Factors affecting HCH and DDT in soils around watersheds of Beijing reservoirs, China

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Abstract The factors that influence the dynamics of hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) in soils around the watersheds of Beijing reservoirs were examined. Compared with other studies on HCH and DDT in soils and established reference values, the concentrations of HCH and DDT in soils around our study area were relatively low. The relationships between HCH and DDT concentrations and land use, soil texture, and soil properties were discussed. HCH and DDT concentrations were higher in arable soils than those in uncultivated fallow soils. Although land use was the most important factor affecting HCH and DDT residues, additional factors such as soil texture and soil total organic carbon were also involved in pesticide retention in soils. The results indicated that the historical agricultural applications of HCH and DDT were the major source of their residues. Atmospheric deposition, as well as long-distance

transportation and inputs from surrounding weathered agricultural soils may also serve as important sources of HCH and DDT residues in the watersheds.

Keywords Hexachlorocyclohexane and dichlorodiphenyltrichloroethane · Soil contamination · Land use · Watershed · Beijing

Introduction

Hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) are persistent hydrophobic contaminants, and are resistant to biotic and abiotic degradation in the environment (Loganathan and Kannan 1994; Kannan et al. 2004; Gonzalez-Lopez et al. 2005). The environmental fate of HCH and DDT residues is an issue that has received considerable attention over the past three decades due to international regulations on residue levels in food and drinking water (Whyllie et al. 2003). Soil is a reservoir for HCH and DDT and is a source of contamination of food and drinking water. A significant proportion of HCH and DDT, typically ranging from 20–70% of a pesticide or its degradation products, may remain in soil following application (Miglioranza et al. 2003b). When HCH and DDT are applied on a field, several factors control their distribution and fate: some may be lost to the

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atmosphere through volatilization, while others may be carried away by surface runoff or photodegraded by sunlight. Upon entering the soil, HCH and DDT may bind to soil components (organic matter, mineral particles), be taken up by plants, degraded, and transported to the groundwater or surface waterbodies (Bergstrom and Stenstrom 1998; Miglioranza et al. 2003a). Therefore, the soil ecosystem around watersheds plays an important role in storage, transport, and cycling of HCH and DDT in the soil–plant and soil–water interaction zones. Several earlier studies focused on how HCH and DDT residues were distributed in the soil (Harner et al. 1999; Feng et al. 2003; Kannan et al. 2003; Gong et al. 2004; Li et al. 2006; Gao et al. 2008), but only a few studies discussed the factors influencing the residue levels and patterns (Oliver et al. 2003; Wang et al. 2005a; Hao et al. 2008; Wang et al. 2008a). Understanding of factors affecting HCH and DDT residues in soils is important for developing strategies for the monitoring and management of persistent organic pollutants.

As one of the largest agricultural production countries, China has been a major producer and consumer of pesticides, until its ban on production and agricultural use was enforced in 1983 (Wong et al. 2005). In Beijing, water is mainly supplied from Guanting Reservoir (GTR) and Miyun Reservoir (MYR). Around the two reservoirs in Beijing, there are many “green fruit bases”. Agriculture in this region is intensive and highly productive, thus agrochemicals were used intensively to improve crop yields in this area in the past (Xue et al. 2005). One report showed that HCH and DDT accounted for 83.3% of total pesticides sold in Beijing before 1979 (Wang et al. 2008b). The widespread notion is that the land uses occurring in the watersheds can impact the water quality of streams and rivers draining the watershed (Bergstrom and Stenstrom 1998). HCH and DDT residues have been studied in different soils of this area (Wang et al. 2005b; Zhang et al. 2005; Xue and Xu 2006), but these reports focused on limited sites in this region and may not reflect the general situation of soil pollution in the Beijing watershed. For understanding of HCH and DDT levels and to develop an effective soil pollution control plan, detailed and systematic investigation is needed.

