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Spatial Distribution of Organochlorine Pesticide Residues in Soils Surrounding Guanting Reservoir, People's Republic of China

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The Stockholm Convention on Persistent Organic Pollutants lists twelve chlorinated carbon-based compounds as priority persistent organic pollutants (POPs) for special investigation (Jones and Voogt, 1999). The list included eight pesticides (aldrin, dieldrin, endrin, DDT, chlordane, heptachlor, mirex and toxaphene), two industrial chemicals (PCBs and hexachlorobenzene), and two families of unintended manufacturing by-products from the use and/or combustion of chlorine and chlorine containing materials (dioxins and furans). Organochlorine pesticides (OCPs), particularly HCH and DDT, were extensively used insecticides in agriculture, forestry and public health, and have become a ubiquitous element of the environment over the past decade. Although these chemicals are now being banned from manufacture and/or restricted in use in most countries, living organisms including human beings can still come in contact with them by breathing contaminated air, eating contaminated food, and drinking or washing in contaminated water (Terry and Laura, 1995; Politov et al. 2000; Singh, 2001).

Guanting Reservoir was Beijing's second largest source of water until 1997, when its use was discontinued because its water quality failed to meet national standards. Although regional surveys continue to monitor DDT and HCH residue in water and sediment (Ma and Wang, 2001; Kang et al., 2001; Wang et al., 2003), documentation for residue concentrations in the soils is less developed. The present work is the result of a preliminary sampling campaign designed to describe and characterize the spatial structure of contamination from two OCPs, HCH and DDT, in soils surrounding Guanting Reservoir. The information will facilitate a better understanding of the sources of OCP contamination in the area since it was banned from use some 20 years ago, and thus serve as a basis for the management and remediation of the watershed in the future.

MATERIALS AND METHODS

This study focuses on a 920 km^2 area around Guanting Reservoir- a watershed located to the northwest of Beijing, China (E115.43°, N40.19°$\sim$E115.97°, N40.50°), including the 98 km^2 reservoir and 820 km^2 of surrounding land. Land uses in the area can be divided between farms, orchards and fallow ground.

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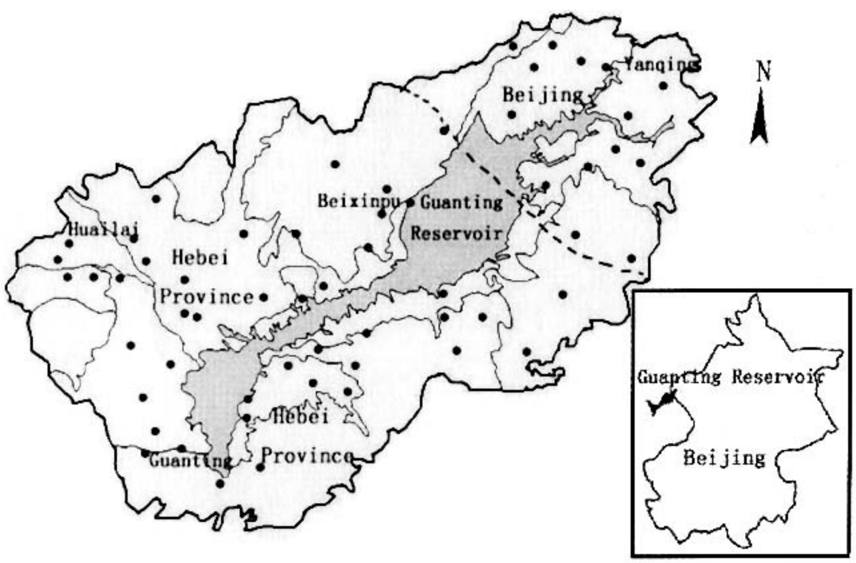

Figure 1. Study area and sample locations in Guanting Reservoir.

Where farming is taking place, the fields are generally planted in corn, with smaller fields and marginal areas used for vegetables. 56 composite geo-referenced samples were obtained in the spring of 2003 (Fig. 1). The composite samples contained 5 increments collected from the upper 20cm of the soil in a cross pattern at 5 m intervals. Sites descriptions were registered when sampled to record the sample location, land use, and major environmental features.

Prior to analysis, the samples were dried at 20℃, sieved through a 2mm mesh and milled using a ball mill. 10g samples were then extracted twice with 100ml hexane: dichloromethane, 7:3 (v:v) for 30 min in an ultrasonic bath. The extracts were centrifuged and decanted to a separating funnel and 10ml concentrated sulfuric acid added to eliminate impurities 2-3 times, and then washed with 50ml 10% sodium chloride solution twice (Kim and Smith, 2001). The extracts were concentrated to ~1 ml by rotary evaporator. Reagent blanks were also analyzed simultaneously with the experimental samples. Gas chromatography was done using a Carlo Erba 500 HRGC fitted with an electron capture detector (63Ni) (GC-6890). Pesticide separation was done using a HP-1 50m×0.32mm id fused silica capillary column with a liquid phase thickness of 0.17μm. The temperature regimen was as follows: 150℃ for 2min, 5℃/min to 200℃, held for 2min, 8℃/min to 270℃ and held for 5min. The carrier gas was helium with a flow rate of 1ml/min. Nitrogen (0.6ml/min) was used as the make up gas for the electron capture detector, and injections made in splitless mode. Compounds recoveries were calculated by adding OCPs standard admixture (obtained from the National Research Center for Certified Reference Materials of China) to the mineral soil, with recoveries in the range of 72.1 ± 4.78%, and a relative standard deviation between 5 and 12%.

