cai *et al*., 1985
1981	Paddy field	307	21–1960					Zhang *et al*., 1983
1982–1983	Paddy field	306	35–3669		147	13–5747		Ma *et al*., 1986
1999–2000		0.59[b]	nd–3.4	2.0	0.98[b]	nd–5.3	2.4	Feng *et al*., 2003
2004	Paddy field	28.5	10.1–41.5	6.5	50.2	19.0–92.6	13.6	This study

nd: Below the detection limit; [a] half-lives of HCH and DDT in 2000 were calculated according to the mean values in 1981–2000; half-lives of HCH and DDT in 2004 were calculated without the mean values in 2000; [b] mean values were calculated according to the data presented in the reference.

DDT were estimated to be about two years in paddy soils (Table 3), which is much lower than the reported half life of DDT. In contrast, the residue levels and therefore the extrapolated half-lives in this study (Table 3) are in accordance with the data reported previously (Dimond and Owen, 1996; Harner *et al*., 1999).

2.4 Degradation of HCH and DDT in soils under three land usages

Technical HCH contains 60%–70% α-HCH, 5%–12% β-HCH, 10%–12% γ-HCH, 6%–10% δ-HCH and 3%–4% ϵ-HCH, while lindane contained almost pure γ-HCH (Willett *et al*., 1998). β-HCH is the most stable and persistent HCH-isomer with respect to microbial degradation (Wu *et al*., 1997; Willett *et al*., 1998; Manz *et al*., 2001; Concha-Graña *et al*., 2006). The ratio of β-HCH/γ-HCH might increase during their degradation process. We tried using the ratio of β-HCH/γ-HCH to reflect the degradation of HCH in soils. As shown in Fig.2a, the ratios were mostly lower than the technical ratios, indicating both technical HCH and lindane were used in this region (Qiu *et al*., 2004). However, no significant difference was observed between the ratios of β-HCH/γ-HCH in soils under three land usages, which showed two possibilities. One is that the land usage has no significant influence on the degradation of HCH in soils. Another is that the land usage might affect the degradation of HCH in soils, but the ratio of β-HCH/γ-HCH is not enough to directly show the influence of land-use on the HCH degradation in soils. Degradation of HCH in the environment is complicated. Although it is clear that their degradation products are different under aerobic and anaerobic conditions, degradation pathways of HCH isomers in the environment are still unclear since identification of their degradation products is a challenge. γ-Pentachlorocyclohexene and γ-tetrachlorocyclohexene have been identified as degradation products of HCH, however, other suspected degradation products, such as cyclopentiltrichloroethene and 4,6,6,6-tetrachloro-1-hexene were also detected in soil (Concha-Graña *et al*., 2006). Thus, further study needs to be conducted to identify degradation products of HCH in soils for a better evaluation of land usage on the degradation of HCH in soils.

DDT is reductively dechlorinated to DDD and dehydrochlorinated to DDE and the metabolites are more stable and persistent than the parent compound (Quensen *et al*., 1998; Yao *et al*., 2006). Ratios of metabolite/parent compound were calculated to understand the degradation pathway of DDT in soils. Ratios of *p*,*p*′-(DDD+DDE)/DDT > *p*,*p*′-DDE/DDT > *p*,*p*′-DDD/DDT (Figs.2b, 2c and 2d) show that the main degradation pathway was from DDT to DDE.

Generally, a value of (DDD+DDE)/DDT ratio greater than 1.0 indicates aged (microbiologically degraded) DDT while a value much less than 1.0 indicates new pesticide application (Harner *et al*., 1999; Tavares *et al*., 1999; Miglioranza *et al*., 2003; Zhang *et al*., 2006). The average value of *p*,*p*′-(DDD+DDE)/DDT ratios were greater than 1.0 (Fig.2b), indicating aged DDT in the soils. However, the ratios with a value lower than 1.0 were found in soil samples from the paddy field (value is 0.91) and fallow land (value is 0.86) in Hengshan. According to the average value of *p*,*p*′-(DDD+DDE)/DDT ratio, the contamination of the paddy fields in Hengshan could be caused by a new input of DDT. Small ratio of *p*,*p*′-(DDD+DDE)/DDT in the fallow land soils could thus be explained by a new DDT deposition caused by its unwished application in paddy fields in the neighborhood. This new input of DDT in Hengshan is most likely the pesticide dicofol which contains DDT related compounds 300 g/kg (Qiu *et al*., 2005). Dicofol is still in restrictive use as a compensation pesticide of DDT to control mites after the usage of DDT was banned in China since 1983 (Qiu *et al*., 2004, 2005; Zhu *et al*., 2005).

