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Regional differences and sources of organochlorine pesticides in soils surrounding chemical industrial parks

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Abstract Concentrations of organochlorine pesticides (OCPs; dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB)) were investigated in 105 soil samples collected in vicinity of the chemical industrial parks in Tianjin, China. OCP concentrations significantly varied in the study area, high HCH and DDT levels were found close to the chemical industrial parks. The intensity of agricultural activity and distance from the potential OCP emitters have important influences on the OCP residue distributions. Principal component analysis indicates that HCH pollution is a mix of historical technical HCH and current lindane pollution and DDT pollution input is only due to technical DDT sources. The significant correlations of OCP compounds reveal that HCHs, DDTs and HCB could have some similar sources of origin.

Keywords Chemical industry · Environmental fate · Organochlorine pesticides · Soil pollution

Introduction

Characterized by persistence, bioaccumulation, toxicity and long-range environmental transport, many organochlorine pesticides (OCPs) are semivolatile and lipophilic and are described as persistent organic pollutants (Loganathan and Kannan 1994). In China, dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) were the most important OCPs, produced for use in agriculture, forestry, and public health for more than four decades (Li et al. 1998a, b). Hexachlorobenzene (HCB) has never been used as pesticides, but it was an intermediate in the production of pentachlorophenol and sodium pentachlorophenate (Wei et al. 2007). HCB is also a by-product of some industrial chlorination processes (Bailey 2001). Until the ban on production and usage of technical HCH and DDT in 1983, China had produced and consumed large amounts of organochlorine pesticides with the production levels of technical HCH being 4 million tons and technical DDT being 0.27 million tons (Hua and Shan 1996; Li et al. 1998b, 2001). After 1983, 3,200 tons of lindane (99% γ-HCH) had been used for agriculture and

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forestry to control pests until 2000 (Li et al. 2001) while DDT was also produced mostly for further production of dicofol (Qiu et al. 2005). Soil is the largest sink of OCPs in the environment and the release of OCPs from soils continues to be a source to other environmental compartments. Although OCPs was phased out of use decades ago, OCP residues can still be found in soils in China (Li et al. 2006b). In the 1970s' scientists and governmental agencies began to monitor POP levels in environmental compartments in China. However, most of the studies focused on agricultural areas (Wang et al. 2005a), and few studies were conducted on pollution characteristic and health risks of the soils surrounding industrial production and storage sites. This research intends to reveal regional differences and sources of OCPs pollution in the areas surrounding chemical industrial parks by examining concentrations of DDTs, HCHs and HCB at Tianjin Binhai new area (TBNA).

TBNA is located in eastern Tianjin, which encomposes three administrative districts: Tanggu District, Hangu District and Dagang District (Fig. 1). In the last few decades, this area has been experiencing rapid urbanization and industrialization. Tanggu District and Hangu District are both famous for chemical industry. There is Dagu chemical industrial park at Tanggu District and Hangu chemical industrial park at Hangu District. Besides large agricultural plantation areas at these two districts, salt ponds at Hangu District cover an area of 139.33 km^2, about three times of the plantation area. More than half of the land use area at Dagang is wetland, and the rest is for agricultural use. Dagang is also an emerging satellite city where some industries like petroleum, petrochemical, and fine chemicals are developing.

There is long history of pollution and complex sources of contamination at TBNA. Large amount of lindane, dicofol, technical HCH and most of HCB and technical DDT in China were produced at Dagu Chemical Industrial Park and Hangu Chemical Industrial Park (Hu and Liu 2003; Tao et al. 2006). Besides, some other manufacturers at TBNA have produced dicofol since 1990 (Hu et al. 2005). There were some waste dumps and storage sites of some OCPs (for example technical DDT and HCB). Effluents from the production facilities were treated ineffectively. Consequently, wastewater discharged from the two parks contributed large amount of DDT and HCH contamination (Li et al. 2006b). Sewage irrigation has been at a large scale in this area for over 30 years because of water shortage (Gong et al. 2004a). Furthermore, agricultural usage of HCHs and DDTs lasted from 1953 to1993 (Tao et al. 2006). Potential OCP pollution sources at TBNA are listed in Table 1.

