Spatial variability and temporal trends of HCH and DDT in soils around Beijing Guanting Reservoir, China

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Received: 23 June 2009 / Accepted: 29 January 2010 / Published online: 13 February 2010
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Abstract Spatial variability and temporal trends in concentrations of the organochlorine pesticides (OCPs), hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT), in surface soils around Beijing Guanting Reservoir (GTR) were studied in 2003 and 2007. Concentrations of the two OCPs in soils around GTR were generally less than reference values set by the Chinese government for the protection of agricultural production and human health. Among the OCPs, β -HCH and p, p' -DDE were the two predominant compounds. This result indicates that the HCH and DDT residues in soils were primarily from historical use. Based on kriging, a spatial

distribution of HCH and DDT around the GTR was observed. Spatial variability indicated how HCH and DDT had been applied and been distributed in the past. Between 2003 and 2007, concentrations of HCH and DDT decreased more rapidly in orchard soils than those in fallow soils.

Keywords Land use · Watershed · Hexachlorocyclohexane and Dichlorodiphenyltrichloroethane · Geo-statistical methods · Kriging

Introduction

Due to international regulations on residue levels in soil, water, sediment and food, the environmental fate of OCP residues is an issue that has received considerable attention over the past three decades. Soil is a reservoir for the OCPs and over time has gradually changed from a major sink to an important emission source of OCPs to food and drinking water. This reemission will continue for many years to come (Tao et al. 2008). Significant proportions of between 20 and 70% of a pesticide or its degradation products can remain in soil following application (Miglioranza et al. 2003b). Spatial variability and temporal investigations of OCP concentrations in various environments are useful in developing a better understanding of OCPs behavior in different ecosystems and in predicting their future impact on environmental and

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human health (Hung et al. 2005). Although in previous studies OCP concentrations have been measured in different soils from different regions of Beijing (Shi et al. 2005; Wang et al. 2005a; Zhang et al. 2005; Zhu et al. 2005; Li et al. 2008), and the spatial variability of concentrations of HCH and DDT has been analyzed (Li et al. 2005; Zhang et al. 2007), studies of temporal trends of HCH and DDT in soils have been limited.

Guanting Reservoir (GTR) is Beijing's second largest water source for agricultural and industrial purposes. Agriculture in this region is both concentrated and productive. The local economy is based primarily on agriculture, and agrochemicals have been used intensively to improve crop yields. Historically, some more persistent OCPs were heavily used in these areas (Xue et al. 2005). The occurrence of OCPs in soils around watersheds is one of the major sources of pollutants in the aquatic environment of the upstream rivers and its tributaries, especially adjacent water bodies (Wan et al. 2005; Poolpak et al. 2008). Therefore, in agricultural areas around watersheds where OCPs were applied in large amounts, monitoring of OCP residues continues. As part of this monitoring program, integrated and systemic studies of concentrations of various organic and inorganic pollutants have been conducted (Wang et al. 2005b; Zhang et al. 2005; Luo et al. 2007). These studies have assessed health risks for the local population who have been living in the neighborhood of the reservoir since 2003. Since the Beijing municipal government and the national government have established the Beijing water environmental protection initiative, one of the plans has been the resumption of using GTR as a drinking water source by 2010. Thus, elucidation of spatial variability and temporal trends of OCPs in soils around reservoirs is of great importance in long-term conservation and management of reservoir ecosystems. Furthermore, to be able to predict future concentrations of OCP in soils estimates of the rate of dissipation were needed.

This paper presents an overview of the spatial variability of OCPs in soils around GTR, and temporal trends through comparison of concentrations of HCH and DDT in 2003 and 2007. The analyses presented in this report will facilitate better understanding of the residue characteristics and tendency effects of HCH and DDT in soils under various conditions around watersheds.

