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# Assessment of 20 Organochlorine Pesticides (OCPs) Pollution in Suburban Soil in Tianjin, China

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**Abstract** Soil contamination with organochlorine pesticides has aroused worldwide concerns considering their high toxicities and long-term persistence. In this study, 87 representative soil samples from suburban areas (Xiqing, Dongli, Jinnan, Beichen) of Tianjin, the third biggest city in China, were collected to evaluate the pollution of 20 organochlorine pesticides. Surface soil samples were air-dried and sieved. Ultrasonic extraction was used for organochlorine pesticides preparation prior to analysis with gas chromatography–mass spectrometry. It was revealed that *p*,*p*′-DDE, *p*,*p*′-DDD, *o*,*p*′-DDT, *o*,*p*′-DDD, hexachlorobenzene, dicofol and *β*-HCH were seven pesticides detected most frequently. DDTs, HCHs and hexachlorobenzene were the predominant pesticide pollutants in soil. Spatial variation of these organochlorine pesticides in soil was illustrated; Pollution levels, characteristics and possible sources were also investigated. Most of other 13 kinds of pesticides were detected and the frequencies of detection were calculated to reveal the pollution status, which ranged from 0.0% (aldrin, dieldrin and endrin) to 34.5% (*p*,*p*′-DDT). These data were helpful to figure out the pollution of organochlorine pesticides and could be further used to evaluate the health risk associated with soil pollution.

**Keywords** Organochlorine pesticides (OCPs) · Soil · Suburban · Tianjin

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Organochlorine pesticides have a wide range of acute and chronic health effects, including cancer, neurological damage, birth defects and endocrine disruption, so organochlorine pesticides had been banned in many countries in consideration of these bad health effects to human being. But many organochlorine pesticides are extremely persistent in the environment. Organochlorine pesticides can accumulate in human bodies through the food chains and finally impact bad influence on human health. Contamination of organochlorine pesticides in environment, especially in agricultural soils, was reported in many studies (Harris et al. 2000), even the use of those organochlorine pesticides had been banned for decades of years.

China is a large producer and consumer of organochlorine pesticides. As one of China's greatest metropolises, Tianjin (N: 38°34′–40°15′; E: 116°43′–118°194′) covers about 11 thousands km$^2$ with a population of more than 11 million. Organochlorine pesticides were once widely used in the agricultural area in suburban Tianjin districts (Xiqing, Dongli, Jinnan, Beichen). Many spices of organochlorine pesticides were detected in the air (Zheng et al. 2010), sediment (Yang et al. 2005) and soil (Wang et al. 2006). But most previous studies on soil focused on the levels, profiles of organochlorine pesticides in whole Tianjin city, including rural counties and urban areas; sampling sites in suburban districts were not systematic and detailed enough; On the other hand, some kinds of organochlorine pesticides were still produced and released to the environment now, e.g., DDT, as a intermediate of dicofol. To our best of knowledge, samples in the latest study on organochlorine pesticides pollution in the soil in this area were collected before 2002 (Wang et al. 2006) and the pollution status had not been monitored and evaluated for many years, it is necessary to conduct new and comprehensive survey.

## Materials and Methods

Sampling sites were illustrated in Fig. 1 according to the GPS values. A total of 87 soil samples (0–10 cm soil layer, 1 kg each) were collected in August 2008 with a stainless steel scoop and stored in PE bags. Each sample was mixed of 20 sub samples collected in the 10 × 10 $m^2$ of sampling site. All soil samples were placed in dark and transported to the laboratory. Soil samples were air dried and then ground. All samples were stored in −20°C after sieved through a 50 mesh sieve.

All organic solvents purchased from Fisher (Fair Lawn, NJ, USA) were pesticide grade. Pesticide standards (1 mL, 1000 mg/L, in acetone or methanol) were kindly presented by Institute of Environmental Protection and Monitoring, Ministry of Agriculture, China. $^2$D-labeled surrogate standards (EPA M-525-IS, 1mL 2.0 mg/mL in acetone) were purchased from Accustandard Inc. (CT, USA). 40 mg/L $^2$D-chrysene was spiked 25 μL before extraction as surrogate in all samples.

