

Concentrations, enantiomeric compositions, and sources of HCH, DDT and chlordane in soils from the Pearl River Delta, South China

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Abstract

Concentrations, and enantiomeric compositions of HCH, DDT and chlordane in 74 soils of the Pearl River Delta, South China were investigated. The mean concentrations of HCHs and DDTs descended in the order: crop soils > paddy soils > natural soils. The concentrations (ng/g dw) of *p,p'*-DDE, *p,p'*-DDT, *p,p'*-DDD and *o,p'*-DDT in crop soils were 0.14–231, 0.07–315, <DL-96.7 and 0.06–73.8, respectively, while those of chlordane were generally below 0.78 for *trans*-chlordane (TC) and 0.75 for *cis*-chlordane (CC). Enantiomeric factors (EF value) were determined for *o,p'*-DDT, α -HCH, TC and CC. Both preferential depletions of (–) enantiomer and (+) enantiomer were observed for *o,p'*-DDT and α -HCH, indicated by EF values either <0.5 or >0.5. An EF value >0.5 generally suggested a preferential degradation of the (–) enantiomers of both TC and CC. The racemic α -HCH observed in the soils with higher HCH concentrations indicated that the transformation from γ -HCH (e.g. lindane) to α -HCH may be an important process in the soils. The isomer ratios of *p,p'*-DDT/(DDE+DDD), *o,p'*-DDT/*p,p'*-DDT and enantiomeric compositions of *o,p'*-DDT suggested that both illegal use of technical DDT and the DDT impurity in dicofol may be responsible for the freshly DDT input in the region. The sources of DDTs were drawn by principal component analysis-multiple linear regression (PCA-MLR). The relative contributions of dicofol-type DDT, residues, and fresh technical DDT were estimated to be 55%, 21% and 17%, respectively. In addition, CC was found to degraded faster than TC in soils from the Pearl River Delta. The study demonstrated that the combination of isomer ratios and enantiomeric composition analysis may provide critical information on the potential sources and fate of organochlorine pesticides in soil.

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Keywords: Soil; HCH; DDT; Chlordane; Enantiomeric fraction; Source; Pearl River Delta; China

1. Introduction

The pollution of organochlorine pesticides (OCPs) are of worldwide concern because of their persistence (Dimond and Owen, 1996), bioaccumulation (Nakata et al., 2002), and negative impacts on human and other animal and plant lives (Jones and de Voogt, 1999).

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Dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) were widely used in China since the 1950s until their production ban in May 1983. The total production of technical HCH (4.9 million tons) and DDT (0.4 million tons) in China, respectively, accounted for 33% and 20% of the global production (Hua and Shan, 1996). Recent observations of OCPs revealed high concentrations of DDTs in the atmosphere in the eastern coast of China, and the current input of fresh DDT to the environment was identified to be mainly of dicofol-type (Jaward et al., 2005; Qiu et al., 2004, 2005; Zhang et al., 2005).

The Pearl River Delta, located in southern China, has gone rapid urbanization and industrialization in the last few decades. It now has a population of more than 38 millions, and a land area of approximately of 40,000 km², contributing 1/9 of the country's Gross Domestic Production in the year of 2005 (GDP, exclusive of Hong Kong and Macau). As one of the most prosperous regions in China, the PRD has a record of the highest pesticide application in the country. The average annual application from 1980 to 1995 reached 37.2 kg ha⁻¹, four times higher than China's average annual application (Huang, 2000). As a region with severe termite problem, chlordanes have been widely used as a termiticide. DDT concentrations in human breast milk from Guangzhou and Hong Kong were reported to be among the highest in the world (Wong et al., 2002). Recent studies revealed that the concentrations of DDT and chlordane in the regional atmosphere were much higher than other parts in East Asia (Jaward et al., 2005). While no significant decrease of DDT concentrations were observed in dated sediment cores from the Pearl River estuary (Zhang et al., 2002), several studies inferred that there were still current fresh inputs of DDT in urban soils and aquatic environment in the Pearl River Delta (Luo et al., 2004; Zhang et al., 2002). Undoubtedly, a better understanding of the sources and fate of OCPs is of critical need for control and management of these pesticides in the subtropical region.

Chemical fingerprints of OCPs have been developed and adopted in identifying/tracking their sources (Harner et al., 1999) and environmental processes, such as their long-range transport (Kallenborn et al., 1998) and air-surface exchange (Bidleman et al., 1998b). Current illegal use of technical DDT and HCH may be traced by their relatively fixed composition patterns. *o,p'*-DDT is indicative of DDTs as impurities in dicofol, a currently widely used pesticide in China (Qiu et al., 2004, 2005). Redistribution, weathering and transport can alter the original composition of OCPs. The relative contents of DDT and its metabolites, DDE and DDD, may provide important information about the freshness of DDTs in the

environment (Harner et al., 1999; Hitch and Day, 1992; Zhang et al., 2002).

