

Dicofol application resulted in high DDTs residue in cotton fields from northern Jiangsu province, China

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Received 1 February 2007; received in revised form 15 April 2007; accepted 16 April 2007

Available online 21 April 2007

Abstract

Dicofol with high impurity of DDT compounds is still widely used in agricultural practice such as cotton cultivation and becomes an important source of DDT pollution in China. In this study, investigations on the DDT residues in cotton fields from northern Jiangsu province, China were conducted. The results showed that DDTs in cotton soil were much higher than other mode of land use. The DDTs levels ranged from 4.2 to 678.6 ng g⁻¹, with a mean concentration of 190.4 ng g⁻¹, of which the most abundant compounds were *p,p'*-DDE (mean of 129.38 ng g⁻¹), *p,p'*-DDT (mean of 26.57 ng g⁻¹) and *o,p'*-DDT (mean of 16.92 ng g⁻¹). The concentrations of *o,p'*-DDT and *o,p'*-DDE were significantly higher ($p < 0.05$) in topsoil (0–10 cm) than in subsoil (10–20 cm), while other DDT compounds were not. Source apportionment showed that dicofol-type DDT accounted for up to 80% of the DDTs residue. All the results indicated that dicofol applications resulted in serious DDT pollution in cotton fields. Our work provided implications for reasons why there was no apparent decrease of DDT level in China.

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Keywords: Organochlorine pesticide; DDT; Dicofol; Cotton field

1. Introduction

Because of their persistence, bioaccumulation, toxicity and long-range atmospheric transport, the pollution of organochlorine pesticides (OCPs) such as DDT is still widely concerned [1–4].

China has been a major producer and consumer of DDT since the 1950s until its production ban in 1983 [5,6]. Over the 30 years the total production of DDT was about 0.4 million tonnes, accounting for nearly 20% of the global production. After 1983, DDT production still continues primarily due to the demand of malaria control and production of dicofol. Additionally, China has requested for specific exemption of DDT under the Stockholm Convention till 2009. Statistical data showed that from 1988 to 2002, the average annual DDT production was about 6000 t in China, of which, nearly 80% was for dicofol production [7]. The dicofol production reduced gradually in recent years (e.g. the production was 1518.3 t in year

2005, only 30% of that in year 2000) and would be completely eliminated in the future several years [8], however, in the production procedure, dicofol contains high impurity of DDT-related compounds, and therefore becomes an important source of DDT in China [9,10]. Dicofol with impurity of DDTs above the national standards is still available in the Chinese market. An investigation on the impurity content in commercial dicofol revealed the average contents of *o,p'*-DDT, intermediate 2,2,2-trichloro-1,1-bis(4-chlorophenyl)-1-chloroethane (α -chloro-DDT), *o,p'*-DDE, and *p,p'*-DDT in the samples were as high as 114, 69, 44 and 17 g/kg dicofol, respectively [7].

Large applications of dicofol in agricultural practice especially in cotton cultivation have resulted in serious environmental pollution in China. A study on the atmospheric concentration revealed that the concentrations of DDT in China were much higher than other parts in East Asia [11]. Air samples collected over Taihu Lake during the summer of 2002 displayed very high concentrations of DDTs and the authors suggested dicofol was the significant important source of DDT [12]. The investigation on the DDT in dated sedimentary cores from the Pearl River estuary, in the south of China, found there was little

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sign of any declining trend in DDT concentrations [10]. High concentrations of DDT were also detected in different food items including marine products, eggs, dried fruits and vegetables [13]. Moreover, a survey on the DDT contamination in human milk revealed that the Chinese population exhibited rather high concentrations of DDTs [14].

As far as the temporal and spatial characteristics of dicofol application were concerned, Jiangsu province might be subject to serious DDT pollution because of the large cotton cultivation areas and the corresponding intensive dicofol application. For example, in 1998, cotton cultivation area was 0.42 million ha. In recent years, cotton cultivation in Jiangsu province is mainly located in the north and accounts for 96.4% of total cultivation areas. Consequently, the DDT pollution in the north was truly higher than in the south [15]. Therefore, it was considered that the north cotton cultivation area was one of the significant source areas of atmospheric DDT in the south of Jiangsu province [12].