The top soils at Hangu and Tanggu had relatively high residues of DDTs and HCHs, especially in areas

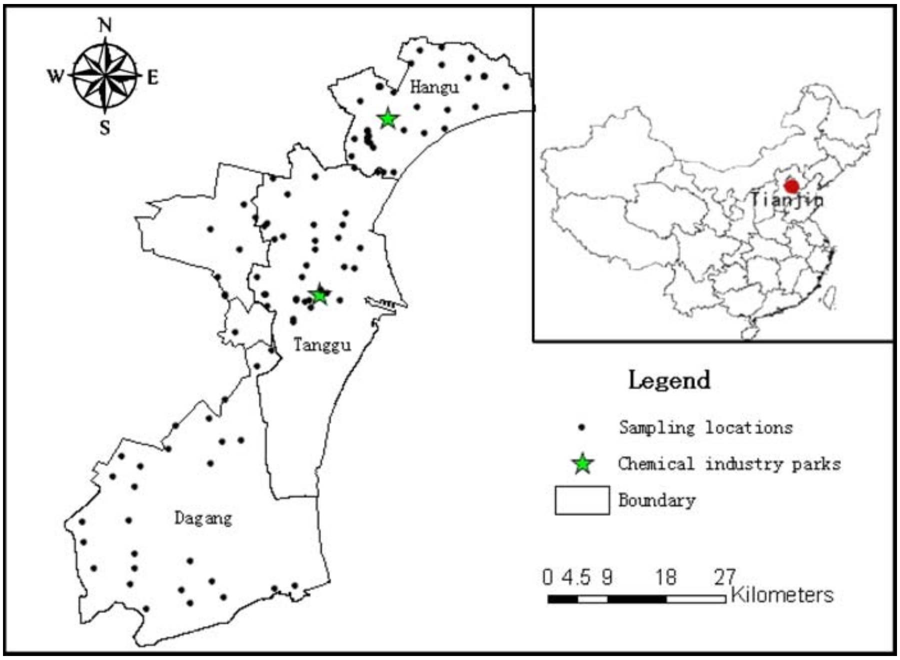

Fig. 1 Map of sampling sites

Table 1 Previous usage of organochlorine pesticides and potential pollution sources in the study area

Pollutants (group)	Usage in China	Potential emission/pollution sources in the study area
HCH: Technical HCH	Mainly used in agriculture, pest control in rice, wheat, soybean, maize, cotton, sorghum and orchard; A small apportion was also used in forestry and public health;	Chemical production (HCH until 1983, lindane until 2000); Extensive application in agriculture and forestry; Wastewater irrigation;
Lindane	Major use on wheat land	Lindane waste dumps;
DDT and its metabolites: Technical DDT	Disease vector; Intermediate of dicofol production; Antifouling paint for ships; Export for controlling malaria; Insecticide in orchards, paddy fields and vegetable fields(until 1983); Mosquito-repellent incense (until 2002);	Chemical production (technical DDT until now); Extensive application in agriculture and forestry; Transportation leakage; Wastewater irrigation; Waste product dumps;
Dicofol (10%DDT impurities)	Acaricide in agriculture (apple, orange and cotton)	Dicofol application on cotton;
HCB	As intermediate producing pentachlorophenol and santobrite; As materials producing fireworks	By-product of chlorine-based chemical industry; Chemical production as intermediate (until 2004); Waste water irrigation; HCB waste storage; Contaminant in some pesticides;

Sources: Hu and Liu 2003; Gong et al. 2004a, b; Li et al. 2006b; Qiu et al. 2005; Tao et al. 2006; Tao et al. 2007; Wei et al. 2007; Wang et al. 2005a and Yang et al. 2008

close to the two large chemical industrial parks (Gong et al. 2004a, b). The sediments of the Dagu Drainage River near Dagu Chemical Industrial Park were seriously contaminated by HCHs (mean 87.7 μg kg^{-1}) and DDTs (mean 35.5 μg kg^{-1}), and high residue levels of γ-HCH and *p*,*p*′-DDT indicated a recent input of these two OCPs into Dagu Drainage River (Yang et al. 2005). Meanwhile, the sediments from immediately downstream of the effluent discharges of Hangu Chemical Industrial Park were severely polluted by DDTs (5,350 μg kg^{-1}) (Tao et al. 2007). These studies indicate that chemical factories are responsible for high residue levels of DDT and HCH in the surrounding areas. More detailed studies of OCPs pollution status and effects surrounding chemical industrial parks are in bad need. This paper was to assess the OCPs contamination status and to evaluate the risks in surrounding areas of chemical industrial parks through systematic soil sampling and analysis. By the use of statistical analyses, the regional differences and effects of different OCP emission sources were also explored. In addition, the potential sources and fates of OCPs were identified by applying Principal Component Analysis (PCA).