Materials and methods

Study area and sample collection

This study focused on a 920 km² watershed around GTR, which is located northwest of Beijing, China (E115.43°–115.97°, N40.19°–40.50°), and includes the 98 km² reservoir and 820 km² of surrounding land. Historically, GTR was used as a drinking water supply until 1997. Due to contamination from industry and agricultural runoff, the quality of water in this reservoir is no longer suitable as a source of drinking water (Xue et al. 2006; Luo et al. 2007; Wang et al. 2007), and currently the water is used primarily for irrigation of crops, including grapes, apricots, corn, wheat, and soy beans.

In May 2003 and May 2007, 56 and 60 soil samples were collected around GTR, respectively (Fig. 1). Although it should be noted that an accurate comparison of OCP residues cannot be made unless the sampling sites and points were all the same, this study nonetheless provided an estimated comparison for HCH and DDT concentrations in soil samples from different years. Throughout the survey, a global positioning system (GPS) was used to locate the sampling sites. Each sample was made from a mixture of five sub-samples collected from the center and at the four corners of an area of about 100 × 100 m². All soil sub-samples were collected at a depth of 0–20 cm using a stainless steel shovel. Grass and other larger materials were removed from the surface of each sample location before the sample was collected. Soils were air dried at room temperature (22–25°C) for 15 days, sieved to <2 mm, and stored at 4°C in pre-cleaned glass jars until analysis.

Reagents and instruments

HCH and DDT were extracted from soil with *n*-hexane and dichloromethane (J.T.Baker, HPLC grade). 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) cartridges containing 1 g of florasil 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

Fig. 1 Location of the sampling sites in the year 2003 (a) and 2007 (b)

Materials of China. The mass of analytes in extracts was quantified by use of internal standard (2, 4, 5, 6-tetrachloro-m-xylene or TCMX) supplied by Supelco (Supelco, Bellefonte, PA). An Agilent 6890 gas chromatograph (GC) equipped a ^{63}Ni electron capture detector (μECD) (Agilent Technologies, Wilmington, DE) was used for identification and quantification of HCH and DDT isomers. The column used was an HP-5 silica capillary column with $30\text{ m} \times 0.32\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$ film thickness.

Sample extraction and cleanup

The analytical method used was similar to that described earlier (Wang et al. 2009). 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 the concentration of $0.08\text{ }\mu\text{g/ml}$ was added. The mixture was extracted twice with 35 ml of hexane/dichloromethane (1:1, v/v) by ultra-sonication for 60 min and then centrifuged. Extracts were concentrated to approximately 2 ml by rotary evaporation and further purified with SPE cartridges loaded with 1 g silica gel and 1 g anhydrous sodium sulfate. Analytes were eluted with 20 ml of hexane/dichloromethane (7:3, v/v). The eluent was concentrated by N_2 to a final volume of 1 ml for GC analysis. Reagent blanks were also analyzed simultaneously with the experimental samples. Meanwhile, several grams of soil were dried for 8 h at 80°C to calculate moisture content.

Chromatographic analysis

The purified extract was analyzed by GC- μECD under split-less injection mode with ultra-pure

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, and 10°C/min to 270°C with a 2-min hold. The four HCH isomers (α , β , γ , δ) and four DDT homologues (p , p' -DDE, p , p' -DDD, o , p' -DDT, and p , p' -DDT) were identified by retention time matched to standards and were quantified based on peak area. Concentrations of $\sum\text{HCH}$ and $\sum\text{DDT}$ were calculated by summing the four HCH isomers and four DDT homologues, respectively, and reported on a dry soil 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. Recovery of the four HCH isomers (α , β , γ , and δ -HCH) and four DDT homologues (p , p' -DDE, p , p' -DDD, o , p' -DDT, and p , p' -DDT) spiked to soil were 73.3, 90.3, 75.8, 85.6% and 80.0, 93.8, 95.4, 96.2%, respectively. 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 of signal-to-noise ratio (S/N). The detection limit ranged from $0.05\text{--}0.20\text{ ng g}^{-1}\text{ dw}$. GC analysis was repeated twice for each replicate sample, and the relative standard deviation (RSD) of replicate analyses was less than 10%.