The present work is a large-scale and systematic investigation of the residue characteristics and factors affecting HCH and DDT in soils around the Beijing

watershed. The objectives of this study were (1) to determine the residue levels and potential ecological risks of HCH and DDT in surface soils surrounding the Beijing watershed, (2) to elucidate how the environmental factors affect HCH and DDT residues in soils, and (3) to identify the sources of HCH and DDT residues. The information collected will facilitate a better understanding of the residue characteristics and factors affecting HCH and DDT in soils under various conditions around watersheds.

Materials and methods

Study area and sample collection

The study area is the watersheds of two Beijing water reservoirs, GTR and MYR (Fig. 1), which supply water to almost 7 million Beijing residents and have been listed as top water-quality protection areas by the government. The GTR is located northwest of Beijing (latitude 40.19°–40.50°, longitude 115.43°–115.97°), with a total area of 130 km² and a watershed area of 43,402 km². It is Beijing's second-largest water source for agricultural and industrial purposes, and historically, it was also used for drinking water until 1997. Since then, however, industrial pollution and contamination from farming have substantially degraded the quality of water in this reservoir (Xue et al. 2006; Luo et al. 2007; Wang et al. 2007c). The MYR is located northeast of Beijing (latitude 40.13°–40.48°, Longitude 116.40°–117.30°), with a total area of 188 km² and a watershed area of 15,788 km², which makes it the largest water source for Beijing, as well as the largest reservoir in north China. At present, nearly all the drinking-water supply of Beijing comes from this reservoir.

In May 2007, 104 soil samples around GTR and MYR were collected. The locations of the sampling sites are shown in Fig. 1. Throughout the survey, a global positioning system (GPS) was used to locate the sampling sites. The sampling sites covered different types of land-use patterns: orchards, farmlands, and fallow areas. Each sample was made from a mixture of five subsamples collected from the four corners and the center in an area of about 100 × 100 m². All soil subsamples 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

Fig. 1 Study area and soil-sampling locations around the watershed of two reservoirs in Beijing

before the sample was collected. The soil samples were air dried at room temperature (22–25°C) for about 15 days, sieved to <2 mm, and stored at 4°C in pre-cleaned glass jars until analysis.

Reagents

For extraction of pesticides from the soil, n-hexane and dichloromethane (J.T. Baker, HPLC grade) were used. 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, Bellefonte, PA, USA) cartridges containing 1 g of florisil were washed with 10 ml of n-hexane before use. A mixture of standard solution containing α -, β -, γ -, δ - HCH isomers, *p*, *p'*-DDE, *p*, *p'*-DDD, *o*, *p'*-DDT, and *p*, *p'*-DDT at 1 mg/g per compound was obtained from the National Research Center for Certified Reference Materials of China. The amount of substances in the extracts was quantified using the internal standard (2, 4, 5, 6-tetrachloro-m-xylene or TCMX) supplied by Supelco (Supelco, Bellefonte, PA, USA).

Sample extraction and cleanup

The analytical method is similar to that described earlier (Wang et al. 2008a). Each soil sample (5.0 g dry weight) was mixed with 1 g anhydrous sodium sulfate. One milliliter of 2, 4, 5, 6-tetrachloro-m-xylene at a concentration of 0.08 $\mu\text{g}/\text{ml}$ was added. The mixture was extracted twice with 35 ml of 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 cartridges loaded with 1 g silica gel and 1 g anhydrous sodium sulfate. The elution was subsequently carried out using 20 ml of hexane/dichloromethane (7:3, v/v). The effluent was concentrated to a final volume of 1 ml for GC analysis. Reagent blanks were also analyzed simultaneously with the experimental samples. In addition, several grams of soil were dried for 8 h at 80°C to calculate moisture content.