2.0 g of soil sample was ultrasonic-extracted for 30 min with 15 mL of acetone: hexane (v: v/1:1) twice. Then the mixture each time was centrifuged for 5 min at 4000 rpm. The supernatant was collected, mixed and evaporated to nearly dry under nitrogen flow. Florisil columns were employed for cleanup according to a Chinese national standard: NY/T 761-2004. The elution was collected and then concentrated to 0.1 mL with gentle nitrogen flow for GC–MS injection.

Organochlorine pesticides were quantified on Agilent 6890 gas chromatography with Agilent 5973 N mass spectrometer with electron impact ion source. Helium was the carrier gas with a constant flow at 1.0 mL $min^{-1}$. 2μL of the extract was injected with 7673 auto sampler in splitless mode. A DB-5MS fused silica capillary column (30 m × 0.25 μm × 0.25 mm) was used to separate the 20 organochlorine pesticides. The ion source and the quadrupole temperature were set at 230°C, 150°C respectively. The oven temperature program were as follow: 60°C, held for 2 min, increased to 200°C at 19°C $min^{-1}$, held for 2 min, then increased to 240°C at 4.5°C $min^{-1}$, held for 2 min, finally increased to 290°C at 2.5°C $min^{-1}$, held for 2 min. SIM mode was used, the parameters in SIM were listed in Table 1.

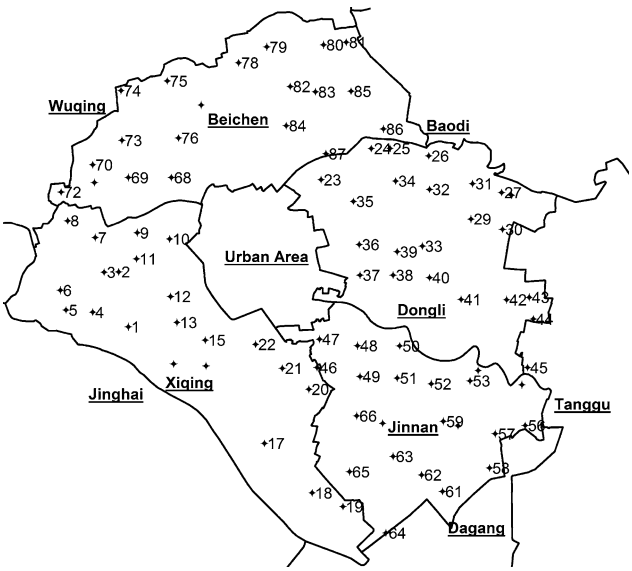


**Fig. 1** Sampling sites

**Table 1** SIM programs and detection frequencies of organochlorine pesticides

| Compounds | R.T. (min) | T.ion | Q.ions | | LOD (μg/kg) |
|---|---|---|---|---|---|
| d-Chrysene | 21.43 | 240 | | | |
| α-HCH | 11.16 | 219 | 181 | 181 | 0.55 |
| Hexachlorobenzene | 11.31 | 284 | 286 | 286 | 0.96 |
| Atrazine | 11.53 | 200 | 215 | 215 | 0.28 |
| β-HCH | 11.68 | 219 | 181 | 181 | 2.65 |
| γ-HCH | 11.76 | 219 | 181 | 181 | 0.61 |
| Quintozene | 11.85 | 295 | 265 | 265 | 0.88 |
| δ-HCH | 12.28 | 219 | 181 | 181 | 3.12 |
| Heptachlor | 13.31 | 272 | 337 | 337 | 0.24 |
| Aldrin | 14.19 | 263 | 293 | 293 | 0.80 |
| Dicofol | 14.45 | 139 | 250 | 250 | 1.35 |
| *p,p′*-DDE | 16.14 | 318 | 316 | 316 | 0.81 |
| Thiodan-α | 16.35 | 339 | 341 | 341 | 0.42 |
| *p,p′*-DDE | 17.10 | 318 | 246 | 246 | 1.32 |
| Dieldrin | 17.15 | 345 | 263 | 263 | 0.39 |
| *p,p′*-DDD | 17.39 | 235 | 165 | 165 | 1.92 |
| Endrin | 17.84 | 345 | 317 | 317 | 0.49 |
| Chlorobenzilate | 18.18 | 251 | 139 | 139 | 0.91 |
| *p,p′*-DDD | 18.48 | 235 | 165 | 165 | 1.27 |
| *p,p′*-DDT | 18.56 | 235 | 165 | 165 | 1.10 |
| *p,p′*-DDT | 19.72 | 235 | 165 | 165 | 0.63 |