Data analyses

The software used for mapping the sampling sites and spatial analysis was ArcGis (ESRI, US). SPSS 11.5 for windows was employed for statistical analysis.

Results and discussion

Concentrations of HCH and DDT in soils around GTR

The concentrations of $\sum$ HCH and $\sum$ DDT in soils were described by minimum, maximum, difference between mean, median, standard deviation, and coefficient of variation (CV) (Table 1). Among these descriptors, CV is the most discriminating factor. The mean concentrations of $\sum$ HCH and $\sum$ DDT were 8.5×10^{-1} and $7.8 \text{ ng g}^{-1} \text{ dw}$, ranging from $<\text{LOD}$ to $5.6 \text{ ng g}^{-1} \text{ dw}$ and $<\text{LOD}$ to $1.2 \times 10^2 \text{ ng g}^{-1} \text{ dw}$, respectively. When CV is $<10\%$, the property shows little variability; if CV is greater than 90% , it indicates relatively great variability (Wei et al. 2008). The large coefficients of variation of HCH and DDT concentrations ($>100\%$) indicated intense variability of HCH

and DDT distribution. This type of patchy distribution is often observed for concentrations of residues in soils and leads to non-normal frequency distributions. To better understand the magnitude of HCH and DDT concentrations in soils around GTR, comparisons of concentrations in this study were compared to those in other locations. Mean concentrations of HCH in the study area were less than concentrations reported for the Pearl River Delta (range: 0.05–24.1, median: 2.94) (Li et al. 2006), Haihe Plain, China (range: 0.02–349, mean: 3.90) (Tao et al. 2008), 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). Concentrations of DDT in this area were greater 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), Haihe Plain, China (range: 0.40–2350, mean: 63.6) (Tao et al. 2008), and central Germany (range: 23.7–173, mean: 72.0) (Manz et al. 2001). In general, concentrations of HCH and DDT in soils around GTR were less than those in other places.

Table 1 Concentrations ($\text{ng g}^{-1} \text{ dw}$) of HCH and DDT components in soils around GTR relative to the target values set by China and the Netherlands

OCPs	Mean	SD	Minimum	Maximum	Median	CV ^c (%)	Target values	
							Chn ^d	Neth ^e
α -HCH	2.0×10^{-2}	0.5×10^{-2}	$<\text{LOD}$	2.7×10^{-1}	0.0	282		3.0
β -HCH	5.9×10^{-1}	9.4×10^{-1}	$<\text{LOD}$	4.6	2.5×10^{-1}	159		9.0
γ -HCH	1.6×10^{-1}	1.9×10^{-1}	$<\text{LOD}$	1.0	1.2×10^{-1}	122		5.0×10^{-2}
δ -HCH	7.0×10^{-2}	2.2×10^{-1}	$<\text{LOD}$	1.5	0.0	305		
$\sum$ HCH ^a	8.5×10^{-1}	1.2	$<\text{LOD}$	5.6	4.4×10^{-1}	139	5.0×10^1	1.0×10^1
p, p' -DDE	3.9	1.1×10^1	$<\text{LOD}$	7.8×10^1	9.5×10^{-1}	275		
p, p' -DDD	1.1×10^{-1}	3.3×10^{-1}	$<\text{LOD}$	1.8	0.0	292		
o, p' -DDT	7.5×10^{-1}	1.8	$<\text{LOD}$	9.0	0.0	242		
p, p' -DDT	3.0	7.4	$<\text{LOD}$	5.1×10^1	1.2	248		
$\sum$ DDT ^b	7.8	1.8×10^1	$<\text{LOD}$	1.2×10^2	2.3	226	5.0×10^1	1.0×10^1

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

^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 CV (%): coefficient of variation