Chromatographic analysis

An Agilent 6890 gas chromatograph (GC) equipped a ^{63}Ni electron capture detector (μECD) (Agilent Technologies, Wilmington, DE, USA) was used for the analysis. The column used was HP-5 silica capillary column with 30 m $\times$ 0.32 mm i.d. $\times$ 0.25 μm film thickness. The purified extract was analyzed by GC- μECD under splitless injection mode with ultrapure nitrogen as the carrier gas and the make-up gas. The injector and detector temperatures were 220 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. HCH and DDT were identified by retention time matched to standards and were quantified based on peak area. The measured HCH and DDT include four HCH isomers and four DDT homologues. The concentrations of $\sum\text{HCH}$ and $\sum\text{DDT}$ are the sum of the four HCH isomers and

four DDT homologues, respectively. The HCH and DDT concentrations in soil are reported on a dry weight basis.

Quality control

For quality assurance and control, procedural blanks and matrixes spiked with the standard solution were analyzed. None of the target compounds were detected in the procedural blanks. All solvents used were distilled in glass (PR grade) and were checked for interferences or contamination prior to use. The recovery rate of HCH and DDT spiked to soil ranged from 73.3 to 96.2%. Extraction efficiency, as indicated by recovery of the surrogate standards (TCMX), was $75 \pm 10\%$. The limits of detection (LOD) were described as three times the signal-to-noise ratio (S/N). The detection limit ranged from 0.05 to 0.20 ng g^{-1} . GC analysis was repeated twice for each replicate sample and the relative standard deviation (RSD) of replicate analyses was less than 10%.

Soil physicochemical characteristics analysis

Soil pH was measured (10 g of air-dried soil suspended in 25 ml deionized water) using a pH meter. Total organic carbon (TOC) and total nitrogen (TN) were analyzed by Universal CHNOS Elemental Analyzer (Elementar Vario EL III, Germany).

Statistical analysis

The software used for mapping the sampling sites was ArcGis (ESRI, US). SPSS 11.5 for Windows was employed for statistical analysis. Correlation analysis was used to explore the relationship between HCH and DDT and selected soil properties.

Results and discussion

Concentrations of HCH and DDT in the study area

The range, mean, and median concentrations of HCH and DDT around the watersheds of Beijing water reservoirs are shown in Table 1. The mean concentrations of $\sum\text{HCH}$ and $\sum\text{DDT}$ were 0.67 and 6.64 ng g^{-1} , ranging from $<\text{LOD}$ to 5.56 ng g^{-1}

and $<\text{LOD}$ to 117 ng g^{-1} , respectively. HCH and DDT were not detected in many locations, or were present only in amounts that were below the detection limit. The high standard deviations of HCH and DDT concentrations indicated high variability of HCH and DDT distribution. In comparison to HCH concentrations in soils from other areas, the mean concentration in the study area was lower than the residual levels reported for the Tibetan plateau (range: 0.18–5.38, mean: 1.97; Fu et al. 2001), the Pearl River delta (range: 0.05–24.1, median: 2.94; Li et al. 2006), central Germany (range: 4.60–11.5, mean: 7.52; Manz et al. 2001) and Romania (range: 2.8–89.5, mean: 26.1; Covaci et al. 2001). DDT levels in this area were higher than those in soils from the Taihu Lake region (range: 0.3–5.3; Feng et al. 2003) and the mountain Andean lakes (range: 0.10–1.10; Borghini et al. 2005), but were significantly lower than those of the Pearl River delta (range: 0.52–414, median: 20.1; Li et al. 2006), central Germany (range: 23.7–173, mean: 72.0; Manz et al. 2001) and Romania (range: 9–187.4, mean: 62.5; Covaci et al. 2001). Overall, the concentrations of HCH and DDT in soils around the Beijing watersheds were lower than those in other places.