However, few efforts have been made on the DDT residue in cotton fields, and it is not known yet to what extent the cotton fields were polluted due to dicofol application. Moreover, there is too little information to answer the questions as follows: (1) Are the DDT residues in soil consistent with the DDT impurity in dicofol? (2) Are the DDTs residue patterns in soil consistent with the pattern in air of southern Jiangsu province e.g. around Taihu Lake? (3) Does the technical DDT historically applied still persist in the cotton field? If anything, what is the proportion for dicofol and technical DDT? In an attempt to provide implications for these questions as well as for the risk assessment and

pesticide management, the DDT residue in the cotton fields of northern Jiangsu province was studied and some characteristics of DDT residue were found.

2. Materials and methods

2.1. Study area and sample collection

Soil samples were collected from Tongzhou and Qidong (see Fig. 1), where the cotton cultivation had a long history and in 2006 the cultivation areas were about 6800 ha, accounting for 86% of the cotton cultivation areas and 10% of the total arable field of Nantong. Nantong is located in the north of Jiangsu province and in the northern bank of the estuary of Yangtze River. The topography of this area is characterized by plain. The climate is northern subtropical. The average annual temperature is 15.1 °C and the normal annual precipitation is 1060 mm. The dominant soil types are silt loam. Twenty-nine cotton soil samples were collected in August 2006, and five vegetable soil samples were also sampled with the expectation that these sites could be used as “background soils”. At each sample location, five cores were scooped with a pre-cleaned stainless steel scoop from a 100 m × 100 m plot and then mixed to provide a composite sample. Topsoil sample (from 0 to 10 cm depth) and subsoil sample (10 to 20 cm) were separately mixed for each sample location. The samples were sealed in polythene bags, air-dried, then passed through 2-mm sieve and stored in cool condition till analysis.

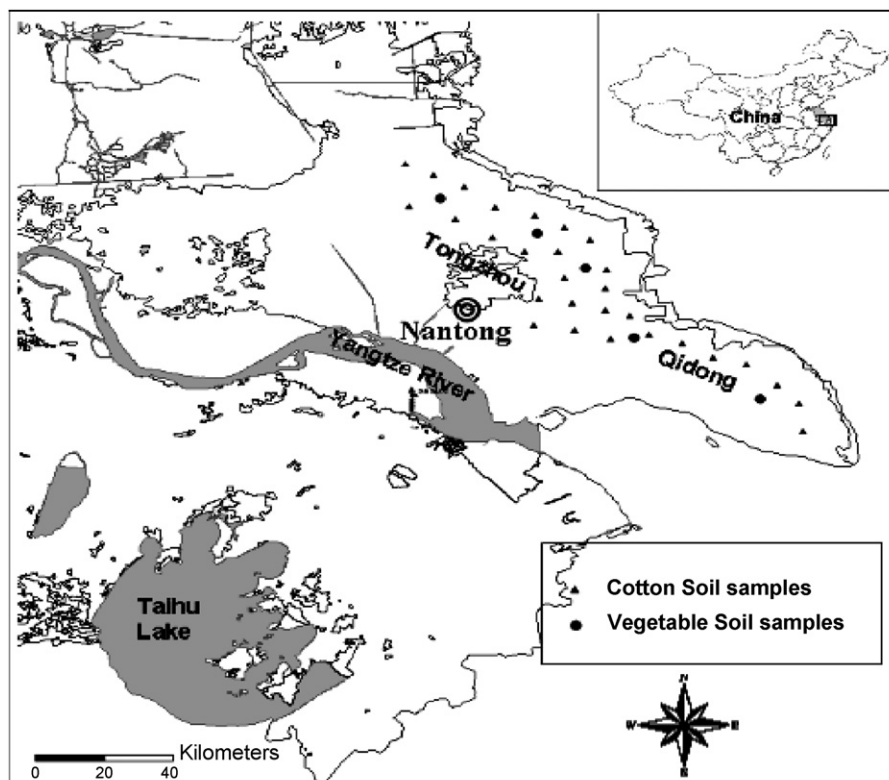


Fig. 1. Map of Nantong showing soil sampling locations.

2.2. Sample extraction and cleanup

The extraction method for DDTs was based on accelerated solvent extraction (ASE). DDTs extraction were performed with an ASE-200 (Dionex, USA) at a temperature of 100 °C, pressure of 1500 psi and static time of 5 min. Hexane/acetone (4:1, v/v) was used as extraction solvent. To eliminate water, about 1 g anhydrous sodium sulfate (Na_2SO_4) was added into each vial of the soil extracts. Then the extract was concentrated first to 2 ml by a rotary evaporator, cleaned up with cartridges containing acid silica gel/anhydrous sodium sulfate, and finally eluted with 15 ml petroleum ether: DCM (9:1). All solvents were spectroscopic grade.

