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Effect of land use change from paddy to vegetable field on the residues of organochlorine pesticides in soils

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The OCPs residues especially DDTs changed significantly with tillage time after the conversion from paddy to vegetable field.

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ABSTRACT

The effect of land use change from paddy to vegetable field on the residues of organochlorine pesticides (OCPs) was investigated. Soil residues of OCPs were analyzed in vegetable fields which had been converted from paddy fields for 0, 5, 10, 15, 20, 30, 50 year in Yixing, China in 2003. The mean concentrations of OCPs followed a sequence of: $\sum$DDTs (13.7 $\mu g\ kg^{-1}$) > $\sum$HCHs (8.6 $\mu g\ kg^{-1}$) > > HCB (2.09 $\mu g\ kg^{-1}$) > α-endosulfan (1.30 $\mu g\ kg^{-1}$) > endrin (1.08 $\mu g\ kg^{-1}$) > PCNB (0.76 $\mu g\ kg^{-1}$) > dieldrin (0.58 $\mu g\ kg^{-1}$). The mean residues of OCPs especially DDTs increased significantly with vegetable planting time after land use change in the first 15 years, then decreased from 20 to 30 years and increased a little afterward. The time under anaerobic and aerobic conditions was suggested to control mainly the change of the residues of OCPs.

1. Introduction

Organochlorine pesticides (OCPs) are of great concern due to their high bioaccumulation potential, ubiquity, persistence in the environment, deleterious effect and high toxicity to non-target organisms (Loganathan and Kannan, 1994; Willett et al., 1998; Jones and de Voogt, 1999). The OCPs were widely used and produced in China from 1960 to 1983 when they were forbidden from being used. It has been estimated that about 4.46 million tons of technical HCHs (1,2,3,4,5,6-hexachloro-cyclohexane) (Li et al., 1998) and 0.435 million tons DDTs (1,1,1-Trichloro-2,2-bis-(p-chlorophenyl) ethane) (Hua and Shan, 1996) entered the environment during 1960–1980. Recent investigations showed that the persistence of DDTs and HCHs has left residual amounts in soils for many areas (Li et al., 2006; Wang et al., 2007; Zhu et al., 2005;Cai et al., 2008).

The OCPs residues in soils showed a temporal and spatial changes in the world (Skrbic and Durisic-Mladenovic, 2007), because the residue level of OCPs depends on the balance of inputs and dissipation (such as decomposition, leaching and volatilization) and is affected by many factors including application history, agricultural practices (Boul et al., 1994; Spencer et al., 1996; Wang et al., 2006), physico-chemical properties of soil such as soil organic matter, pH and water content (Boul, 1996; Wenzel et al., 2002; Gong et al., 2003, 2004; Zhang et al., 2006), as well as meteorological factors such as temperature, rainfall and solar radiation (Samuel and Pillai, 1989; Haynes et al., 2000). In China, there was a large spatial variability in the residues of OCPs at the regional scale (Gong et al., 2003, 2004; Zhao et al., 2005; Li et al., 2006). The spatial distribution of soil residual concentrations of DDTs and HCHs in China shows a regional pattern of south > central > north, which is consistent with the use pattern of the pesticides (Wang et al., 2005). The largest amount of pesticide application was in Southeast China with the average annual usage of the active ingredients of OCPs varying from 2.4 to 4.5 kg ha^{-1}(Cao et al., 2007).

Land use patterns affect the application history and the dissipation of OCPs through changing the soil conditions, consequently affected the OCPs residues in soils. Wang et al. (2005) found that the soil residues of HCHs and DDTs in vegetable fields were larger than that in the farmland in South and Central China. Li et al. (2006) investigated the residues of HCHs and DDTs in soils in the Pearl River Delta in SE China, and found that their mean concentrations decreased in the order of upland crop soil > paddy soil > natural soil. Wang et al. (2007) found that the total OCPs residues were higher in agricultural soils than in uncultivated fallow land soils in the Tai Lake region in East China, and the ratios of p,p′-(DDD + DDE)/DDT in soils were in an order of paddy

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Table 1
The mean values of main properties of soil samples