A remarkable progress in this field in recent years is the use of the enantiomeric compositions of some chiral pesticides, in particular, such as α -HCH, *o,p'*-DDT, TC, CC, etc. (Bidleman and Falconer, 1999; Kurt-Karakus et al., 2005). Enantiomers have identical physicochemical properties, but often have different toxicological properties and rates of metabolism (Hegeman and Laane, 2002; Muller and Kohler, 2004). Chiral OCPs are frequently degraded enantioselectively in soil by microbial activity, resulting in the accumulation of nonracemic residues (Hegeman and Laane, 2002). The enantiomeric composition can be expressed as EF (Harner et al., 2000), defined as $A_+/(A_+ + A_-)$, where A_+ and A_- correspond to the peak areas of the (+) and (-) enantiomers. A racemic pesticide with an EF value close to 0.5, i.e. without significant enantioselective degradation, can be regarded to be fresh in the environment or to be equal degradation of both enantiomer.

After several decades of application, OCPs in the current environment media are the mixture of historical residues, and fresh inputs from current illegal uses and impurity in other pesticides. The significant diversity of fingerprints of various sources made it possible to apportionment their sources by multiple statistical analysis, like principal component analysis (PCA) with multiple linear regression analysis (Larsen and Baker, 2003; Li et al., 2006; Manz et al., 2001).

In this study, chemical fingerprints including conventional isomer ratios and enantiomeric compositions were applied to identify the potential sources of DDT, HCH and chlordanes in the soils from the Pearl River Delta. The relative contribution of historic residues, current illegal usage of technical DDT and dicofol-type DDT were studied by multivariate analysis tool (e.g. PCA-MLR). The results will be of particular values for understanding the sources and environmental fate of OCPs in an important source region at a global scale.

2. Materials and methods

2.1. Soil sampling

74 soil samples, consisting of 37 crop soils, 14 paddy soils and 23 natural soils, were collected in September 2002 (Fig. 1). The locations of the crop soils were relatively evenly distributed across the region. The majority of the paddy soils are distributed in the relatively less developed areas in the northern and eastern parts of the region. The crop soils were predominantly used for

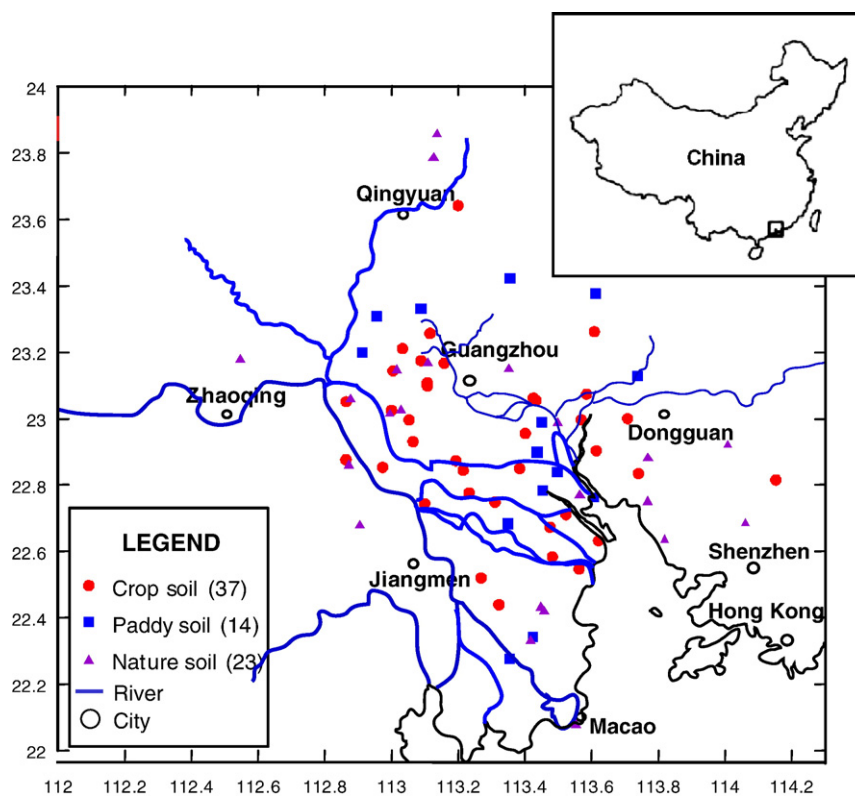


Fig. 1. Map of the Pearl River Delta with sampling locations.

fruit and vegetable production, and the paddy soils for rice culture. The natural soils were generally collected from uncultivated and/or remote sites, in forests or on mountaintops. These soils were generally thin and sandy. The crop and paddy soils consisting of 3–5 subsamples were collected between the depths of 0 and 15 cm, which was representative of the plough layer. Each of the natural soils was made of nine subsamples obtained between 0 and 5 cm. All soil samples were collected using a hand auger and then stored in polyethylene bags. The soil samples were kept at $-18\text{ }^{\circ}\text{C}$ until analysis.