2.3. DDTs analysis

Quantification was achieved by Agilent 6890 gas chromatography equipped with a ^{63}Ni electro-capture detector (ECD) and an HP-5 fused capillary column (30-m length, 0.32-mm internal diameter, and 0.25- μm film thickness). The samples were quantified using external standard. To assure data quality, spike recovery samples containing known quantitation of the pesticide mixture standards were used to evaluate extraction efficiency. Average recoveries of the selected compounds ranged from 91% for *o,p'*-DDE to 98% for *p,p'*-DDT. Laboratory blank values for all the compounds were generally low and posed no problem to the analytical quantitation. The overall reproducibility was evaluated using the replicate analyses ($n=3$). The coefficient of variation (CV) was between 0.01 and 0.35 for the different compounds, and it was less than 0.3 in 90% of the cases. Thus, the reproducibility of the measurements was considered to be satisfactory.

3. Results and discussion

3.1. DDT residues in cotton soil

For cotton topsoil samples (0–10 cm), *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT were detected in all the samples, *o,p'*-DDT were detected in 28 of 29 samples, and *o,p'*-DDE was detected in 27

of 29 samples. The mean concentrations, median concentrations and concentration ranges of each DDT compound in cotton soil were summarized in Table 1. It showed that the total DDTs ($\sum\text{DDT}$, the summation of *o,p'*-DDE, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT) in cotton topsoil ranged from 6.29 to 678.60 ng g^{-1} , with a mean concentration of 185.66 ng g^{-1} . The most abundant compound was *p,p'*-DDE (1.72–545.90 ng g^{-1}), followed by *p,p'*-DDT (1.34–108.63 ng g^{-1}) and *o,p'*-DDT (ND ~57.26 ng g^{-1}). The concentration of the DDTs was higher by a factor of about 4 when compared with the DDTs concentrations in Alabama soils reported by Harner et al. [16].

with regard to the cotton subsoil samples (10–20 cm), the total residues of DDTs ranged from 4.20 to 623.80 ng g^{-1} , with a mean concentration of 195.00 ng g^{-1} , quite similar to the residue level in topsoil. Moreover, most of the DDT compositions in subsoil resembled these in the topsoil, e.g. the predominant compounds in subsoil were also *p,p'*-DDE (1.83–500.90 ng g^{-1}), *p,p'*-DDT (0.76–123.92 ng g^{-1}) and *o,p'*-DDT (ND ~27.74 ng g^{-1}). It was very interesting to note that the independent-samples *t* test showed that the residue levels of *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD were not significant different ($p>0.05$) between topsoil and subsoil, while the residue levels of *o,p'*-DDT and *o,p'*-DDE were significantly higher ($p<0.05$) in topsoil than that in subsoil (see Table 2). This interesting observation would be discussed later.

One-sample Kolmogorov–Smirnov test for all the 58 cotton soil samples (including topsoil and subsoil) showed that the frequency distribution of DDTs residues in the cotton soil was normal ($p<0.05$). The wide variability in soil concentrations probably reflected differences in historical pesticide application [16]. According to National Environmental Quality standards for Soils of China (GB15618-95), the DDTs contents in 15 samples were lower than the first grade (<50 ng g^{-1}), and contents in 37 samples were between the first and the second grade (<500 ng g^{-1}), and those in six samples were between the second and third grade (<1000 ng g^{-1}) (see Fig. 2). Namely, about 74.1% of the cotton soil samples were moderately polluted, and about 10% were seriously polluted. Therefore, it suggested that pesticide management and remediation measurement should be taken to control the