Materials and methods

Reagents and instruments

For extraction of pesticides from the soil, *n*-hexane and dichloromethane (J.T.Baker, HPLC) were used for residue analysis. The anhydrous sodium sulfate (analytical grade) and silica gel (60 mesh, for column chromatograph) were activated at 180°C for 24 h. Solid Phase Extraction (SPE, 6 ml, Supelco) containing 1 g of florisil was washed with 10 ml *n*-hexane before use. A mixture of standard solution containing α, β, γ, δ-HCH, *o*,*p*′-DDT, *p*,*p*′-DDT, *p*,*p*′-DDE, *p*,*p*′-DDD and HCB standard solution with 1 g kg^{-1} per compound were purchased from National Research Center for certified Reference Materials of China.

2,4,5,6-Tetrachloro-*m*-xylene (TCMX) was used as the surrogate standard (Supelco, Bellefonte, PA, USA). Agilent6890 gas chromatograph (GC) equipped a ^{63}Ni electron capture detector (μECD; Agilent Technology Co., USA) was used for the analysis. The column used was HP-5 silica capillary column with 30 m×0.32 mm i.d×0.25 μm film thickness.

Soil sampling

In October 2006, 105 samples including 39 at Tangu, 38 at Hangu and 28 at Dagang (see Fig. 1) were collected. The soil sampling sites were performed to have even distribution, and some series of soil samples were collected surrounding the chemical industrial parks for the study. The sampling sites covered different types of land use such as industrial park, wetland, salt pond and farmland. Each sample was mixed with five subsamples collected from five locations in an area of about 100×100 m^2 (at the four corners and the center). All the soil samples were collected at a depth of 0–20 cm using a stainless steel shovel. Grass and other sundries were removed from the surface of each sample location before the sample was collected. The soil samples were air dried at room temperature (22–25°C) about 10 days, sieved to <2 mm, and stored at 4°C.

Sample extraction and cleanup

Soil sample (2.0 g dry weigh) was mixed with 1 g anhydrous sodium sulfate. One milliliter of 2,4,5,6-tetrachloro-*m*-xylene at the concentration of 0.08 μg ml^{-1} was added. The mixture was extracted twice with 35 ml hexane/dichloromethane (1:1, *v*/*v*) by ultrasonication for 60 min and then centrifuged. Extracts were concentrated to about 2 ml by rotary evaporation, and further purified with SPE loaded with 1 g silica gel and 1 g anhydrous sodium sulfate. The elution was subsequently carried out using 20 ml hexane/dichloromethane (7:3, *v*/*v*). The eluate was concentrated to a final volume of 1 ml for GC analysis. Meanwhile, several grams of soil were dried 8 h at 80°C to obtain dry-weight data.

OCPs analysis

The purified extract was analyzed using GC-μECD under the splitless mode with ultrapure nitrogen as the carrier gas and make-up gas. The injector and detector temperatures were 220°C and 300°C respectively. The oven temperature was initially set at 100°C with a 2-min hold, ramped at 10°C/min to 160°C with a 2-min hold, 4°C/min to 230°C with a 5-min hold, 10°C/min to 270°C with a 2-min hold. OCPs were identified by retention time matched to standards and were quantified using peak area integration. OCPs measured include four DDT homologues, four HCH isomers and HCB. Concentration of ΣDDT and ΣHCH were the sum of the four DDT homologues and four HCH isomers, respectively. The OCP concentrations in soils are shown on a dry weight basis.

Quality control

For quality assurance and quality control, the procedural blanks and matrixes spiked with the standard solution were analyzed. None of the target compounds were detected in the procedural blanks. The spiked concentration levels of OCPs for the recovery study were 80 μg kg^{-1}. The recoveries of OCPs spiked to soil ranged from 78.1% to 93.0% (Table 2) by three replicates. The limits of detection (LDs) were described as three times of signal-to-noise ratio (S/N). The detection limit was 0.05 to 0.24 μg kg^{-1} (Table 2). GC analysis was repeated twice for each replicate sample and the relative standard deviation of replicate samples was less than 20%. Extration efficiency, indicated by recovery of the surrogate standards (TCMX), was 75±10%.