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

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

Concentrations of HCH and DDT in soils were compared with the soil quality reference values recommended in China and in the Netherlands (Table 1). According to the Guideline of Chinese Environmental Quality Standard for soils (GB15618-1995), the maximum permitted concentration of both HCH and DDT in the soil should be less than the second grade ($5.0 \times 10^2 \text{ ng g}^{-1} \text{ dw}$) in order to ensure the safety of agricultural products and to prevent food contamination from HCH and DDT, which can cause detriment to human health, while the first grade ($5.0 \times 10^1 \text{ ng g}^{-1} \text{ dw}$) is for protection of regional ecology and maintaining the natural environmental background. Concentrations of $\sum \text{HCH}$ in all samples were less than the first grade ($5.0 \times 10^1 \text{ ng g}^{-1} \text{ dw}$) set by the Guideline of Chinese Environmental Quality Standard and Dutch target values ($1.0 \times 10^1 \text{ ng g}^{-1} \text{ dw}$) (NMH 2000). Mean concentrations of α -HCH, β -HCH, and γ -HCH were also less than the suggested limit of Dutch target values. While for $\sum \text{DDT}$ concentrations in 58 samples were less than the first grade classification, those in two samples were between the first and the second grade, and there were 11 soil samples that exceeded the Dutch target values but were less than the intervention values ($4.0 \times 10^3 \text{ ng g}^{-1} \text{ dw}$) (NMH 2000).

The mean percentages of HCH isomers in soils were as follows: $\beta\text{-HCH} > \gamma\text{-HCH} > \delta\text{-HCH} > \alpha\text{-HCH}$. The relatively great proportion of β -HCH (70% of $\sum \text{HCH}$) observed in this study indicates that technical HCH has not been used in this region recently (Zhu et al. 2005). The predominance of β -HCH among HCH in most soil samples suggested that the HCH is mainly due to historical uses (Toan et al. 2007). The order of contribution of individual constituents to the total concentration of $\sum \text{DDT}$ was: $p, p'\text{-DDE} > p, p'\text{-DDT} > o, p'\text{-DDT} > p, p'\text{-DDD}$, with the $p, p'\text{-DDE}$ accounting for the greatest proportion of $\sum \text{DDT}$ (50%). This indicated that the DDT in soils was due to historical applications. The pattern on constituents observed further suggests that significant aerobic degradation of DDT occurred in soil. The greater concentration of DDE found in the soil in this area was also related to the longer persistence of DDE than that of DDD or the 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 large proportion of

$p, p'\text{-DDT}$ (39% of $\sum \text{DDT}$) indicated a more recent input of DDT occurred at some locations. This could be explained by the fact that after cessation of use of DDT in agriculture, input from weathered agricultural soils and atmospheric deposition may have served as a continuous source (Villa et al. 2003; Gioia et al. 2005; Yang et al. 2008).

Spatial distribution and residue trends of HCH and DDT in soils

Knowledge of spatial distribution and residue trends of contaminants is essential for site assessment and subsequent risk assessment. Geo-statistical methods such as kriging have been applied to investigate the spatial variability of continuously varying environmental parameters to develop distribution maps. Kriging is a linear interpolation procedure that provides a best linear, unbiased estimator (BLUE) for spatially varying quantities. The procedure, then, facilitates estimates at un-sampled locations (Lin 2002). Spatial distributions of HCH and DDT concentrations around GTR are presented as kriging maps (Fig. 2).

The distribution patterns of $\sum \text{HCH}$ were similar for 2003 and 2007 (Fig. 2a, c). After 4 years degradation, $\sum \text{HCH}$ concentrations in soils were significantly greater in the central area compared to other regions. This area is more mountainous as well as having more orchards than other areas. In the past, a considerable amount of pesticides was used in this area. As a result, concentrations of HCH in this area were greater than those in other areas. Moreover, it has been reported that a pesticide factory was once located near this area, which might also have been a source of OCPs (Wang et al. 2007). At the upstream region of GTR (the northeast corner of the map), $\sum \text{HCH}$ concentrations were significantly less than those in other areas in 2007, which were also similar to those of 2003. In general, the differences in the spatial distribution of HCH were not significant between 2003 and 2007. Restriction of the use of HCH has brought a general decrease in $\sum \text{HCH}$ concentrations in soil, but the rate of decrease has been slow.