2.2. Analytical procedure

2.2.1. Analysis of OCPs

In the laboratory, soil samples were thawed and freeze-dried for 24 h, pulverized and sieved through a 100-meshed stainless steel mesh. About 50 g of the subsamples were Soxhlet-extracted for 48 h with dichloromethane (DCM) (both DCM and hexane obtained from Merck and Co., Inc.). A mixture of surrogate standards of 2,4,5,6-tetrachloro-*m*-xylene (TCmX) and decachlorobi-

phenyl (PCB209) was added to each of the samples prior to extraction. Activated copper granules were added to the collection flask to remove elemental sulfur. The extract was concentrated and solvent-exchanged to hexane and purified on an 8 mm i.d. aluminum/silica column packed, from the bottom to top, with neutral aluminum (6 cm, 3% deactivated), neutral silica gel (10 cm, 3% deactivated), 50% (on a weight basis) sulfuric acid silica (10 cm), and anhydrous sodium sulfate. Before used, neutral aluminum, neutral silica gel, and anhydrous sodium sulfate were Soxhlet-extracted for 48 h with DCM, and then baked for 12 h in 250, 180, and $450\text{ }^{\circ}\text{C}$, respectively. The column was eluted with 50 ml of dichloromethane/hexane (1:1) to yield the organochlorine pesticides fraction. The fraction was concentrated to 0.2 ml under a gentle nitrogen steam. A known quantity of pentachloronitrobenzene (PCNB) was added as an internal standard prior to GC-MS analysis.

GC-MS analysis was carried out on an Agilent-5975 GC-MSD system with a CP-Sil 8 CB capillary column (50 m, 0.25 mm, 0.25 μm), operating under single ion monitoring (SIM) mode. Helium was used as the carrier gas at $1.2\text{ mL}\cdot\text{min}^{-1}$ under constant-flow mode. Helium

was filtered with moisture, hydrocarbon, and oxygen filters before entering the GC system. The oven temperature began at 60 °C for 1 min and increased to 290 °C (10 min hold time) at a rate of 4 °C·min⁻¹. Split/splitless injection of a 1 µL sample was performed with a 5 min solvent delay time. Injector temperature was at 250 °C. The inlet degradation of DDT was checked daily and controlled within 15%.

2.2.2. Chiral analysis

Enantiomer analysis was done by GC-MS (GC-NIMS) on an Agilent 6890 GC 5975 MSD with methane at a nominal pressure of 1.0 Torr. The column used was a BGB-172 (20% *tert*-butyldimethylsilylated β-cyclodextrin in OV-1701) column (Analytik AG, Switzerland). The analytical method was previously described elsewhere (Bidleman et al., 1998a). Ions monitored were α-HCH, 255/257; CC and TC, 408/410; *o,p'*-DDT, 246/248. To ensure peak purity, ion ratios for each compound were compared to the racemic standard (Ehrenstorfer Laboratories, Augsburg, Germany) which was run in every 8 samples during chiral analysis, and were always within 5%. Average EF values of the standards were 0.504±0.001 for α-HCH, 0.500±0.004 for TC, 0.501±0.004 for CC, and 0.501±0.007 for *o,p'*-DDT. Replicate analysis was done for four samples. The precision of the enantiomer analysis for these replicates was high, with the relative standard deviation (RSD) ranging between 0.9 and 2.7%.

2.2.3. Quality control

Method blanks (solvent), duplicate samples and spiked blanks (standards spiked into solvent) were analyzed. In addition, surrogate standards were added to each of the samples to monitor procedural performance and matrix effects. The recovery ratios for the surrogates in the samples conform to the reported ranges by US EPA. The average recoveries were 76±11% and 85±7% for TCmX and PCB209, respectively. The concentrations

of OCPs were corrected according to the recovery ratios for the surrogates.

3. Results

3.1. Soil pH

The average soil pH of the crop, paddy and natural soils were 5.88 (4.06–7.22), 5.76 (5.69–5.90), and 4.56 (4.07–5.18), respectively.

3.2. Soil Total organic carbon (TOC)

Total organic carbon (TOC) content ranged from 0.27% to 2.02% for crop soils, 0.58% to 1.56% for paddy soils and 0.32% to 4.94% for nature soils.

3.3. Concentrations of HCH, DDT and Chlordane

Descriptive statistics of OCPs concentrations of the crop, paddy and natural soils are presented in Table 1. The mean concentrations of total HCHs and DDTs descended in the order: crop soils > paddy soils > natural soils, whereas, only pesticides in the natural soils were significantly ($p < 0.001$) lower than crop soils and paddy soils. The total HCH concentrations in the crop soils ranged from 0.05 to 24.1 ng/g with a median value of 2.94 ng/g, while the total DDT concentrations spanned several orders of magnitude, ranging from 0.52 ng/g to 414 ng/g with a median value of 20.1 ng/g. In the paddy soils, the total HCH concentrations ranged from <DL to 10.5 ng/g with a median value of 3.01 ng/g, and the total DDT 2.23 to 232 ng/g with a median value of 24.7 ng/g. The concentrations of total HCHs and total DDTs in the nature soils ranged from <DL to 4.03 ng/g (median 0.39 ng/g), and from 0.27 to 7.99 ng/g (median 3.23 ng/g), respectively. Levels of chlordanes in the soil samples ranged from <DL to 13.7 ng/g for TC and from <DL to 15.5 ng/g for CC (Table 1). The majority of the soils