The concentrations of HCH and DDT in our soils were compared with the soil-quality reference values recommended in China and in the Netherlands (Table 1). According to the Guidelines of Chinese Environmental Quality Standard for Soils (GB15618-1995), and the Dutch target values (NMH 2000), the concentrations of $\sum\text{HCH}$ in all samples were lower than the first grade (50 ng g^{-1}) of the Chinese environmental quality standard and Dutch target values (10 ng g^{-1}). The mean concentrations of $\alpha\text{-HCH}$ and $\beta\text{-HCH}$ were also within the limit of Dutch target values. The mean concentrations of $\sum\text{DDT}$ in 101 samples were below the first grade (50 ng g^{-1}), those in three samples were above the first grade but beneath the second grade (500 ng g^{-1}), and there were 16 soil samples exceeded the Dutch target values (10 ng g^{-1}) but were much lower than the intervention values ($4,000 \text{ ng g}^{-1}$). According to the Guideline of Chinese Environmental Quality Standard, the maximum permitted concentration of both HCH and DDT in the soil should be less than 500 ng g^{-1} in order to ensure the safety of agricultural products and to prevent food contamination from pesticides, which can damage human health. The data of this study showed that the levels of HCH and DDT in soils

Table 1 Concentrations (ng g⁻¹ dw) of HCH and DDT in soils around the Beijing watershed

OCPs	Mean	SD	Minimum	Maximum	Median	Detection rate (%)	Target values	
							Chn ^d	Neth ^e
α -HCH	0.01	0.04	<LOD	0.27	0.00	10.77		3
β -HCH	0.46	0.75	<LOD	4.58	0.28	59.31		9
γ -HCH	0.14	0.17	<LOD	1.01	0.12	62.19		0.05
δ -HCH	0.05	0.21	<LOD	1.53	0.00	11.23		
$\sum$ HCH ^a	0.67	0.95	<LOD	5.56	0.40	83.73	50	10
<i>p</i> , <i>p'</i> -DDE	3.11	8.61	<LOD	78.07	0.78	81.69		
<i>p</i> , <i>p'</i> -DDD	0.16	0.65	<LOD	5.71	0.00	17.46		
<i>o</i> , <i>p'</i> -DDT	0.59	1.58	<LOD	9.04	0.00	34.54		
<i>p</i> , <i>p'</i> -DDT	2.72	6.65	<LOD	50.73	0.97	91.19		
$\sum$ DDT ^b	6.64	15.3	<LOD	116.74	1.91	93.31	50	10
Ratio1 ^c	0.04	0.13	0.00	0.73	0.00			
Ratio2 ^c	1.00	1.10	0.00	5.49	0.64			

Mean, SD, minimum, maximum and median were calculated assuming less than LOD (limits of detection) were equal to zero for statistical purpose

^a $\sum$ HCH = α -HCH + β -HCH + γ -HCH + δ -HCH

^b $\sum$ DDT = *p*, *p'*-DDE + *p*, *p'*-DDD + *o*, *p'*-DDT + *p*, *p'*-DDT

^c Ratio1 = α -HCH/ γ -HCH; Ratio2 = (*p*, *p'*-DDE + *p*, *p'*-DDD)/*p*, *p'*-DDT

^d Chn: Chinese environmental quality standard for soils (GB15618-1995)

^e Neth: The Netherlands target values for soil remediation (2000)

around GTR were significantly lower than the mandatory safe values. Although almost all of the HCH and DDT concentrations in soils were much lower than the Chinese Environmental Quality Standard, the HCH and DDT concentrations, especially DDT, in some sites were higher than the Dutch target values for soil remediation. As a result, further soil remediation may be essential for improving soil quality to reach the international standard for producing and exporting agricultural products in this region.