$\sum \text{DDT}$ concentrations in soils decreased from northwest to southeast (Figs. 2b, d). The trends analysis indicated that the mean concentration of $\sum \text{DDT}$ followed a significant decreasing trend between 2003 and 2007, which was greater than that of HCH concentrations. At the upstream region of GTR,

Fig. 2 Spatial distribution map of HCH and DDT levels in 2003 (a, b) and 2007 (c, d)

Σ DDT concentrations in soils in 2007 were significantly less than those of 2003, which indicated that Σ DDT decreased more significantly in this region. The relatively great DDT concentration was mainly due to manufacturing of DDT at the upstream region of GTR. The factory was established in 1968 and remained in operation till 1982. Since there were no direct point sources of HCH in this region, concentrations of HCH in soils were less than those in other areas both historically and currently. At the northwest corner of the GTR, relatively great concentrations of Σ DDT were also observed in 2007. In this region, orchards account for more than 50% of all land uses. The results of this analysis suggest that occurrence and distribution of the Σ DDT are dependent on a combination of historical application, retarded degradation, and possible new input (Wang et al. 2007).

Spatial variability of HCH and DDT in soils under different land-use types

Understanding the occurrence and spatial variability of toxic substances can further illuminate the role of

anthropogenic activities in releasing these compounds to the environment and provide information to assist in devising effective strategies to mitigate potential health effects (Marvin et al. 2004). Different land-use types usually cause different pollution statuses of OCPs because of different OCP application quantity, OCP remediation capacities, cultivation pattern, and soil properties (Harner et al. 1999; Gong et al. 2004; Wang et al. 2005a; Gaw et al. 2006). Soils from different land-use types were analyzed in order to determine the spatial variability of the OCP concentrations in different soils. The sampling sites covered three different types of land-use patterns: orchards, farmlands, and fallow land. The average concentrations of Σ HCH and Σ DDT in soils under three land-use types in 2007 are presented (Fig. 3).

Mean concentrations of Σ HCH in soils decreased in the following order: fallow > orchard > farmland. The lesser concentrations of Σ HCH in soils from arable soils (orchard and farmland) indicated that after the ban on HCH application, the residue concentrations of Σ HCH in arable soils have significantly decreased. The greater concentrations of

Fig. 3 Relative concentrations of HCH and DDT ($\text{ng g}^{-1} \text{ dw}$) in soils under different land-use types

$\sum\text{HCH}$ in fallow soils might result from the drift and volatilization of HCH from the nearby agricultural areas (Miglioranza et al. 2003b), followed by atmospheric deposition (Harner et al. 1999). Pesticides can be delivered from the atmosphere to terrestrial environments via dry or wet deposition on the soils (Shegunova et al. 2007). Since the fallow soils studied here were mostly alkali soils and not covered by vegetation, HCH concentrations may not decrease naturally. Furthermore, extensive cultivation and irrigation may result in accelerated biodegradation or dissipation of HCH from arable soils (Harner et al. 1999). Concentrations of $\sum\text{DDT}$ in soils under three land-use types differed from those of $\sum\text{HCH}$. The mean concentrations of $\sum\text{DDT}$ decreased in the following order: orchard > farmland > fallow. Concentrations of $\sum\text{DDT}$ in arable soils were significantly ($p < 0.05$) greater than those in fallow soils, which suggests that DDT was mostly used for agricultural activities in this region in the past years. The greatest concentrations of $\sum\text{DDT}$ were all found in orchard and farmland soils, where it has been confirmed that fruit and vegetable cultivation used greater concentrations of OCPs, including DDT.