Statistical analysis

Statistical Package for the Social Sciences 12.0 for windows was employed for statistical analysis. Be-

Table 2 The detection limit (μg kg^{-1}) and recovery (%) of the method

OCPs	Detection limit	Recovery
α-HCH	0.15	82.2
β-HCH	0.20	81.4
γ-HCH	0.05	83.9
δ-HCH	0.05	89.8
o,*p*′-DDT	0.10	89.7
p,*p*′-DDT	0.10	91.9
p,*p*′-DDE	0.10	93.0
p,*p*′-DDD	0.20	87.1
HCB	0.24	78.1

cause the data were non-normally distributed (even after log transformation), non-parametric Mann–Whitney and Kruskal–Wallis tests were used to identify differences in OCP concentrations between regions. Kendall correlation analyse was performed to determine if there was statistically significant correlation between the compounds of OCPs. Principal component analysis was used to explore the sources and fates of OCPs.

Results

Concentrations of DDTs, HCHs and HCB

OCP residue levels in soil samples from TBNA are summarized in Table 3. ΣDDT was detected in 79 samples, ΣHCH in 102 samples and HCB in 25 samples. The mean concentrations of ΣDDT, ΣHCH and HCB were higher than those reported earlier in China (Table 5). Especially, ΣHCH concentrations were 14.5 times as much as that in Tianjin (Gong et al. 2004b). The extremely high ΣDDT and ΣHCH concentrations in several samples close to the chemical industrial parks indicate that these sites are heavily polluted. According to the National Environmental Quality Standards for Soils of China, the concentrations of ΣHCH in 63 samples were lower than the first grade (50 µg kg^{-1}), those in 30 samples were between the first and the second grade (500 µg kg^{-1}), those in six samples were between the second and third grade (1000 µg kg^{-1}) and those in six samples were worse than the third grade. While for ΣDDT, the concentrations in 91 samples were lower than the first grade (50 µg kg^{-1}), those in ten samples were between the first and the second grade (500 µg kg^{-1}), those in two samples were between the second and third grade (1000 µg kg^{-1}) and those in only two samples were worse than the third grade. The serious OCP contamination may cause toxic exposure and health risks to the local communities. The mean concentration of HCB was 7.62 µg kg^{-1}, and HCB had the highest concentrations (731 µg kg^{-1}) in a site at Hangu. If this sample was excluded, the mean concentration of HCB was only 0.67±1.75 µg kg^{-1}. It was lower than that in agricultural soils in Central Germany (0.57–3.75 µg kg^{-1}; Manz et al. 2001) and higher than that in soils from Hong Kong (0.007–0.31 µg kg^{-1}; Zhang et al. 2006) and the USA (<1 µg kg^{-1}; Kannan et al. 2003). It indicates that there is no extensive HCB soil pollution at TBNA.

Compositions of DDT and HCH

DDT and its metabolites

Technical DDT and Dicofol containing high DDT-related compound impurities were the main sources of DDT pollution in China. Technical DDT is typically composed of 77.1% *p,p′*-DDT, 14.9% *o,p′*-DDT, 4% *p,p′*-DDE and some other trace impurities (Kannan et al. 1995). A survey of the dicofol in Chinese market found that the ratio of *o,p′*-DDT: *p,p′*-DDT was 7.0. Therefore, sources of DDTs (from technical DDT or dicofol impurities or a mixture) can be identified according to the ratios of *o,p′*-DDT: *p,p′*-DDT (Yang et al. 2008). The mean concentrations of individual compound in soil samples were as follows: *p,p′*-DDD > *p,p′*-DDE > *p,p′*-DDT > *o,p′*-DDT, but

Table 3 Concentration (µg kg^{-1}, dry weight) of organochlorine pesticides in study area soils

	Mean	SD	Median	Minimum	Maximum
α-HCH	16.9	115	0	ND	1,080
β-HCH	6.84	18.7	2.75	ND	156
γ-HCH	636	4870	27.9	ND	49,900
δ-HCH	9.51	93.5	0	ND	958
ΣHCH	666	5010	36.0	ND	51,300
P,p′-DDE	19.3	63.0	1.90	ND	415
P,p′-DDD	40.9	226	0	ND	1,900
O,p′-DDT	2.32	8.45	0	ND	65.2
P,p′-DDT	11.3	27.3	0	ND	168
ΣDDT	73.9	298	5.30	ND	2,420
HCB	7.62	71.3	0	ND	731

Mean, SD, maximum and minimum were calculated assuming non-detect measurements were equal to zero