Table 1
HCH, DDT and chlordane concentrations in crop soils, paddy soils, and natural soils from the Pearl River Delta (DL: detection limit)

Subgroup	ng/g	α-HCH	β-HCH	γ-HCH	δ-HCH	<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>p,p'</i> -DDT	<i>o,p'</i> -DDT	TC	CC
Crop soils (37)	Mean	1.08	2.49	0.90	0.50	21.9	7.22	20.9	6.34	0.62	0.71
	Median	0.80	1.26	0.54	0.42	7.82	2.70	4.64	0.80	0.42	0.40
	Range	<DL-3.48	0.05–16.0	<DL-4.43	<DL-1.28	0.14–231	0.06–73.8	0.07–305	<DL-96.7	<DL-6.13	0.10–7.74
Paddy soils (14)	Mean	0.89	1.76	0.62	0.38	19.4	23.4	2.98	0.91	0.42	0.36
	Median	0.78	1.14	0.45	0.26	12.6	7.64	1.05	0.33	0.47	0.40
	Range	<DL-2.76	<DL-7.01	<DL-2.03	<DL-1.02	1.64–66.6	0.07–163	0.19–22.4	0.12–4.92	<DL-0.76	<DL-0.56
Natural soils (23)	Mean	0.25	0.27	0.11	0.20	0.82	0.53	1.40	0.46	1.53	1.61
	Median	0.17	0.11	0.04	0.14	0.71	0.48	1.12	0.41	0.45	0.38
	Range	<DL-1.46	<DL-1.11	<DL-0.75	<DL-0.70	<DL-2.22	0.05–1.40	0.09–4.20	0.05–1.22	<DL-13.7	<DL-15.5

were below 0.78 ng/g for TC and 0.75 ng/g for CC, except for six soils that had higher values for both the compounds.

The DDT concentrations in crop and paddy soils in this study were similar to those reported in paddy soils in Dehradun of India (13–238 ng/g) (Babu et al., 2003), lower than those reported in soils (range from 3.58 to 831 ng/g) in Guangzhou (Chen et al., 2005), Tianjin (range from 628.1 to 2840.5) (Gong et al., 2002), the US Corn Belt (range from n.d. to 11 800 ng/g) (Aigner et al., 1998), Romania (range from 9.0 to 1542.2 ng/g) (Covaci et al., 2001) and Vietnam (average 110 ng/g) (Thao et al., 1993).

The HCH concentrations are similar to that in vegetable soils of Guangzhou (0.19–42.3 ng/g) (Chen et al., 2005), much lower than those in Tianjing (386.5–4689.1 ng/g) (Gong et al., 2002) and Dehradun of India (122–638 ng/g) (Babu et al., 2003). Moreover, given the factor that China is one of the largest HCH users, the natural soils showed HCH concentrations comparable to residual levels in archived background soils in UK (0.1–10 ng/g; (Meijer et al., 2001) and European high altitude mountains (HCHs: 0.08–0.49 ng/g; (Grimalt et al., 2004), and in Korea (<3 ng/g, (Kim and Smith, 2001). This might give the evident of the global transport of POPs from low latitude areas to high latitude areas (Valle et al., 2005; Wania and Mackay, 1995).

The TC and CC concentration in the soils were higher than those from Lake Tai in China (0.04±0.01 ng/g) (Nakata et al., 2005) and in archived soils in UK (range from <0.05 to 1.6 and from <0.07 to 1.0 ng/g) (Meijer et al., 2001). The median value were similar to that of soils from US corn belt (0.49 and 0.43 ng/g) (Aigner et al., 1998), but the highest value are much lower than those of soils from US corn belt (560 and 199 ng/g) (Aigner et al., 1998).

The spatial distribution of HCHs and DDTs was similar, with higher levels found at the center of the Pearl River Delta. The soils with higher concentrations of chlordane scattered across the region. In addition, the concentrations of OCPs in the soils showed no significant correlation with the total organic carbon (TOC) content and pH value of soils.

3.4. Enantiomer fractions

Results of enantiomeric composition analysis of the soils are presented in Table 2. A wide range of EFs was found with values below and above racemic (EF=0.500). For chlordane, soils of different land-use in this study generally showed the preferential degradation of the (–) enantiomer, both for TC and CC (EF>0.5). This was

Table 2

Summary statistics for EFs of α -HCH, *o,p'*-DDT, TC and CC in the Pearl River Delta soil samples

Soils	EF	α -HCH	<i>o,p'</i> -DDT	TC	CC
Crop (37)	Mean	0.515	0.546	0.545	0.545
	Std	0.104	0.102	0.112	0.069
	Range	0.424–	0.265–	0.237–	0.409–
		0.910	0.801	0.885	0.740
	N	33	30	32	32
Paddy (14)	Mean	0.495	0.499	0.567	0.541
	Std	0.033	0.151	0.077	0.043
	Range	0.411–	0.154–	0.487–	0.482–
		0.531	0.797	0.734	0.602
	N	13	14	9	9
Natural (23)	Mean	0.557	0.534	0.555	0.561
	Std	0.187	0.058	0.057	0.110
	Range	0.382–	0.180–	0.427–	0.352–
		0.904	0.789	0.729	0.813
	N	18	22	20	20