Table 1
DDTs residue levels in cotton soil and vegetable soils

Soil group	Horizon	ng g^{-1}	<i>o,p'</i> -DDE	<i>o,p'</i> -DDT	<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>p,p'</i> -DDT	$\sum\text{DDT}^a$
Cotton soil	Topsoil	Mean \pm S.D.	2.59 \pm 1.77	16.92 \pm 14.43	129.38 \pm 144.03	2.54 \pm 1.75	26.57 \pm 25.12	185.66 \pm 173.45
		Median	2.29	12.93	88.97	2.04	21.07	141.68
		Range	ND–6.34	ND–57.26	1.72–545.90	0.46–8.16	1.34–108.63	6.29–678.6
	Subsoil	Mean \pm S.D.	1.68 \pm 1.06	11.12 \pm 8.42	139.10 \pm 150.05	2.65 \pm 2.09	31.40 \pm 33.92	195.00 \pm 185.12
		Median	1.33	7.98	90.85	1.96	22.6	128.05
		Range	ND–4.00	ND–27.74	1.83–500.90	0.33–8.02	0.76–123.92	4.20–623.8
vegetable soil	Topsoil	Mean \pm S.D.	0.83 \pm 0.53	1.99 \pm 1.53	6.02 \pm 4.10	1.59 \pm 1.09	3.52 \pm 2.10	13.96 \pm 7.08
		Median	0.88	2.00	5.05	1.52	3.18	12.76
		Range	ND–1.58	ND–4.60	2.17–13.34	0.46–3.01	1.34–7.56	6.29–25.79
	Subsoil	Mean \pm S.D.	0.70 \pm 0.19	2.56 \pm 1.48	6.24 \pm 3.27	0.98 \pm 0.86	2.97 \pm 1.59	13.46 \pm 6.13
		Median	0.63	2.26	5.33	0.51	2.88	12.75
		Range	0.51–0.98	0.68–4.59	1.83–11.98	0.33–2.45	0.76–5.82	4.19–23.36

^a $\sum\text{DDT}$, the summation of *o,p'*-DDE, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT.

Table 2

The independent-samples *t* test of DDTs in the topsoil and subsoil for both cotton and vegetable soils

Land use mode		<i>o,p'</i> -DDE	<i>o,p'</i> -DDT	<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>p,p'</i> -DDT
Cotton	<i>F</i>	5.976	4.088	0.076	0.046	0.405
	<i>p</i> -value	0.017*	0.048*	0.783	0.83	0.527
Vegetable	<i>F</i>	2.896	0.061	0.220	1.792	0.074
	<i>p</i> -value	0.117	0.809	0.648	0.208	0.790

* Difference is significant at the 0.05 level.

DDT pollution in the north cotton cultivation area of Jiangsu province.

3.2. Comparison of DDT residue in cotton soil with vegetable soil

As shown in Table 1, the mean contents of total DDTs in cotton soil were higher than vegetable soil at least by a factor of 20. Especially, the differences were significant for the residue content of *p,p'*-DDE, *o,p'*-DDT and *p,p'*-DDT in cotton soil and vegetable soil. For example, the mean residue of *p,p'*-DDE in vegetable soil was only about 6 ng g⁻¹ for both the topsoil and subsoil, on the contrary, the mean residue in cotton soil was up to nearly 130 ng g⁻¹ for both horizons. Additionally, all the five DDT compounds in vegetable topsoil were not significantly different from subsoil, in contrast, *o,p'*-DDT and *o,p'*-DDE in cotton topsoil were significantly higher than in cotton subsoil (see Table 2).

Therefore, it indicated that the DDTs residue in cotton soil was much higher when compared with other mode of land use. This observation was in good agreement with the fact that the majority of technical DDT and dicofol were applied in cotton fields. Other studies also obtained similar results. Lin et al. [15] reported that the concentration of DDT residue in cotton fields was much higher than in rice fields. Shivaramaiah et al. [17] found the residue levels of *p,p'*-DDE in the cotton growing valleys of northern New South Wales, Australia was relatively high, and revealed that there was an apparent correlation between current residue levels and mode of land use. Hoh and Hites [3] also held that the historical heavy application of DDT on cotton in the southern United States had made this area a signifi-

cant source region responsible for the contamination of northern United States.

3.3. Reasons for the characteristics of DDTs residue in cotton soil

As is known, technical DDT consists of *p,p'*-DDT (85%) and *o,p'*-DDT (15%), while dicofol, often contains *p,p'*-DDT, *o,p'*-DDT, α -chloro-DDT, *p,p'*-DDE, and *o,p'*-DDE as impurities. Furthermore, in dicofol, *o,p'*-DDT has a higher proportion than *p,p'*-DDT as impurity [7,12]. A survey on the formulated dicofol in Chinese market found that the ratio of *o,p'*-DDT to *p,p'*-DDT was as high as 7.0 [7]. The relatively fixed components of both technical DDT and dicofol make it feasible to analyze the reasons for the characteristics of DDTs residue in soil [6].