The mean percentages of HCH isomers in soils were as follows: β -HCH > γ -HCH > δ -HCH > α -HCH. A relatively high proportion of β -HCH (69% of $\sum$ HCH) confirmed that the technical HCH had not been used in this region recently (Zhu et al. 2005). The predominance of β -HCH among HCH in most soil samples suggested that HCH was mainly from historical inputs (Toan et al. 2007). The mean ratio of α -HCH/ γ -HCH was 0.04 with a maximum of 0.73, and the ratios were zero in 90% of the samples, which were much lower than the α / γ -HCH ratio found in the technical HCH mixture, possibly indicating an input of lindane in the past several years or that more α -HCH has evaporated into atmosphere from soil with

time (Gao et al. 2008). The mean composition of DDT compounds in soils was as follows: *p*, *p'*-DDE > *p*, *p'*-DDT > *o*, *p'*-DDT > *p*, *p'*-DDD, with the *p*, *p'*-DDE accounted for a major composition of DDT (48% of $\sum$ DDT). This indicated that the DDT contamination of the soil occurred in the past and that a substantial amount of aerobic degradation of DDT has already taken place. During the dry season, because of the aerobic soil conditions, the active oxidative transformation of *p*, *p'*-DDT to *p*, *p'*-DDE was expected (Toan et al. 2007). The higher concentration of DDE found in this area was most likely related to the longer persistence of DDE than that of DDD and their parent compound, DDT. The predominance of metabolites with respect to parent compounds suggested a contamination mainly by runoff from aged and weathered agricultural soils (Miglioranza et al. 2004). The ratio of (*p*, *p'*-DDE + *p*, *p'*-DDD)/*p*, *p'*-DDT was <1 in 63% of the soil samples, and the high proportion of *p*, *p'*-DDT (41% of $\sum$ DDT) indicated a recent input of DDT had occurred at some sampling sites. This could be explained by that after the ban on the use of HCH and DDT in agricultural production was enforced, the

input of agricultural application had been cut, while the input from weathered agricultural soils and atmospheric deposition may have served as continuous sources of the residue (Villa et al. 2003; Gioia et al. 2005).

Effect of land use on the HCH and DDT residues

Land use is a pivotal factor that affects HCH and DDT residues because different land uses can lead to the differences in the quantity of HCH and DDT applied, HCH and DDT remediation capacities, cultivation pattern, and soil physico-chemical and biological properties (Harner et al. 1999; Gong et al. 2004; Wang et al. 2005a; Gaw et al. 2006). Soils collected from different land-use patterns were analyzed to determine the effects of land use on HCH and DDT residues. Soil samples in the study area were categorized into three types of land uses as orchards, farmlands, and fallow lands. The average concentrations of HCH and DDT in soils under three land uses are presented in Table 2. The total concentration of HCH in soils varied only slightly among land use categories, which may be due to the relatively higher vapor pressure of HCH making it much easier to volatilize than DDT from soil to atmosphere (Zhang et al. 2006). The levels of DDT in soils under the three land-use types differed from those of HCH. The mean levels of $\sum$ DDT decreased in the following order: orchard > farmland > fallow. The total concentrations of DDT in arable soils were significantly ($p < 0.05$) higher than those in fallow soils, suggesting that DDT was mostly used for agricultural activities in this region over the past years. In addition, the highest levels of HCH and DDT were all found in orchard soil, which confirmed that fruit and vegetable cultivation used high levels of HCH and DDT. The lower pesticide concentrations detected in fallow soils might be due to drift of pesticides and volatilization from the nearby agricultural areas (Miglioranza et al. 2003b), followed by atmospheric deposition (Harner et al. 1999). From the atmosphere, pesticides can be delivered to the terrestrial environment via dry or wet deposition (Shegunova et al. 2007).

The relative concentrations of the parent compounds and their metabolites/isomers can provide useful information on the origin of these compounds, the history of how they were imputed into the