Note: Std. standard deviation, N. number of samples.

opposite to the pattern observed in agricultural soils and archived soils in the UK, and most of the background soils reported in the literatures (Aigner et al., 1998; Kurt-Karakus et al., 2005; Meijer et al., 2001). For *o,p'*-DDT, preferential depletion of either enantiomer (EF<0.5 or >0.5) was observed, similar to those observed in agricultural soils from a variety of locations such as Alabama, the Midwestern US, British Columbia, Hawaii (Bidleman et al., 2000) and in background soils around the world (Kurt-Karakus et al., 2005). For α -HCH, the racemic residues were observed in most agricultural soils, but a preferential degradation of (–) enantiomer (EF>0.5) observed in most of the natural soils. In addition, the EF values showed no significant correlation with the total organic carbon (TOC) content and pH value of soils.

4. Discussion

4.1. Sources and potential fate of HCHs

Two types of hexachlorocyclohexane products are manufactured throughout the world: technical HCH containing about 55–80% α -HCH, 5–14% β -HCH, 8–15% γ -HCH and minor proportions of minor isomers, and lindane (γ -HCH>99%). The production of technical HCH was banned in 1983 in China; lindane is currently used for pest control. Based on the composition of the two main HCH pesticide formulations, a high α/γ -ratio of HCHs in soils should indicate the input of technical HCH and a low ratio for the use of lindane.

In the studied soils, the mean values of α/γ -ratios of HCHs were 1.9, 2.6 and 1.0 in crop, paddy and nature soils, respectively (refer to Table 1), which were lower

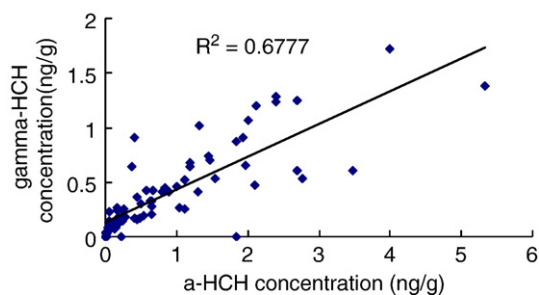


Fig. 2. Relationship of α -HCH and γ -HCH in soil samples.

than that of technical HCH, indicating that the HCHs in the studied soils were a cocktail of technical HCH and lindane application. Among the HCH isomers, β -HCH is the most persistent and less volatile isomer and tends to accumulate in soils (Buser and Muller, 1995; Li, 1999). As shown in Table 1, β -HCH isomer predominated the HCH compositions in the studied soils, with mean percentages of 44.2 and 44.3 in crop and paddy soils, respectively. This was much higher than that of technical HCH (5–14% of β -HCH), indicating a past (historical) local technical HCH contamination, rather than current input.

It is interesting to note that, even in the mixture of past technical HCH and current lindane application, a significant correlation between α -HCH and γ -HCH was still observed in the studied soils (Fig. 2). And the α -HCH in higher concentration samples were racemic or close to racemic, with EFs ≈ 0.5 (Fig. 3), which in turn indicated a fresh source of α -HCH, contrary to the past application of technical HCH. The *in situ* transform from γ -HCH to

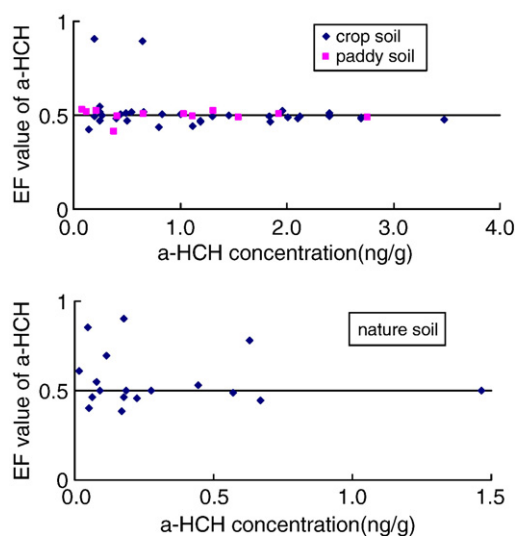


Fig. 3. Enantiomer fraction of α -HCH in soil samples (A: crop and paddy soil, B: nature soil).

α -HCH seems to be the best explanation here, both in terms of maintaining the correlation between each other, and deriving racemic α -HCH.