One of the predominant characteristics of DDTs residue in cotton soil was that *p,p'*-DDE was the most abundant compound of the residue. According to Table 1, *p,p'*-DDE accounted for 68% of the total DDTs. It is well documented that *p,p'*-DDE is the metabolite of *p,p'*-DDT in aerobic condition and is more persistent than *p,p'*-DDT in the environment. At the same time, it is noteworthy that one of the impurities of dicofol, α -chloro-DDT, could also degrade into *p,p'*-DDE in the environment [18,19]. Therefore, it was reasonable to consider that the abundance of *p,p'*-DDE in cotton soil resulted from both technical DDT and dicofol. This viewpoint could be supported by the following qualitative estimates. Firstly, given *p,p'*-DDE was only derived from technical DDT, then *o,p'*-DDT, the “impurity” in technical DDT, should have very similar residue pattern (*o,p'*-DDE/*o,p'*-DDT) to the *p,p'*-DDT residue pattern (*p,p'*-DDE/*p,p'*-DDT) in the soil after the same time span, because it was reported that the environmental behaviors of *p,p'*-DDT and *o,p'*-DDT were quite similar, e.g. they declined at similar rates in the environment [16]. However, the observed residue patterns were significantly different (the ratio of *o,p'*-DDE to *o,p'*-DDT was about 0.15, while the ratio of *p,p'*-DDE to *p,p'*-DDT was about 4.9). Thus, the assumption that all the *p,p'*-DDE come from technical DDT was invalid. Secondly, given *p,p'*-DDE was only derived from dicofol, then the residue of *o,p'*-DDT in cotton soil should be higher than *p,p'*-DDT due to the fact that dicofol contained higher *o,p'*-DDT than *p,p'*-DDT as impurity in Chinese market. While it was showed in Table 1 that the mean concentration of *o,p'*-DDT was lower than *p,p'*-DDT by a factor of 1.6. Hence, it was valid to hold that both historical technical DDT and current dicofol application contributed to the abundance of *p,p'*-DDE in cotton soil.

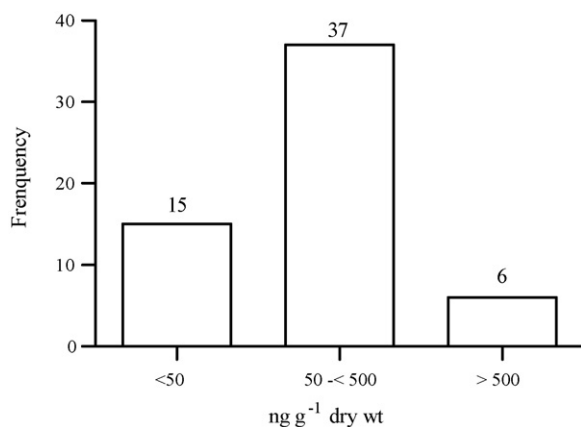


Fig. 2. Frequency distribution of total DDTs in the cotton soil samples.

Another predominant characteristic of DDTs residues in the cotton soil was that *o,p'*-DDT and *o,p'*-DDE were significantly higher ($p < 0.05$) in topsoil than that in subsoil. This observation was very impressive because other DDT compounds such as *p,p'*-DDE, *p,p'*-DDT were supposed to show the similar trend, however, none of them did. The only explanation for this observation might be that dicofol was being used and became an important source of DDT pollution in the cotton fields. Because the soils were sampled in August, the very growing season when pesticides were largely applied to control the mites, and the soil profile was not subject to mechanical mixing, therefore, the topsoil seemed likely to provide clues to the characteristic of pesticide used: containing considerable *o,p'*-DDT as impurity. As far as the pesticides currently used on cotton fields were concerned, only dicofol met such characteristic. Some studies implied that the cotton cultivation area we investigated appeared to be responsible for the atmospheric DDT contamination in southern Jiangsu, e.g. around Taihu Lake [12], then one question would be raised: was the DDT isomer pattern (*o,p'*-DDT/*p,p'*-DDT) in topsoil consistent with that in the air around Taihu Lake? The *o,p'*-DDT/*p,p'*-DDT in the air around Taihu Lake was about 7, similar to the ratio in dicofol [12], while *o,p'*-DDT/*p,p'*-DDT in cotton topsoil was only 0.64, which was unexpectedly different from the former. There might be two reasons which could possibly explain the difference: (I) The relatively high atmospheric DDTs around Taihu Lake was more likely the results of dicofol spray drift and post-application volatilization from cotton leaf in growing season, rather than that of volatilization of DDTs from soil. The spray drift was like an “impulse” input to which the ambient air responded quickly and resulted in the isomer pattern in air similar to dicofol; (II) The ratio of *o,p'*-DDT/*p,p'*-DDT in the air was supposed to be similar to that in cotton topsoil, however, *p,p'*-DDT was still persistent in the cotton topsoil due to the historical application of technical