Spiked tests indicated that recoveries of 20 organochlorine pesticides were from 75.7% to 107.9% with RSD (n = 3) from 4.7% to 16.4%. The detection limits of this method ranged from 0.28 ng/g to 3.12 ng/g depending on the analytes (Table 1). The recoveries of surrogates in all samples ranged from 72.2% to 115.7%.

## Results and Discussion

The total concentrations of tested organochlorine pesticides in Xiqing, Dongli, Jinnan, Beichen ranged in 0.1–690.9, N.D.-285.8, N.D.-298.8, 0.2–253.4 ng/g and the averages of total concentrations were 94.3, 61.8, 50.2, 44.8 ng/g

**Table 2** Statistics of concentrations of organochlorine pesticides in soils in suburban Tianjin: (ng/g)

| Compounds | Min. | Max. | Median | Average | Detection frequency (%) |
|---|---|---|---|---|---|
| α-HCH | N.D. | 6.54 | N.D. | 0.16 | 3.4 |
| Hexachlorobenzene | N.D. | 5.30 | 1.02 | 1.48 | 93.1 |
| Atrazine | N.D. | 23.55 | N.D. | 0.44 | 8.0 |
| *β*-HCH | N.D. | 92.74 | N.D. | 4.10 | 64.4 |
| *γ*-HCH | N.D. | 24.45 | N.D. | 0.83 | 8.0 |
| Quintozene | N.D. | 5.82 | N.D. | 0.25 | 5.7 |
| *δ*-HCH | N.D. | 71.73 | 2.47 | 5.52 | 33.3 |
| Heptachlor | N.D. | 6.20 | N.D. | 0.07 | 1.1 |
| Aldrin | N.D. | 5.61 | N.D. | 0.09 | 0.0 |
| Dicofol | N.D. | 145.21 | 1.50 | 10.92 | 64.4 |
| *p*,*p*′-DDE | N.D. | 16.03 | N.D. | 1.31 | 33.3 |
| Thiodan-α | N.D. | 8.79 | N.D. | 0.12 | 2.3 |
| *p*,*p*′-DDE | N.D. | 323.47 | 3.47 | 22.50 | 95.4 |
| Dieldrin | N.D. | 10.38 | N.D. | 0.24 | 0.0 |
| *p*,*p*′-DDD | N.D. | 98.96 | 0.57 | 5.00 | 56.3 |
| Endrin | N.D. | N.D. | N.D. | N.D. | 0.0 |
| Chlorobenzilate | N.D. | 79.42 | N.D. | 1.54 | 2.3 |
| *p*,*p*′-DDD | N.D. | 93.37 | 1.35 | 4.57 | 90.8 |
| *p*,*p*′-DDT | N.D. | 126.59 | 0.63 | 3.01 | 63.2 |
| *p*,*p*′-DDT | N.D. | 73.55 | N.D. | 1.84 | 34.5 |

respectively. Total organochlorine pesticides contaminated areas were distributed in the west and east outskirts of Tianjin. Maximum concentration of total organochlorine pesticides in three districts were a bit higher than those of Shanghai (24 kinds organochlorine pesticides, 3.16 to 265.24 ng/g) (Jiang et al. 2009). Table 2 showed that *p*,*p*′-DDE, *p*,*p*′-DDD, *o*,*p*′-DDT, *o*,*p*′-DDD, hexachlorobenzene, dicofol and *β*-HCH were seven pesticides detected most frequently. DDTs and HCHs were still the predominant pesticides in soil and this coincided well with Gong' study in 2002 (Gong et al. 2002). *p*,*p*′-DDT degrades to *p*,*p*′-DDE in aerobic environment and to *p*,*p*′-DDD in anaerobic environment. Surface soil samples in aerobic environment were collected in this study and this might elucidate the highest detection frequency of *p*,*p*′-DDE.