Soil layer	Year[a]	pH (H_2O)	SOC (g kg^{-1})	TN (g kg^{-1})	TP (g kg^{-1})	TK (g kg^{-1})	CEC (cmol kg^{-1})	Clay (<2 μm) (%)	Silt (2–50 μm) (%)
0–15 cm	0	5.7	14.1	1.50	0.57	10.67	17.0	0.07	82.45
	5	4.4	12.0	1.89	1.45	9.77	16.0	0.46	71.77
	10	5.1	17.5	1.90	0.98	11.10	18.9	0.14	81.14
	15	5.7	27.4	2.78	2.50	10.92	18.8	0.29	71.00
	20	5.3	22.2	2.28	2.39	10.96	19.8	0.35	79.24
	30	5.3	18.3	1.87	1.93	9.70	15.9	0.24	81.46
	50	5.5	16.9	1.96	1.49	10.37	18.6	0.12	83.67
15–30 cm	0	6.8	6.58	0.78	0.50	12.32	16.2	0.32	74.45
	5	5.8	9.93	1.07	0.73	9.61	14.6	0.36	69.64
	10	6.5	7.71	1.02	0.62	13.00	17.9	0.67	88.99
	15	5.7	17.6	1.68	1.31	11.07	18.1	0.51	82.54
	20	5.4	13.0	1.60	1.50	11.26	18.5	0.49	79.03
	30	5.9	9.10	1.04	1.06	9.46	17.5	0.34	87.75
	50	5.3	14.1	0.93	0.85	10.13	16.9	0.32	74.45

SOC: soil organic carbon, TN: total nitrogen, TP: total phosphorus, TK: total potassium, CEC: cation exchange capacity.
[a] Year refers the year under vegetable planting after conversion from paddy field.

field > forest land > fallow land, which indicates that land use has an influence on the degradation of DDT in soils.

In the last two decades, many paddy soils with a long history of rice planting have been converted to vegetable cultivation to meet the demand for vegetables with increasing urbanization in China. According to the China Agricultural Yearbook (ECCAY, 1982, 2004), the cultivated land for rice planting decreased from 33.3 M ha in 1981 to 26.5 M ha in 2003, whereas the area for vegetable planting increased from 3.5 to 17.9 million ha. Some researchers have studied the residues of OCPs in vegetable soils (Chen et al., 2005; Gonzalez et al., 2005) and in paddy soils (Babu et al., 2003) separately. A comparison of OCPs residues between paddy soil and other land use has been reported recently (Li et al., 2006; Wang et al., 2007). However, the impact of the pattern and history of land use change on the residues of OCPs has not been investigated so far. In this paper, Yixing city was selected as a case study area, which is located in the middle of the Yangtse River Delta region and is undergoing the large loss of paddy soil due to urbanization (Pan and Zhao, 2007). We compared the OCPs residues in a series of soils with different ages of vegetable planting since the conversion from paddy field, with the aim to assess the impact of land use change on the OCPs residues in soil.

2. Material and methods

2.1. Investigation area and soil sampling

The investigation area is located in Yixing city, Jiangsu province, China (31°22′18″N, 119°49′45″E). The area is near the Tai Lake and in the middle of the Yangtze River Delta. It has a subtropical monsoon climate with the average annual temperature of 15.7 °C and the average annual rainfall of 1158 mm.

Soil samples were collected from paddy and vegetable fields in Yicheng town, Yixing city in 2003. All the fields sampled were in a vegetable production base. Different tillage ages after conversion from paddy fields to vegetable fields were selected as follows: 0, 5, 10, 15, 20, 30, 50 years, with three replicates for each tillage age. The continuous paddy fields were used as the control treatment with 0 conversion age. All the fields had been used as paddy fields for more than 100 years before the conversion. The paddy soil belong to Fe-leachi Stagnic Anthrosols (CSTRG/ISSCAS and CRGCST, 2001) which are derived from the fluvio-limnic deposition.