The potential for γ -HCH to be transformed into other isomers of HCH was well documented (Walker et al., 1999). In particular, γ -HCH may be transformed by sunlight and through biological degradation in soil into α -HCH (Benezet and Matsumura, 1973; Malaiyandi and Shah, 1980; Newland et al., 1969; Steinwandter and Buss, 1975). In sewage sludge under anaerobic conditions, it was observed that a small percentage of γ -HCH in the active sludge during incubation could be transformed into α - or δ -HCH by nonenantioselective isomerization, though the rate of conversion was extremely slow (Buser and Muller, 1995). The Pearl River Delta is located in the subtropical zone with strong ultraviolet radiation in summer and the anaerobic environment dominates in most times in the agricultural soils. Our

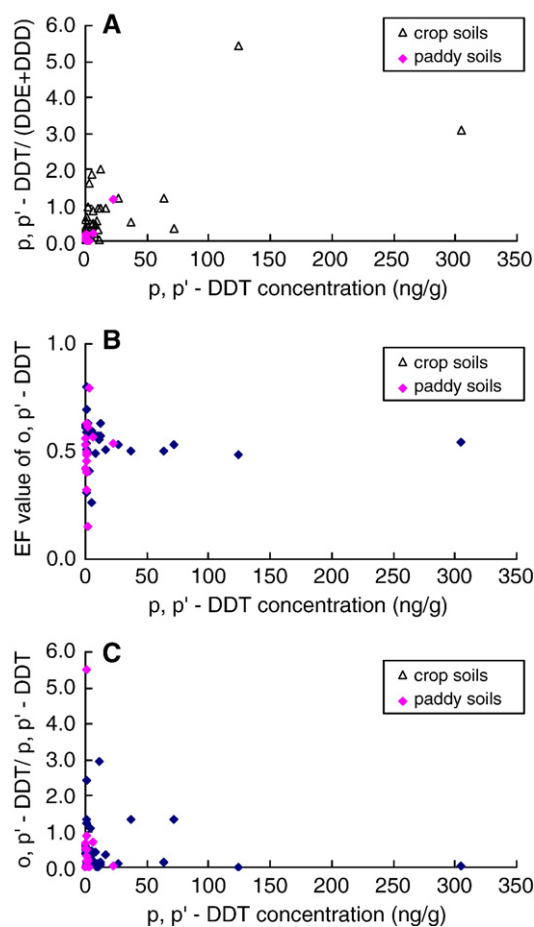


Fig. 4. p,p' -DDT concentrations in crop and paddy soil samples with the ratios of p,p' -DDT/(DDE+DDD) (A), EF values of o,p' -DDT (B) and the ratios of o,p' -DDT to p,p' -DDT (C).

results suggested that the transformation from γ -HCH into α -HCH under such natural conditions may be significant in the studied soils.

4.2. Sources of DDTs

In soil, DDT is microbially transformed to the stable and toxic metabolites DDE and DDD. The rate of transformation depends on several factors, including soil type, temperature, moisture and organic carbon content (Hitch and Day, 1992). In general, a small value of DDT/(DDE+DDD) ratio is indicative of aged (microbially degraded) DDT, and a value much greater than one indicates fresh application. In this study, the DDT/(DDE+DDD) ratios varied among the soils of different land-uses. For agricultural soils, crop soils had more p,p' -DDT relative to its metabolites than paddy soils (Fig. 4A), and generally showed DDT/(DDE+DDD) ratios larger than one. High DDT contents relative to DDD and DDE suggested that DDT may be freshly introduced into the crop soils. Besides isomer ratios,

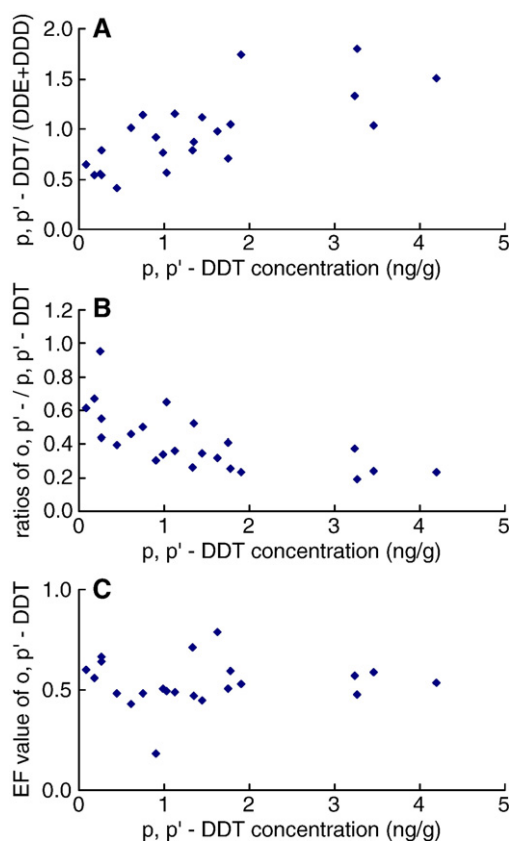


Fig. 5. p,p' -DDT concentrations in nature soil samples with the ratios of p,p' -DDT/(DDE+DDD) (A), the ratios of o,p' -DDT to p,p' -DDT (B) and EF value of o,p' -DDT (C).

Table 3

Factor pattern for DDTs in soils from the Pearl River Delta

	Factor 1	Factor 2	Factor 3
p,p' -DDE	0.81	0.41	0.16
p,p' -DDD	0.22	0.96	0.07
o,p' -DDT	0.94	0.09	0.12
p,p' -DDT	0.16	0.08	0.98
Loading	55.4	21.1	16.6

enantiomeric fractions of o,p' -DDT could be as another feasible approach to provide further information about whether it is being currently applied or residue from past application (Kurt-Karakus et al., 2005).