The concentrations were in the ranges of N.D.-92.74 ng/g for HCHs (sum of α-, *β*-, *γ*- and *δ*-HCH, median 7.03 ng/g), N.D.-616.98 ng/g for DDTs (sum of *p*,*p*′-DDT, *p*,*p*′-DDD, *p*,*p*′-DDE and *p*,*p*′-DDT, median 7.03 ng/g). The maximum values in the study were much higher than those in Shanghai (N.D.-10.38 ng/g; 0.77–247.45 ng/g) (Jiang et al. 2009) and Taiyuan (1.4–45 ng/g; 1.8–100 ng/g) (Fu et al. 2009). For HCHs the maximum and median values were much higher than those in Beijing (1.36 to 56.61 ng/g; median 5.25 ng/g) (Zhu et al. 2005). The average concentration of *p*,*p*′-DDE (22.50 ng/g) was also much higher than that in Hongkong (0.41 ng/g) (Zhang et al. 2006). It indicated that although the ban on the use of organochlorine pesticides, especially HCHs and DDTs, resulted in reduction of these pesticide residues in soils, there were still high amounts of pesticide residues in soils in Tianjin, compared to other big cities in China. Statistics results of concentrations of individual organochlorine pesticides in soils of suburban Tianjin were shown in Table 2. From Table 2, low detection frequencies or non-detectable levels of certain organochlorine pesticides (aldrin, dieldrin, endrin, quintozene, heptachlor, and et al.) indicated a positive phasing out of these organochlorine pesticides which were not further discussed in this work.

Spatial distribution of four typical organochlorine pesticides: dicofol, hexachlorobenzene, *β*-HCH and *p*,*p*′-DDE in soil was illustrated in Fig. 2. For dicofol, concentrations varied significantly at different sites even in same district. The highest concentration (145.21 ng/g) was found in Dongli while most of other sites were found with low concentrations which indicated recent introduction of dicofol at some sampling locations. Average concentrations of dicofol in Xiqing, Dongli, Jinnan, Beichen were 8.56 ng/g, 11.93 ng/g, 12.60 ng/g, 10.54 ng/g separately. Hexachlorobenzene was detected frequently in all four districts. The highest concentration (5.3 ng/g) was found in Dongli, concentrations were relatively low and varied not significantly in all sites which hinted that residues of this compound in most soil samples originated from historical application. Average concentrations of Hexachlorobenzene in Xiqing, Dongli, Jinnan, Beichen were 1.87 ng/g, 1.30 ng/g, 1.76 ng/g, 0.92 ng/g separately. Several sites with high