environment, and possible degradation pathways involved (Wang et al. 2007b). Among all HCH isomers, β -HCH is the most stable and persistent to microbial degradation. The ratio of β -HCH/ γ -HCH can increase during the degradation process. We used the ratio of β -HCH/ γ -HCH to reflect the degradation of HCH in soils (Fig. 2). There was no significant difference in the ratios of β -HCH/ γ -HCH in soils under the three land-use types, which indicated that land use might not have a significant influence on the degradation of HCH in soils, or the ratio of β -HCH/ γ -HCH does not represent the influence of land uses on HCH degradation in soils (Wang et al. 2007a). Since DDT levels in the natural environment will decrease with time and the major metabolites are expected to be DDE and DDD, the ratio of metabolite/parent compound can be used to understand the degradation pathway of DDT in soils (Wang et al. 2007a). The ratios of (DDD + DDE)/DDT in soils under three land uses were: Orchard $\approx$ Farmland > fallow (Fig. 2). The small ratio of (DDD + DDE)/DDT in the fallow soils suggested that degradation of DDT was the slowest (Miglioranza et al. 2003a). This could also be explained by the fact that the fallow soils were not subject to mechanical mixing (e.g., plowing and disking) or fertilization, which would otherwise enhance microbial action (Harner et al. 1999). The accumulation patterns of HCH and DDT in different soils represented a dynamic balance between deposition and erosion in association with tillage management practices and the effects of natural processes such as rainfall and flooding (Miglioranza et al. 2003a).

Effect of soil textures on the HCH and DDT residues

The fact that HCH and DDT are still present in measurable concentrations in many of the sampled soils means that these residues resisted degradation, leaching, and volatilization due to strong sorption (Hilber et al. 2008). The intensity of HCH and DDT degradation depends upon several environmental factors and soil parameters such as total organic carbon (TOC), soil texture, soil pH, water content and temperature, as well as the structure of the pesticides (Manz et al. 2001; Wenzel et al. 2002; Miglioranza et al. 2003a; Hilber et al. 2008). In this study, soil samples were categorized into four types of textures

Table 2 Concentrations (ng g⁻¹ dw) of HCH and DDT in soils under three land-use types

OCPs	Orchard (<i>n</i> = 39)		Farmland (<i>n</i> = 51)		Fallow (<i>n</i> = 14)	
	Mean	SD	Mean	SD	Mean	SD
α -HCH	0.01	0.02	0.01	0.04	0.03	0.06
β -HCH	0.57	1.01	0.37	0.40	0.45	0.93
γ -HCH	0.15	0.16	0.16	0.17	0.07	0.13
δ -HCH	0.03	0.08	0.05	0.21	0.14	0.41
Σ HCH	0.76	1.13	0.59	0.57	0.70	1.46
<i>p</i> , <i>p'</i> -DDE	4.67	12.80	2.47	4.91	1.11	1.83
<i>p</i> , <i>p'</i> -DDD	0.12	0.31	0.21	0.86	0.13	0.47
<i>o</i> , <i>p'</i> -DDT	0.82	1.93	0.37	1.12	0.71	1.93
<i>p</i> , <i>p'</i> -DDT	3.50	8.98	2.43	5.29	1.62	1.90
Σ DDT	9.10	21.02	5.61	11.41	3.56	5.27

Fig. 2 Ratios of β -HCH/ γ -HCH and (DDD + DDE)/DDT in soils under different land-use types

(loam, light loam, sandy loam, and sandy soil) to delineate the influence of soil texture on HCH and DDT residue levels. The concentrations of HCH and DDT by different soil textures are given in Fig. 3.

For HCH and its isomers, the highest levels were found in sandy loam soil, which may be explained because the sandy loam soil together with intensive cropping in this soil (Sparovek et al. 2001). No significant difference was found in HCH residues among the other soil textures. This mainly results from HCH's higher water solubility, vapor pressure, and high Henry's law constant than that of DDT. In this regard, HCH has a stronger ability to degrade and transfer from soil into liquid and atmosphere (Shi et al. 2005). For DDT and its metabolites, the residues in loamy soil were significantly higher than those in

sandy soil, which were similar to the soils from GTR in the previous study (Wang et al. 2005a). This could be explained because, compared to sandy soil, loamy soil can hold more moisture and organic materials, which have the effect of strengthening the ability of the soil particles to adsorb DDT, as well as the ability of decelerating the degradation and cleanup process of this pollutant. In general, it is assumed that the influence of soil texture on the absorption of HCH and DDT is minor compared to the influence from land uses.