ND Non-detect

the concentrations of *p*,*p*′-DDD were extremely high in four samples collected near Dagu Chemical Industrial Park. If these samples were excluded, the order would be *p*,*p*′-DDE > *p*,*p*′-DDT > *p*,*p*′-DDD > *o*,*p*′-DDT. It seemed that for most of the areas of TBNA, the conditions of soil usage tend to be aerobic, but anaerobic dechlorination dominated in sampling soils collected near Dagu Chemical Industrial Park. The average ratio of *o*,*p*′-DDT: *p*,*p*′-DDT was 0.21, which was lower than its ‘starting’ value of 0.27, suggesting that dicofol-type DDT pollution was non-existent or just little although there have been some dicofol manufacturers in this area since 1990. A small value of DDT: (DDE + DDD) ratio indicates aged (microbiologically degraded) DDT while a value much greater than 1.0 means fresh application. The DDT: (DDE + DDD) ratios ranged from 0 to 11.1 with a mean of 0.19, implying the existence of aged DDT in most of the soil samples in the study area. However, the DDT: (DDE + DDD) ratios in 20 soil samples were greater than 1.0. ΣDDT concentrations in all these samples were less than 40 μg kg^{-1} except for one sample from Tianjin Harbor (308 μg kg^{-1}), which was much lower than the mean ΣDDT concentrations at TBNA. The microbial transformation rate of DDT to its metabolites DDE and DDD depends on several factors including soil type, temperature, moisture and organic carbon content. Some soils in the southwestern USA contained high proportion of parent DDT due to their poor metabolite capability (Aigner et al. 1998). Therefore, high DDT: (DDE + DDD) ratios in some soil samples at TBNA indicate inhibition of degradation of DDT to DDE and DDD. The high concentrations of ΣDDT at Tianjin Harbor probably are due to export of large amount of technical DDT to some countries to protect Malaria through Tianjin Harbor (Wei et al. 2007).

The isomers of HCH

Technical HCH and lindane were two types of HCH products manufactured and used in China. Technical HCH contains about 55–80% of α-HCH, 5–14% of β-HCH, 8–15% of γ-HCH and minor proportions of other isomers (Senthilkumar et al. 2001) while the major component of lindane is γ-HCH (>99%). Therefore, a high α/γ-ratio of HCHs in soils indicates the input of technical HCH and a low ratio indicates the use of lindane.

In the soil samples from TBNA, γ-HCH was the dominating isomer (95%), concentrations of α-HCH were the second highest among the four HCH isomers. Concentrations of both β-HCH and δ-HCH were very low. The ratios of α/γ-HCHs in the samples ranged from 0 to 3.58 with a mean of 0.027, which were much lower than the α/γ-HCHs ratio of technical HCH, indicating that lindane dominated the HCH inputs. Meanwhile, because there was α-HCH and δ-HCH, a small portion of HCHs in the soils probably arises from the technical HCH input. As for β-HCH, the equatorial disposition of the chlorines confers the greatest physical and metabolic stability to this isomer, and then persists in the environment. A high proportion of β-HCH means that there is a lack of new sources. However, the ratio of β-HCH/ΣHCH ranged from 0–0.69 with a median of 0.061. The low β-HCH and high γ-HCH concentrations indicate that recent lindane inputs might be present in the study area.

Discussion

Regional differences in the pollution loads

The distribution of various OCPs in the soils from the three regions (Tanggu, Hangu and Dagang) is shown in Table 4.

ΣDDT concentrations in Dagang soils ranged from 0 to 20.5 μg kg^{-1} with a mean of 3.48 μg kg^{-1}, which was significantly lower than that in soils from Beijing urban soils (56.8 μg kg^{-1}; Li et al. 2006c), Guanting Reservoir (9.81 μg kg^{-1}; Wang et al. 2005b) and paddy soils from the Pearl River Delta (2.23–232 μg kg^{-1}; Li et al. 2006a), but higher than that in soils from Tibet (0–2.83 μg kg^{-1}; Fu et al. 2006), and similar to that in natural soils from the Pearl River Delta (ranged from 0.27 to 7.99 μg kg^{-1}, median 3.23 μg kg^{-1}; Li et al. 2006a). This indicates that Dagang was slightly polluted by DDTs because this district is far from point sources and has little agricultural activity. The low DDT: (DDD + DDE) ratio (0.52) could be attributed to past DDT uses at Dagang.

ΣDDT levels in Hangu soils ranged from 0 to 85.2 μg $kg^{-1}$with a mean of 12.3 μg kg^{-1}, which was significantly higher than the levels at Dagang and lower than that at Tanggu. The DDT concentrations were similar to concentrations in agricultural soils of Guanting Reservoir (0–76.0 μg kg^{-1}; Wang et al.