Ratios of *p*,*p*′-(DDD+DDE)/DDT in soils under three

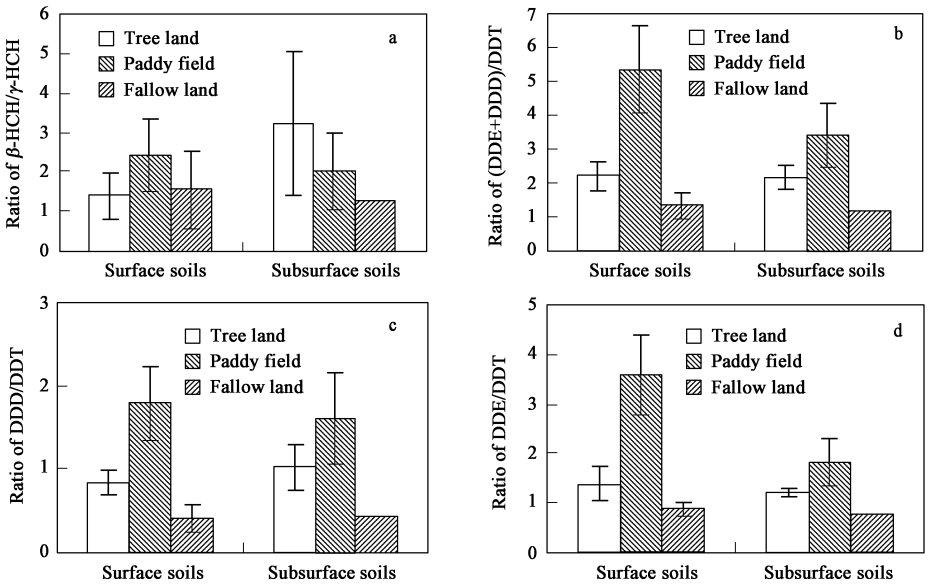

Fig. 2 Ratios of β-HCH/γ-HCH (a), *p*,*p*′-(DDD+DDE)/DDT (b), *p*,*p*′-DDD/DDT (c) and *p*,*p*′-DDE/DDT (d) in soils under three land usages.

land usages were: paddy field > tree land > fallow land (Fig.2b). Degradation of DDT was the slowest in the fallow land soils, indicating that remediation of the fallow land soils might be retarded. This could be explained by that the fallow land soils were not subject to mechanical mixing (e.g., plowing and disking) which would otherwise enhance microbial action (Harner *et al*., 1999). Ratios of *p*,*p*′-DDD/DDT in paddy soils were higher than those in tree land soils, indicating that degradation of DDT could be accelerated under reductive conditions as it was observed in former studies (Boul *et al*., 1994; Yao *et al*., 2006). In paddy soils, agricultural practices generate alternations of aerobic and anaerobic periods (Cary and Trolard, 2006), which could promote dechlorination of DDT to DDE and DDD (Quensen *et al*., 1998; Yao *et al*., 2006).

2.5 Effect of soil property on the HCH and DDT degradation

The fate of organic compounds in soils depends on chemical-specific parameters, environmental factors and on soil parameters such as temperature, soil type, pH, water content and organic matter (Manz *et al*., 2001; Wenzel *et al*., 2002; Miglioranza *et al*., 2003). pH-value can affect the concentrations of OCP in soil by influencing the microbiological activity in the soil (Wenzel *et al*., 2002). Increase of organic matter content in soil can increase the amount of microbial biomass and thus can induce the degradation of organochlorine pesticides (Wu *et al*., 1997; Zhang *et al*., 2006). On the other hand, a larger amount of organic chemicals can be adsorbed on the organic matter of soils with a higher amount of humus (Zhang *et al*., 2006). As the doses of the applied pesticides in the various sites were probably varying in the past, the ratios of metabolites and parent compounds of the pesticides in soils were calculated to receive a "dose independent degradation pattern"; this value was compared with soil pH and TOC.

Multiple analysis of linear regression between pH, TOC and ratios of metabolite/parent compound including the factor of land usages were calculated. The results showed that no influence of pH on OCP residue in soils was observed. Moreover, no correlations between concentrations of TOC and ratios of both β-HCH/γ-HCH and *p*,*p*′-(DDD+DDE)/DDT were found, indicating that the residue levels of HCH and DDT were a reflection of OCPs application history and dissipation rates rather than air-soil equilibrium in the Taihu Lake region, which was similar to OCP residues in soils in Alabama (Harner *et al*., 1999) and in Beijing (Zhu *et al*., 2005).

3 Conclusions

The usage of HCH and DDT in China has been banned for 20 years and this sanction resulted in a tremendous decrease of OCP concentrations in soils of the Taihu Lake region, nevertheless high residues of HCH and DDT in soils still need further remediation measures. Ratios of metabolites to parent compounds showed mostly aged residue of DDT in soils in this region. Depending on land usage and agricultural management the degradation of contaminants increased in soils which showed intensive soil cultivation and intensive fluctuation of soil humidity like in the paddy fields; in contrast, in "undisturbed" soil systems like fallow land the decontamination process in general was slower. It can be concluded that intensive soil cultivation without applying agro-chemicals is a suitable method for a long-lasting soil decontamination of persistent organic chemicals like DDT.

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