Table 3

The correlation analysis among the DDT compounds

Compound	Correlation coefficients				
	<i>o,p'</i> -DDE	<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT
<i>o,p'</i> -DDE	1	0.364**	0.239	0.805**	0.277*
<i>p,p'</i> -DDE	0.364**	1	0.271*	0.480**	0.675**
<i>p,p'</i> -DDD	0.239	0.271*	1	0.087	0.519**
<i>o,p'</i> -DDT	0.805**	0.480**	0.087	1	0.464**
<i>p,p'</i> -DDT	0.277*	0.675**	0.519**	0.464**	1

* Correlation is significant at the 0.05 level (two-tailed).

** Correlation is significant at the 0.01 level (two-tailed).

DDT, which led to small ratio of *o,p'*-DDT/*p,p'*-DDT. Whatever the reasons were, the fact that *o,p'*-DDT and *o,p'*-DDE in topsoil was significantly higher than in subsoil clearly demonstrated that *o,p'*-DDT pollution was becoming serious, and some attention should be paid to the *o,p'*-DDT pollution in the cotton cultivation area.

The third characteristic was that there were fairly strong positive correlations among the DDT compounds. For example, *p,p'*-DDE was significantly correlated with *p,p'*-DDT, *o,p'*-DDT and *o,p'*-DDE at the 99% confidence level, respectively. Relationships among the DDT compounds were shown in Table 3 and Fig. 3. It seemed that the strong correlation among DDT compounds was due to: (1) the fact that *p,p'*-DDT could transformed into *p,p'*-DDE, and *o,p'*-DDT could transformed into *o,p'*-DDE; (2) the fact that components in both technical DDT and dicofol were relatively fixed and therefore the contents of DDTs in soil should be highly correlated.

3.4. Source apportionment of DDT

Under most conditions, *p,p'*-DDE in the environment was considered to solely originate from the degradation of *p,p'*-DDT,

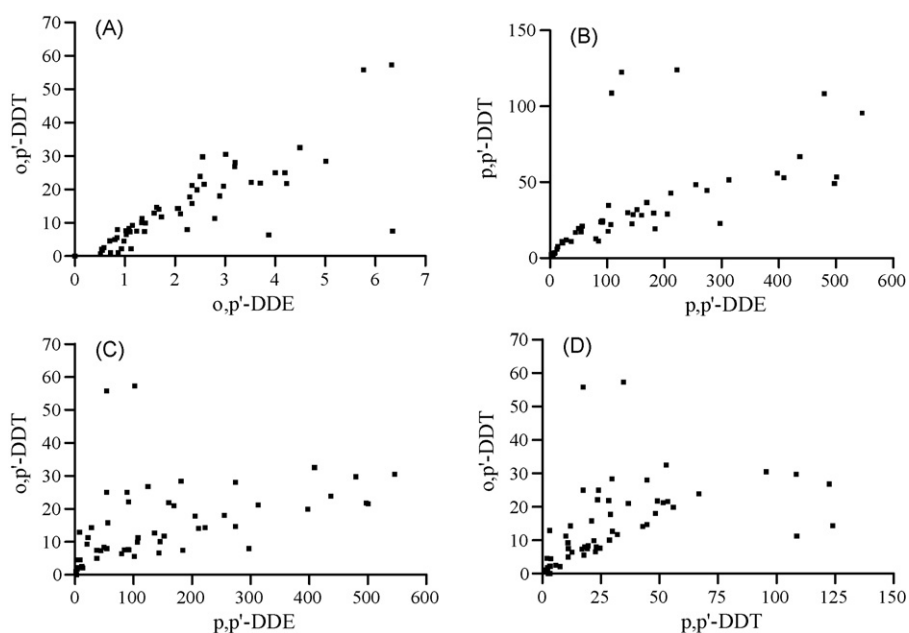


Fig. 3. Correlations among DDT compounds.