Table 4 Regional differences of OCPs residues (μg kg^{-1})

	Tanggu (n=39)			Hangu (n=38)			Dagang (n=28)		
	Mean	SD	Median	Mean	SD	Median	Mean	SD	Median
α-HCH	33.0	172	1.20	12.8	75.3	0	0.04	0.20	0
β-HCH	14.5	29.1	3.95	2.75	2.57	2.43	1.75	2.13	0.91
γ-HCH	193	350	51.8	1,540	8,080	35.8	15.7	34.8	2.67
δ-HCH	0.760	2.19	0	25.5	155	0	0.04	0.20	0
ΣHCH	241	422	70.0	1,580	8,300	38.6	17.6	36.1	5.61
P,p′-DDE	46.5	97.9	5.29	4.83	8.66	1.90	1.11	1.47	0
P,p′-DDD	108	364	2.89	1.48	2.47	0	1.04	2.37	0
O,p′-DDT	5.45	13.2	0	0.710	2.33	0	0.17	0.88	0
P,p′-DDT	24.5	41.0	9.04	5.27	8.48	2.77	1.17	2.56	0
ΣDDT	184	473	17.2	12.3	18.7	6.28	3.48	4.60	2.90
HCB	0.93	1.46	0	19.9	118	0	0.32	1.34	0

2005b). However, the land uses at Hangu were mostly fallow and salt pond where there are no agricultural activity and direct industrial pollution of DDTs. The DDT residues at these sites could originate from atmospheric deposition from point sources. The high *p,p′*-DDT concentration (0.577–1.98 ng m^{-3}; Wu et al. 2005) in total suspended particles at Hangu also supports the results.

ΣDDT levels in Tanggu soils ranged from 0 to 2,420 μg kg^{-1} with a mean of 241 μg kg^{-1}. It was similar to that found in urban and industrial soils of Poland (4.3–2,400 μg kg^{-1}; Falandysz et al. 2001), but higher than that in other places in China (Table 5). Several orders of magnitude variation in concentrations of DDTs were found in soil samples near Dagu Chemical industrial park, which showed that chemical industrial point sources had significant effects on the distribution of DDTs.

Kruskal–Wallis test showed that concentrations of DDT and its metabolites were significantly different among the three regions ($P<0.01$, Table 6). Possibly the differences in soil types and the distances from point sources (Table 1, Fig. 1) caused these differences. There was a significant ‘regional effect’ with respect to the concentrations of DDT and its metabolites between Tanggu and Dagang. The chemical plants and waste dumps at Tanggu may be important sources of DDT pollution. The concentrations of DDT and its metabolites at Hangu were not significantly different from that at Dagang. It indicated that the chemical industrial park at Hangu had a little effect on local DDT inputs.

The distribution of the average concentrations of HCHs showed different degrees of pollution as: Hangu > Tanggu > Dagang. The low α/γ-HCHs ratio of the three regions indicated that there were new

Table 5 Soil OCP residues of other areas and countries (mean concentrations, μg kg^{-1})

Locations	Characteristic	DDTs	HCHs	HCB	References
Tianjin (China)	Whole area	49.6	45.8	–	Gong et al. 2004a, b
Guangting Reservoir (China)	Agricultural soils	9.81	0.69	–	Wang et al. 2005b
Chennai (India)	Dumping-site	26	31	0.31	Minh et al. 2006
Beijing urban city (China)	Urban soil	56.8	7.53	1.58	Li et al. 2006c
Central Germany	Agricultural soils	23.7–173	4.60–11.5	0.57–3.75	Manz et al. 2001
Kraków (Poland)	Close to industrial areas	260	11	1.7	Falandysz et al. 2001
Saõ Paulo State (Brazil)	Forest soils	0.12–11	0.05–0.92	–	Rissato et al. 2006
South Carolina and Georgia (USA)	Cotton soils	0.11–45	<1	<1	Kannan et al. 2003
South India	Agricultural soils	<0.1–35	<0.1–4.8	ND–0.2	Senthilkumar et al. 2001