Temporal trends in concentrations of $\sum\text{HCH}$ and $\sum\text{DDT}$ in soils under different land-use types

Temporal trend studies are a tool employed to trace the history of contamination and to predict future trends of contaminants in the environment (Loganathan and Kannan 1994). In this study, we used concentrations of $\sum\text{HCH}$ and $\sum\text{DDT}$ from a previous study in the same region (Wang et al. 2005a) to determine temporal trends in concentrations of these two OCPs. While an accurate comparison of pesticide concentrations can only be made if the sampling sites were the same, the information in the study by Wang et al. (2005a) provided an estimate of concentrations in soils under different land-use types during different years (Fig. 4).

$\sum\text{HCH}$ and $\sum\text{DDT}$ in orchard soils were greater but decreased more rapidly during the past 4 years than in fallow soils. Restriction on use and/or production of HCH and DDT in orchards is the most likely explanation for the observed decrease (Polder et al. 2008). Concentrations of $\sum\text{HCH}$ in farmland and fallow soils, and $\sum\text{DDT}$ in fallow soils did not obviously decline. In some of the representative sites for the farmland and fallow soils the OCP concentrations actually increased

Fig. 4 Temporal trends of $\sum\text{HCH}$ and $\sum\text{DDT}$ concentrations ($\text{ng g}^{-1} \text{ dw}$) in soils under three land-use types

to some extent. An explanation for this is that it was after the ban on the continuous use of HCH and DDT in agriculture, such that the input from agricultural application decreased, while the input from weathered agricultural soils and atmospheric deposition served as continuous sources (Villa et al. 2003; Gioia et al. 2005). Elevated concentrations of $\sum$ HCH and $\sum$ DDT were found in fallow soils, and there was no significant decline in their concentrations from 2003 to 2007. This might be due to 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 concentrations of $\sum$ HCH and $\sum$ DDT in the different soils represented a dynamic balance between deposition and erosion in association with tillage management practices and effects of natural processes such as rainfall and flooding (Miglioranza et al. 2003a). In this regard, if common agriculture practices are followed without applying $\sum$ HCH and $\sum$ DDT, the practices themselves will facilitate the degradation of $\sum$ HCH and $\sum$ DDT in soils.

Conclusions

The results of this study elucidated the spatial variability and temporal trends of concentrations of $\sum$ HCH and $\sum$ DDT in soils around Beijing GTR. Compared with established reference values of OCPs for soils, the concentrations of $\sum$ HCH and $\sum$ DDT in soils around our study area were relatively less. The results indicated that the earlier agricultural application in this region was the main source of HCH and DDT. Based on kriging maps, a spatial distribution of $\sum$ HCH and $\sum$ DDT around the GTR was observed. The trend analysis indicated the mean concentration of $\sum$ DDT showed a significant decreasing trend over the 4-year period, which decreased more than those of $\sum$ HCH. Compared with the residue concentrations of $\sum$ HCH and $\sum$ DDT in 2003, concentrations decreased more in orchard soils than those in fallow soils in 2007. With the help of traditional statistical and geo-statistical methods, continual monitoring and further studies of $\sum$ HCH and $\sum$ DDT in various environmental compartments, including biota and abiotic samples, are needed to reveal the trends, environmental behavior, and ecological risks of HCH and DDT in soils around the watershed.

Acknowledgments This study was supported by the National Basic Research Program of China ("973" Research Program) with grant no. 2007CB407307, the Knowledge Innovation Program of the Chinese Academy of Sciences with grant no. KZCX2-YW-420-5 and no. RCEES-QN-200707, and the National Natural Science Foundation of China with grant no. 40601089. Prof. Giesy was supported by the Canada Research Chair program. The authors are grateful to Professor Kurunthachalam Kannan, Wadsworth Center, Albany, New York, for his constructive comments. We also thank the editors and reviewers for their careful work and comments that improved this manuscript.

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