Soil samples were collected from the surface layer (0–15 cm) and the sub-surface layer (15–30 cm). Each sample was a composite of 8–10 sub-samples that were mixed, sieved (2 mm) and freeze-dried prior to analysis. De Boer and Smedes (1997) found that the storage conditions had little impact on the contents of chlorobiphenyls and DDT components in the wet biological samples which were stored in screw-cap jars at −5, −25 and −70 °C and in the freeze-dried sample which was stored in the dark at ambient temperature up to 2 year. Each sample was divided into two portions, one for OCPs analysis and the other for soil-geochemical analysis. The hydrometer method was used to determine texture and soil particle size. Soil pH was obtained from a 1:2.5 water–soil slurry and determined by a pH meter (Jackson, 1964). Total *P* was determined according to the colorimetric method with molybdenum vanadate as the color reagent (Jackson, 1964).

Table 1 shows the basic properties of the soil samples. The texture of all soils was silt according to the USDA texture classification, with a mean content of silt (0.002–0.05 mm) of 79.1%. The soil nutrient content was higher in surface layer than the sub-surface layer. Mean soil organic C contents in the surface and sub-surface layer were 20.2 and 13.4 g kg^{-1}, respectively. Soil cation exchange capacity (CEC) was similar in the two layers. All soils were acidic especially in the surface layer which had a mean value of pH of 5.3.

2.2. Reagents and instruments

Standard samples of organochlorine pesticides including α-, β-, γ- and δ-HCH [hexachlorocyclohexane], o,p′-DDT [1,1,1,-trichloro-2(p-chlorophenyl)-2-(o-chlorophenyl)ethane], o,p′-DDE [1,1-dichloro-2-(p-chlorophenyl)-2-(o-chlorophenyl) ethylene], p,p′-DDT [1,1,1,-trichloro-2,2-bis(p-chlorophenyl)ethane], p,p′-DDD [1,1-dichloro-2,2-bis (p-chlorophenyl)-ethane], p,p′-DDE [1,1-dichloro-2,2-bis (p-chlorophenyl)ethylene], α-endosulfan, dieldrin, endrin, HCB [hexachlorobenzene] and pentachloronitrobenzene (PCNB) were purchased from Dr. Ehrenstorfer (Germany) and National Research Center for Certified Reference Materials of China at concentrations of 100.0 mg l^{-1}, respectively. 2,4,5,6-tetrachloro-m-xylene (TCMX) was purchased from Supelco (Bellefonte, PA, USA) and was used as a surrogate for organochlorine pesticides. The standards were further diluted with hexane to prepare working standards. Hexane (HPLC-graded) was from Tedia Company, USA. All other solvents were of the analytical grade and were redistilled before use. Anhydrous sodium sulphate (Na_2SO_4, AR, Nanjing Chemical Reagent Plant, P.R. China) was used as a desiccant. Silica gel (60 ∼ 100 mesh, Dalian Chemical and Physical Institute, P.R. China) and Florisil (E. Merck Company, 60 ∼ 100 mesh) were activated in an oven at 225 °C for 12 h, then deactivated by adding 5% deionized water, and other chemical reagents were of the analytical grade as required.

2.3. Organochlorine pesticides analysis

Analytical procedures were adapted from the standard operating procedures specified in the State Environmental Protection Administration of China methodology guidelines (SEPA, 1993). Ten grams of freeze-dried soil samples in glass

Table 2
The detection limit, recovery and repeatability of the method

OCPs	Detection limit (ng/g)	Recovery (%)[a]	Repeatability (% RSD)
α-HCH	0.10	85.8	3.01
β-HCH	0.10	87.4	3.67
δ-HCH	0.10	85.9	4.04
o,p′-DDT	1.0	98.9	3.36
p,p′-DDT	1.0	96.5	4.83
p,p′-DDD	1.0	92.8	3.25
o,p′-DDE	0.10	100.5	4.22
p,p′-DDE	0.10	101.8	4.07
α-endosulfan	0.10	83.4	2.75
HCB	0.05	102.2	3.99
Diel	0.10	87.2	3.14
Endrin	0.50	97.5	3.22
PCNB	0.08	98.4	4.05

[a] Values as mean of three determinations.