Table 4
Principal component analysis (PCA) for the source apportionment of DDT in cotton soil

Compounds	Component	
	Factor 1	Factor 2
<i>o,p'</i> -DDE	0.898	0.123
<i>p,p'</i> -DDD	−0.058	0.817
<i>o,p'</i> -DDT	0.944	0.168
<i>p,p'</i> -DDT	0.301	0.855
<i>p,p'</i> -DDE	0.458	0.653
Loading (%)	54.6	22.1

therefore, the very small concentration ratio of *p,p'*-DDT/*p,p'*-DDE (e.g. much less than 1) was indicative of aged DDT and a value much greater than 1 indicated fresh application [20,21]. However, in areas with both technical DDT residue and dicofol application, *p,p'*-DDE was derived not only from the degradation of *p,p'*-DDT but also from the degradation of dicofol (actually, one of its impurities, α -chloro-DDT) in the environment. Thus, the *p,p'*-DDE/*p,p'*-DDT ratio was not a valid method to evaluate the source apportionment of DDT in cotton cultivation areas, and other approach should be taken to apportion the sources. Principal component analysis (PCA) was primarily used for data reduction or structure detection. This analysis approach had been widely used to apportion the different sources of pollutants in environment [22,23].

In our work, PCA was conducted for five DDT compounds (*p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *o,p'*-DDE). As shown in Table 4, only two factors were extracted and accounted for 77.4% of the total variance in the data set. Factor 1 explained 54.3% of the total variance, was highly associated with both *o,p'*-DDT and *o,p'*-DDE, and was moderately associated with *p,p'*-DDE. As was known, *o,p'*-DDT was considered to be the major impurity compound in dicofol, *o,p'*-DDE was the metabolite of *o,p'*-DDT, and *p,p'*-DDE was the metabolite of both *p,p'*-DDT and α -chloro-DDT, therefore, Factor 1 was mostly related to dicofol usage. Factor 2, which accounted for 22.1% of total variance, was highly associated with *p,p'*-DDT and *p,p'*-DDD, and was moderately associated with *p,p'*-DDE. Thus Factor 2 may be related to the historical technical DDT application. Additionally, it was worth noting that *p,p'*-DDE was moderately associated with both Factors 1 and 2, which once again indicated the abundance of *p,p'*-DDE was due to both technical DDT and dicofol.

After the detection of source structures, contribution of individual source to the total DDT in the soil could be attained by multiple linear regressions. It was found that dicofol-type DDT accounted for about 80% of the total DDT in most of the cotton soil. The results implied that dicofol application had resulted in serious pollution in cotton cultivation area. Dicofol-type DDT input in the environment seemed likely the main reason why in China there was no apparent decrease of DDTs level after two decades since the ban of technical DDT application in agricultural practice. Therefore, more strict management should be focused on both the dicofol production and application.

4. Conclusions

The DDT compounds residues in cotton soil were much higher than in vegetable soil. The total DDTs in cotton soil (including topsoil and subsoil) ranged from 4.2 to 678.6 ng g^{−1}, with a mean concentration of 190.4 ng g^{−1}, and the most abundant compound was *p,p'*-DDE, *p,p'*-DDT and *o,p'*-DDT. There were no significant differences between cotton topsoil and subsoil for *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD, however, *o,p'*-DDT and *o,p'*-DDE in cotton topsoil were significant higher than in subsoil. Moreover, there were significant and fairly strong positive correlations among DDT compounds. All the results indicated that the DDT pollution in cotton fields were serious and was a mixture pollution of historical technical DDT and current dicofol, in which, dicofol accounted for 80%. Our work provided implications for reasons why there was no apparent decrease of DDT level in China even after decades since the ban of technical DDT application.

Acknowledgments

This research was funded by Innovative Research Group and Outstanding Youth Fund of National Natural Science Foundation of China (nos. 40621001 and 40325001), National Natural Science Foundation of China (no. 40571075), CAS International Partnership Project (no. CXTD-Z 2005-4), and National Basic Research and Development program of China (no. 2002CB410805).

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