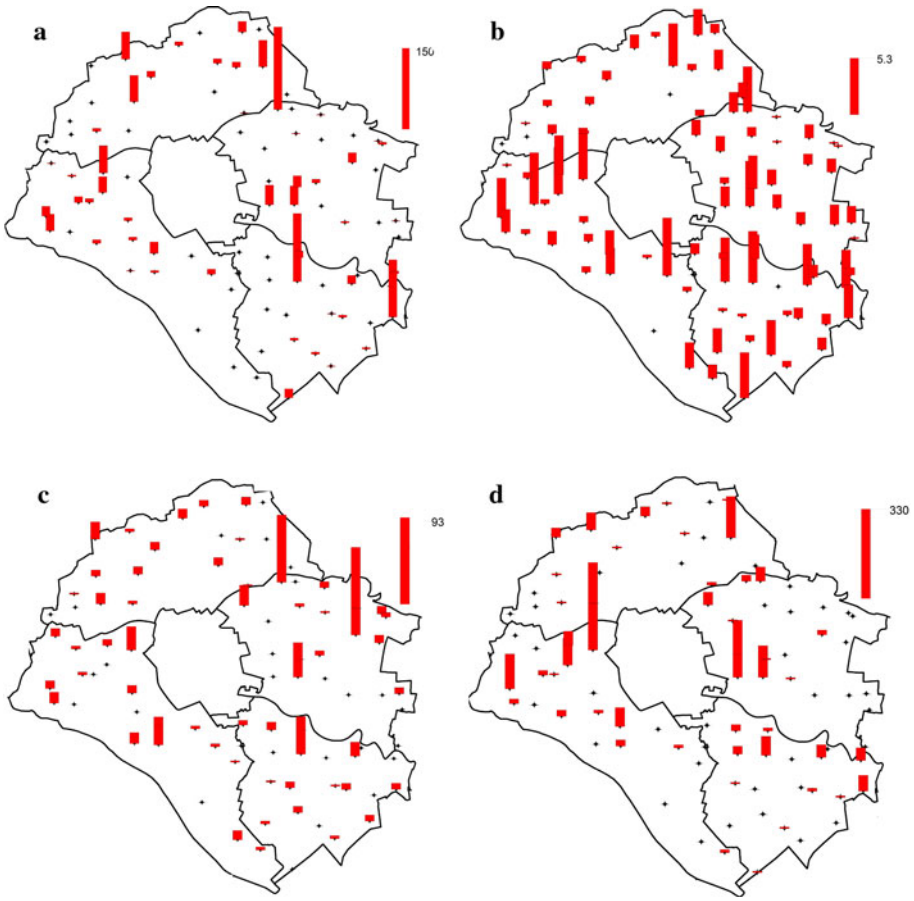


**Fig. 2** Distribution of dicofol (**a**), hexachlorobenzene (**b**), $\beta$-HCH (**c**) and $p,p'$ DDE (**d**) in the soil samples in suburban Tianjin (ng/g)

concentrations of $\beta$-HCH and $p,p'$-DDE were found among which the highest (92.74 ng/g, 323.47 ng/g) occurred in Dongli and Xiqing separately. Average concentrations were 3.66 ng/g, 6.34 ng/g, 3.95 ng/g, 2.08 ng/g for $\beta$-HCH and 37.09 ng/g, 19.64 ng/g, 14.59 ng/g, 17.86 ng/g for $p,p'$-DDE in Xiqing, Dongli, Jinnan, Beichen. Furthermore, pollution levels of these organochlorine pesticides at all sites were illustrated clearly with four maps in Fig. 2 which should be very helpful for local government to take corresponding remediation steps.

The saturated vapor pressure at 20°C of $\alpha$-HCH ($3.3 \times 10^{-6}$ kPa) and $\gamma$-HCH ($2.1 \times 10^{-5}$ kPa) are significantly higher than that of $\beta$-HCH ($3.7 \times 10^{-7}$ kPa). That's to say, in the soil-air interface, $\alpha$-HCH and $\gamma$-HCH are more readily to diffuse to the air. $\beta$-HCH has symmetrical structure, high stability and is not readily to degrade as other isomers. In the degradation of HCHs, other isomers can easily transform to $\beta$-HCH to get the most stable structure. So the percentage of $\beta$-HCH in the soil will keep increasing with the time going. In many studies, the ratios of $\beta$-/($\alpha$+$\gamma$)-HCH were used to identify the historical pollution sources (Willett et al. 1998; Zheng et al. 2009). $\beta$-/($\alpha + \gamma$)-HCH $> 0.5$, it is the indicator of historical pollution; and if it is less than 0.5, it is the indicator of new introduction of HCH. Considering that $\alpha$- and $\gamma$-HCH in many sites were not detected in this study, the values of ($\alpha + \gamma$)-HCH were zero and $\beta$-/($\alpha + \gamma$)-HCH were meaningless, the values of $\beta$-($\alpha + \gamma$)*0.5 were used as indicator (Fig. 3a). 28 values were positive and 7 values were negative which indicated that historical pollution still accounted for most of HCH pollution.