ND Not detected

Table 6 Kruskal–Wallis and Mann–Whitney tests among three regions

OCPs pollutants	Kruskal–Wallis test	Mann–Whitney test		
		Hangu vs.Tanggu	Tanggu vs. Dagang	Hangu vs. Dagang
α-HCH	0.000	0.003	0.000	0.009
β-HCH	0.000	0.001	0.000	0.092
γ-HCH	0.000	0.203	0.064	0.000
δ-HCH	0.176	0.731	0.000	0.104
ΣHCH	0.000	0.053	0.000	0.000
p,p′-DDE	0.001	0.044	0.000	0.026
p,p′-DDD	0.001	0.003	0.001	0.404
o,p′-DDT	0.002	0.015	0.003	0.283
p,p′-DDT	0.000	0.008	0.000	0.010
ΣDDT	0.000	0.006	0.000	0.019
HCB	0.024	0.080	0.012	0.334

Difference is significant at the 0.01 levels

sources of lindane. The mean γ-HCH concentrations at Hangu, Tanggu and Dagang soils were 1,540, 193 and 15.7 μg kg^{-1} respectively. Even the mean HCH concentration at Dagang was higher than that in Beijing urban area (7.53 μg kg^{-1}; Li et al. 2006c), Guangting Reservoir (0.69 μg kg^{-1}; Wang et al. 2005b) and crop soils of Pearl River Delta (0.05–24.1 μg kg^{-1}; Li et al. 2006a). Due to the long distances from point sources and slight agricultural activity at Dagang, γ-HCH contaminant at Dagang was mostly from atmospheric deposition of γ-HCH point sources. This is different from DDTs pollution status at Dagang because of higher vapor pressure of γ-HCH than that of DDTs.

ΣHCH concentrations in soils of Hangu and Tanggu were much higher than that in the whole Tianjin area (45.8 μg kg^{-1}). Although ΣHCH concentrations at Hangu and Tanggu were lower than the concentrations (more than 2,000 μg kg^{-1}) in old HCH formulation factories of Spain (Concha-Graña et al. 2006), such high concentrations were seldom detected in agricultural or urban soils in other studies. This shows that the soils at Hangu as well as at Tanggu were heavily contaminated by HCHs.

Kruskal–Wallis test showed a general nonhomogeneity of HCH concentrations among the three regions. However, the distribution of δ-HCH concentrations had no significant difference among the three regions. The most possible reason was that proportions of δ-HCH both in technical HCH and in lindane were very small. According to Mann–Whitney tests, ΣHCH concentrations in Dagang soils were significantly lower than that in Tanggu soils, while γ-HCH concentrations between Dagang and Tanggu soils were not significantly different. It was possibly because γ-HCH at Dagang and Tanggu had similar sources (the atmospheric deposition) although the two regions had different distances from 'point sources' such as chemical industrial parks. Meanwhile, α-HCH concentrations at Tanggu were significantly higher than those at Hangu and at Dagang. Technical HCH application, as the result of heavy agricultural activity, leads to larger amount of other HCH isomers inputs at Tanggu than that at other regions.

The mean residue levels of HCB (19.9 μg kg^{-1}) at Hangu were much higher than that at Tanggu (0.93 μg kg^{-1}) and Dagang (0.32 μg kg^{-1}). However, if the site with extremely high HCB concentration (731 μg kg^{-1}) was excluded, the mean level of HCB at Hangu would be 0.65 μg kg^{-1}. The Kruskal-Wallis and Mann-Whitney tests showed that there was no significant 'regional difference' of HCB concentrations. The similar distribution of HCB residue levels in three regions indicated that the HCB production plants and HCB formation as a by-product had little effect on soil residues in the study area.

Pollutants input identification using statistical analysis

Principal component analysis was made to reduce a set of original variables and to extract a small number of latent factors. PCA could be used to find out different sources and degradation behavior of OCPs in the environment (Škrbić and Đurišić-Mladenović 2007; Manz et al. 2001).

By using PCA for the data of DDT concentrations, the first two factors accounted for 97.3% of the total