Fig. 3 Concentrations (ng g⁻¹ dw) of HCH and DDT in soils with different textures

Table 3 Correlations between HCH and DDT and selected soil properties

	α -HCH	β -HCH	γ -HCH	δ -HCH	Σ HCH	p, p' -DDE	p, p' -DDD	o, p' -DDT	p, p' -DDT	Σ DDT
TOC	0.35**	0.27**	0.25**	0.03	0.28**	0.19	−0.02	0.08	0.14	0.19
TN	0.02	0.05	0.07	−0.11	0.03	0.07	−0.09	−0.05	0.03	0.05
pH	0.06	0.04	−0.01	0.20**	0.08	0.02	0.07	0.01	−0.12	−0.04

** Correlation is significant at the 0.01 level

Effect of soil physicochemical properties on HCH and DDT residues

Soil physicochemical properties play a role in determining the concentrations of pollutants. These parameters affect both the current concentration in the soil system as well as possible adsorption onto various soil components (Zhang et al. 2005). The increase of organic carbon content in soil can increase the amount of microbial biomass and thus can induce the degradation or absorption (Wang et al. 2007a). As a result, total organic carbon (TOC) content could affect the residue levels of HCH and DDT in soils (Zhang et al. 2006). Soil pH can affect the concentrations of HCH and DDT in soil by influencing the microbiological activity in the soil (Wenzel et al. 2002). There have been few reports about the relationship between HCH and DDT residues and total nitrogen (TN) content in soil. In this study, the physicochemical properties of soil (TOC, TN, and pH) were analyzed to examine the possible relationship with HCH and DDT residues.

The results of correlation analyses among HCH, DDT, TOC, and pH are listed in Table 3. Significant positive correlations among α -HCH, β -HCH, γ -HCH, Σ HCH and β -HCH/ γ -HCH with TOC, and between δ -HCH and pH were observed. The correlation between HCH and TOC suggests binding of HCH to soil organic matter (Zhu et al. 2005). A correlation between pH and δ -HCH was found, but such relationships were not found for DDT and other HCH isomers, indicating that soil pH has no obvious effect on DDT and HCH residues in the study area. There were no significant correlations between DDT concentrations and TOC content, HCH and DDT concentrations and TN, which indicated that the residue levels were a reflection of DDT application history and dissipation rates rather than air-soil

equilibrium, which is similar to the agricultural soils from Alabama, USA (Harner et al. 1999) and Georgia, USA (Kannan et al. 2003) and different from the surface soils from Tianjin, China (Gong et al. 2004). These results show that the degradation of HCH and DDT is complex and is affected by many factors. It is therefore impossible to use a single soil-geochemical factor to predict the distribution of HCH and DDT residues in soils at the regional scale (Hao et al. 2008).

Conclusions

The results of this study elucidated the distribution and factors affecting HCH and DDT in soils from orchards, farmlands, and fallow land around the Beijing watershed. Compared to the earlier studies of HCH and DDT in soils and established reference values, the pollution due to HCH and DDT was generally low in soils around our study area. Land uses and soil characteristics account for the considerable differences in HCH and DDT accumulation among the studied soils. HCH and DDT concentrations were higher in arable soils than those in uncultivated fallow soils. HCH residues were highest in sandy loam soil, compared to DDT residues, which were highest in loamy soil. A significant positive correlation ($p < 0.01$) between TOC and HCH indicated that TOC could enhance absorption of HCH in soils. The results indicated that HCH and DDT residues in soils were mainly from the historical application. Atmospheric deposition, as well as long-distance transportation and surrounding weathered agricultural soils, may also serve as sources of HCH and DDT residues. Further soil remediation will be essential for improving soil quality of arable land to safeguard the quality of food.

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