$p,p'$-DDT/$p,p'$-DDT can be used to identify the DDTs input through dicofol production (Zheng et al. 2009). In technical DDTs, $p,p'$-DDT occupy 15% of total components, $p,p'$-DDT occupy 85%. The photo-degradation rate of $p,p'$-DDT in the environment is in the same with that of $p,p'$-DDT, so $p,p'$-DDT/$p,p'$-DDT in the environmental should be about 0.175. China has banned the production of DDTs in 1983. But as a by-product of dicofol production, DDTs were still released to the environment. $p,p'$-DDT was the predominant isomers in the dicofol production ($p,p'$-DDT/$p,p'$-DDT was about 7) which should greatly improve the ratios of $p,p'$-DDT/$p,p'$-DDT in the environment (Qiu et al. 2005). In this study, the minimum ratio of $p,p'$-DDT/$p,p'$-DDT was 0.33, much higher than 0.175, and $p,p'$-DDT at 84 of total 87 sites were higher than $p,p'$-DDT (Fig. 3b). It revealed the new input of DDTs might be caused by the production and application of dicofol which

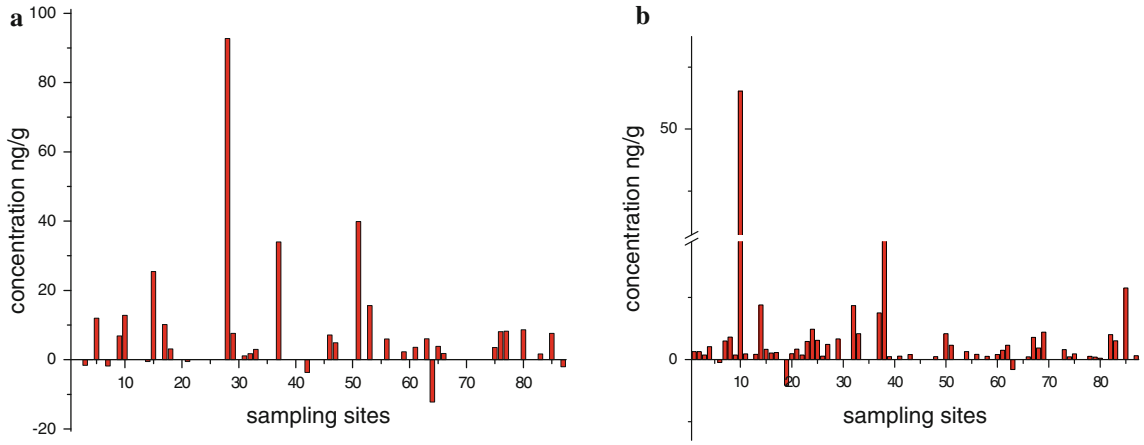


**Fig. 3** Concentrations (ng/g) of ($\beta$-($\alpha$+$\gamma$)*0.5)-HCH (**a**); ($p$,$p'$-DDT–$p$,$p'$-DDT) (**b**)

was in well agreement to the high detection frequency of dicofol in Table 2.

In conclusion, $p$,$p'$-DDE, $p$,$p'$-DDD, $p$,$p'$-DDT, $p$,$p'$-DDD, hexachlorobenzene, dicofol and $\beta$-HCH were seven pesticides detected most frequently in the suburban soil samples in Tianjin. There were still high amounts of DDTs and HCHs residues, compared to other big cities in China. Pollution levels of four widely-used organochlorine pesticides at all sites were illustrated with maps. Recent introduction of dicofol was found at some sampling locations. Concentrations of hexachlorobenzene were relatively low and varied not significantly at all sites. It seemed that residues of hexachlorobenzene in most soil samples originated from historical application and historical pollution also should account for most of HCHs pollution. On the contrary, new input of DDTs might be caused by the recent production and application of dicofol. Aldrin, dieldrin, endrin, quintozene, heptachlor were at non-detectable levels in this area and were not further discussed in this study.

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