As shown in Fig. 4B, the EF values of o,p' -DDT in the soils with high p,p' -DDT concentrations were mostly close to 0.5, indicating a fresh input of (racemic) o,p' -DDT to the soils. This was consistent with the high DDT/(DDE+DDD) ratios.

Both direct application of technical DDT and DDT-containing dicofol may introduce DDT to the environment. As technical DDT contains less o,p' -DDT ($\approx 15\%$) than p,p' -DDT ($\approx 85\%$), and dicofol has reverse pattern (Qiu et al., 2005), fresh input of DDTs from technical DDT hence can be distinguished from dicofol by the o,p' -DDT/ p,p' -DDT ratio. As shown in Fig. 4C, both high and low values of o,p' -DDT/ p,p' -DDT ratios were found, implying that both dicofol-type DDT and technical DDT by illegal use may be present in the crop soils.

The total DDT concentrations in natural soils were significantly lower than those in agricultural soils (Table 1). p,p' -DDT predominated and comprised of 40% of total DDTs. Among the 25 natural soil samples analyzed, 10 of them displayed ratios of DDT/(DDE+DDD) larger than 1 (Fig. 5A), implying that there was possible recent DDT input to the soils. The ratios of o,p' -DDT/ p,p' -DDT (ranged from 0.19 to 0.95 with a mean value of 0.42) in natural soils were lower than that of dicofol, but higher than that of technical DDT (Fig. 5B). In the environment, o,p' -DDT metabolizes more quickly than p,p' -DDT (Martijn et al., 1993), this will result in observed lower o,p' -DDT/ p,p' -DDT ratios than those of the product formulas. The mixing of technical DDT and dicofol-type DDT can also result in an o,p' -DDT/ p,p' -DDT ratio between the two origins. The EF value of o,p' -DDT can provide more information about biodegradation of o,p' -DDT. As shown in Fig. 5C, o,p' -DDT present in the natural soils was generally a mixture of bio-degraded (aged) and fresh ones. It is interesting that the o,p' -DDT in those four soil samples with higher p,p' -DDT concentrations displayed EF values close to 0.5, and the lowest o,p' -DDT/ p,p' -DDT ratios.

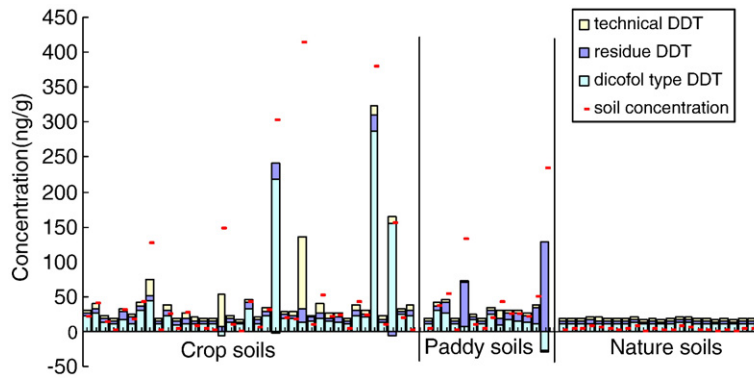


Fig. 6. Patterns of DDTs in soils by principal component analysis/multiple linear regression (PCA/MLR).

This may be indicative of a new input from illegal use of technical DDT in the study area.

Principal component analysis (PCA) with multiple linear regression (MLR) analysis could be used to apportionment the different sources of organic pollutants in environment (Larsen and Baker, 2003; Li et al., 2006; Manz et al., 2001). This approach applied to DDT in soils might be some limitation for that DDT and its metabolites behavior were not in same way. However, due to their persistent in environment, DDT sources in soils might be apportionment by PCA-MLR (Larsen and Baker, 2003; Li et al., 2006; Manz et al., 2001). Factor analysis was conducted for 4 DDT isomers. The first three factors accounted for 94% of the total variance in the data set. Factor 1 explained 55% of the total variance. As shown in Table 3, *p,p'*-DDE and *o,p'*-DDT formed a closely associated group. *o,p'*-DDT was considered to be the major impurity compound in dicofol, and *p,p'*-DDE was the conversion of *p,p'*-Cl-DDT which was another major compound in dicofol (Qiu et al., 2005). Therefore, factor 1 was mostly related to dicofol usage. The second factor, which accounted for 21% of total variance, is highly dominated by *p,p'*-DDD, and moderately involved by *p,p'*-DDE. *p,p'*-DDD was a very minor isomer

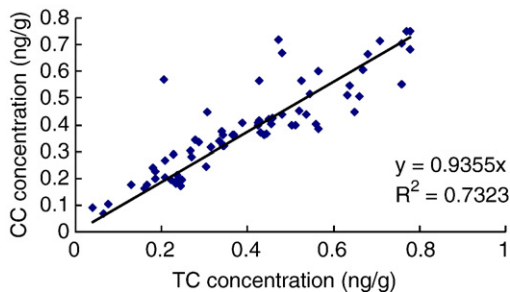


Fig. 7. Relationship of TC and CC in most soil samples with low concentrations.

compared with other isomers in technical DDT and dicofol, and was metabolite of *p,p'*-DDT as well as *p,p'*-DDE. So this factor may be related to the residue of technical DDT. The factor 3 explained 17% of the total variance, and was mainly controlled by *p,p'*-DDT which was the predominant compound in technical DDT. Therefore, this factor may be related to fresh technical DDT usage.