Table 7 Correlations between OCPs in soils of study area

	α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCH	*p,p*′-DDE	*p,p*′-DDD	*o,p*′-DDT	*p,p*′-DDT	ΣDDT	HCB
α-HCH	1.000										
β-HCH	0.364[a]	1.000									
γ-HCH	0.297[a]	0.206[a]	1.000								
δ-HCH	0.122	0.188[b]	0.097	1.000							
ΣHCH	0.342[a]	0.285[a]	0.919[a]	0.137	1.000						
p-DDE	0.345[a]	0.350[a]	0.071	0.212[b]	0.115	1.000					
p-DDD	0.284[a]	0.373[a]	0.081	0.269[a]	0.124	0.491[a]	1.000				
o-DDT	0.348[a]	0.332[a]	0.094	0.311[a]	0.170[b]	0.416[a]	0.440[a]	1.000			
p-DDT	0.418[a]	0.388[a]	0.188[a]	0.150	0.242[a]	0.582[a]	0.416[a]	0.526[a]	1.000		
ΣDDT	0.391[a]	0.359[a]	0.121	0.214[a]	0.164[b]	0.735[a]	0.593[a]	0.475[a]	0.749[a]	1.000	
HCB	-0.098	0.294[a]	0.160[b]	0.150	0.184[b]	0.196[b]	0.252[a]	0.110	0.131	0.164[b]	1.000

[a] Correlation is significant at the 0.01 level (2-tailed)

[b] Correlation is significant at the 0.05 level (2-tailed)

variance in the data set. Factor 1 explained 73.2% of the total variance. Four DDT isomers were all included in Factor 1. Most of *p,p*′-DDE (0.951), *p,p*′-DDT (0.926), *o,p*′-DDT (0.832) and more than half of *p,p*′-DDD (0.687) were involved in Factor 1. According to the composition and degradation rules of technical DDT, factor 1 was mainly related to aerobic degradation of "new" technical DDT. The second factor, which accounted for 24.1%, was dominated by *p,p*′-DDD (0.719), moderately by *p,p*′-DDE (0.252) and little negatively related to *p,p*′-DDT (-0.313) and *o,p*′-DDT (-0.534). *p,p*′-DDD was a very minor isomer compared with other isomers in technical DDT, and was a metabolite of *p,p*′-DDT as well as *p,p*′-DDE. Therefore, this factor could mostly relate to the anaerobic degradation of "old" technical DDT.

By using PCA for the data of HCH concentrations, 90.7% of total variance was explained by the first two factors. The first PC, accounting for 65.8% of total variance, had large positive coefficients for α-HCH (0.934), β-HCH (0.936) and δ-HCH (0.927) and a portion of γ-HCH (0.150). It was similar to the composition of technical HCH. Therefore, PC1 was mainly related to technical HCH sources. In PC2, which explained 24.9% of total variance, the absolute loading of γ-HCH (0.987) was significant and the loadings of α-HCH (-0.096), β-HCH (0.040) and δ-HCH (-0.103) were little. Considering the γ-HCH content (99%) of lindane, PC2 explained the sources of lindane, which indicated that HCHs pollution is a mixture of technical HCH and lindane at TBNA.

Correlations between individual compounds

Although the distributions of DDT and HCH concentrations were different in the study area, there existed positive correlations between the concentrations of ΣDDT, ΣHCH and HCB (Table 7). Different OCPs compounds production plants are commonly located within the same chemical industrial park (Table 1). In addition, HCB has been found as an impurity in several chlorinated pesticides, including technical HCH and lindane (Bailey 2001). Therefore, the correlations probably indicate that DDTs, HCHs and HCB have some similar sources within the study area. The studies of OCPs in remote Austrian forest soils (Weiss et al. 2000) and Beijing urban soils (Li et al. 2006c) drew similar conclusions. The concentrations of γ-HCH had no correlation with ΣDDT concentrations. Because HCHs in soils were the cocktail of technical HCH and lindane (99% γ-HCH), it could be concluded that technical HCH had similar sources with DDT but did not have similar sources with lindane, which was consistent with the facts that most of the sites with high γ-HCH residues were not agricultural areas.

Conclusions

The residue levels of HCHs, DDTs and HCB were investigated in the soils from chemical industrial areas in China. The high concentrations of HCHs and DDTs revealed that this area was seriously contaminated.

According to the National Environmental Quality Standards for Soils in China, the levels of OCPs at this region could cause long-term ecotoxicological damage. Regional differences in the OCPs pollution were identified: Tanggu had the highest concentration of DDTs and Hangu had the highest concentration of HCHs, while Dagang was less polluted by OCPs. There were significant regional differences in ΣHCH and ΣDDT concentrations in the three regions. These differences were probably caused by the different intensities of agricultural activity and distances from the point sources. Ratios between OCPs isomers and principal component analysis were used to distinguish the sources and fates of DDTs and HCHs. All the results indicated that the HCH pollution was a mixture pollution of historical technical HCH and current lindane sources, and DDT pollution input was due only to technical DDT sources. The correlations of OCPs compounds revealed that HCHs, DDTs and HCB could come from the similar sources.

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