Individual contribution of different sources to the total DDT in the soils was obtained by multiple linear regressions. As shown in Fig. 6, dicofol-type and

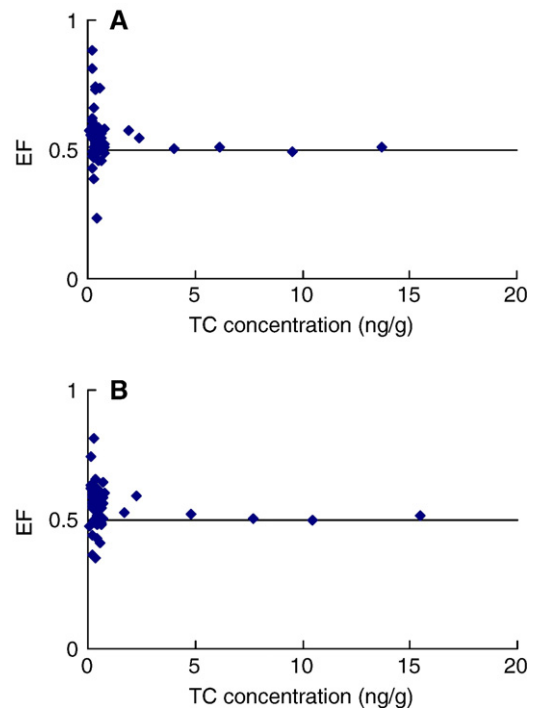


Fig. 8. TC (A) and CC (B) concentrations in soil samples with EF values.

technical DDT were freshly introduced to crop soils; residue of DDT contributed the largest proportion of DDTs in paddy soils, and cocktail of three types DDT coexisted in natural soils.

4.3. Chlordanes

Technical chlordane was used mostly as an agricultural pesticide on corn and citrus, for home lawns and gardens, as well as a termiticide in house foundation. Previous studies revealed that chlordane is widespread in the environment (Aigner et al., 1998; Bidleman et al., 2000; Hegeman and Laane, 2002; Jantunen et al., 2000). There have been very few work concerning chlordane contamination in the environment of China (Nakata et al., 2005), though it has been widely used in termite control. The most abundant components in the technical mixture are TC and CC. Though in a previous study, a TC/CC ratio of 1.18 in the technical mixture was reported (Jantunen et al., 2000), that of 0.76–0.87 in a technical chlordane mixture commercially available in the Pearl River Delta was observed in this study.

In the studied soils, the ratios of TC/CC ranged from 0.36 to 1.47. For the majority of the soils with lower chlordane concentrations, TC and CC concentrations correlates significantly with each other (Fig. 7), displaying a median TC/CC ratio of 1.04. However, for the four soil samples with highest value (both TC and CC >4 ng/g), the ratios ranged from 0.79 to 0.91, and were different from most of the reported data (Aigner et al., 1998; Meijer et al., 2001), but were compared with the ratio (TC/CC=0.76–0.87) of commercial technical chlordane in Guangzhou market. The enantiomeric fractions of TC and CC in those four soils were racemic (Fig. 8). For another two soils with a bit high chlordane concentration (ranged from 1.72 to 2.43 ng/g), the TC/CC ratios changed to 1.06 and 1.11, and their enantiomeric compositions turned to be nonracemic (Fig. 8). This indicated that the degradation of CC might be faster than TC in soils of the PRD region.

5. Conclusion

The present study examined the distribution and profile of HCH, DDT, and Chlordane in the crop, paddy and natural soils of the Pearl River Delta, South China. Enantiomeric fractions of α -HCH, *o,p'*-DDT, TC, and CC of most of the soils were also analyzed. In the PRD, HCH and DDT enrichment in both the crop and paddy soils may indicate the influence of cultivation in the past, and present inputs, and the elevation of TC and CC in some soils may indicate the chlordane usage in house

foundation. The relatively low concentration of DDT, HCH and chlordane in soils of the tropic region compared to temperate or cold region might be the evident of the global transportation of this kind pollutant. Isomer ratio combined the enantiomeric fraction might indicate the OCPs environmental fate. It was found that the transform from γ -HCH into α -HCH under such natural conditions might be significant in the studied soils. The sources of DDTs were drawn by principal component analysis-multiple linear regression (PCA-MLR). The relative contributions of current dicofol-type DDT application, past DDT residues, and fresh technical DDT usage were calculated to be 55%, 21% and 17%, respectively. The variations of isomer ratios and enantiomeric fractions of chlordane in soils compared with that of the commercial technical chlordane in Guangzhou market implied that CC might degrade faster than TC in the soils from the Pearl River Delta.

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