Data were submitted to descriptive statistical analysis to define their frequency distribution, and multiple comparisons used to examine relationships between different land uses. The theoretical variogram and spherical model were calculated using Geo-EAS (Environmental Monitoring Systems Lab., U.S. EPA). Contour maps of the total concentration of OCPs in the soil were then constructed using ArcGis (ESRI, U.S).

RESULTS AND DISCUSSION

The descriptive statistics of the OCPs and their isomers relative to soil samples are given in Table 1. Four isomers of HCH were detected in this research. The minimum values of all HCH isomers were 0ng/g, with a maximum value for α-HCH of 0.78ng/g, β-HCH of 2.74ng/g, γ-HCH of 1.41ng/g, and δ-HCH of 3.55ng/g, respectively. Total soil HCH content ranged from 0 to 7.33ng/g, with a mean of 0.69ng/g and a standard deviation of 1.34. Minimum values for the four DDT isomers were 0ng/g, with maximum value for pp'-DDE, pp'-DDD, op'-DDT, and pp'-DDT of 52.20ng/g, 39.09ng/g, 33.08ng/g, and 3.37ng/g, respectively. Total soil DDT content ranged between 0 and 57.90ng/g, with a mean of 9.82ng/g and a rather large standard deviation (10.91). The major OCP in soil samples was DDT, accounting for ~93% of total pesticide concentration. DDT is very resistant to biodegradation and absorbs strongly onto soil particles (Keith, 1997). The current work indicated that it was highly persistent in the top layers of the study area.

Table 1. Concentrations (ng/g) of HCH and DDT in soils around Guanting Reservoir.

Items	α-HCH	β-HCH	γ-HCH	δ-HCH	pp'-DDE	pp'-DDD	op'-DDT	pp'-DDT	∑HCH	∑DDT
Mean	0.06	0.37	0.06	0.19	4.71	0.24	1.73	3.13	0.69	9.82
Standard deviation	0.14	0.69	0.20	0.61	9.42	0.61	6.06	6.70	1.34	10.91
Min value	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Max value	0.78	2.74	1.41	3.55	52.20	3.37	39.09	33.08	7.33	57.90

Although the use of HCH and DDT ceased in China in 1983, the results described in this paper indicates that even after a period of nearly 20 years, residues still persist in topsoil samples. The history of pesticides application in this region is not clearly known, but it is reasonable to assume that pesticides containing HCH and DDT were used in considerable quantities.

The α-HCH/γ-HCH ratio can serve as an indicator of previous HCH use (Kim et al, 2002). A low value indicates that HCH was applied abundantly at a relatively distant location and transported to the detection region by air, while a high value indicates that HCH or a HCH surrogate (such as Lindane) was applied locally. The α-HCH/γ-HCH ratio for the current research was 0.55. This suggests that pollution from HCH in the Guanting Reservoir area was probably induced by some HCH-like pesticide, and that a significant transformation between different homologues must have occurred. Further, in comparison to α-HCH, relative higher β-HCH content was detected throughout the sample area, reinforcing the persistent and stable nature of β-HCH in the environment.

DDT isomers have long persistence in environment, and gradually degrade to DDE and DDD. The percentage of DDE to DDD has been regarded as an indication of either no or decreasing new inputs into the environment (Aguilar, 1984). The linking of different DDT isomers in the Guanting area was: pp'-DDE >pp'-DDT>op'-DDT>pp'-DDD, with a (DDE+DDD)/DDT value of 1.02. The predominance of the DDE isomer in the results indicates that extensive contamination by DDT occurred in the past. However, the relatively high concentration of pp'-DDT (3.13ng/g) indicated that a new input of DDT compounds must have occurred in this region.

To determine the variability of OCPs by land use different soils the data were grouped by land use type (Table 2). Total HCH content in land devoted to orchards was higher than that for the other two uses (farming or fallow ground), and no significant difference detected in HCH content between farming and fallow ground. The pattern of DDT concentration in soils was as follows: orchard>farm>fallow. There was a significant difference between the farm, fallow and orchard by the results of multiple comparisons. This indicates that considerable amounts of pesticide were still being applied in orchards in this region, and some DDT or HCH surrogates were apparently involved in these pesticides. The results of a survey conducted simultaneously with the soil sampling revealed that a large amount of dicofol (a DDT substitute) was still being used on orchards in this region.

Table 2. Concentrations of HCH and DDT in soils under different cultivation.

Items	Farm 27	Orchard 17	Fallow 12
∑HCH (ng/g)	0.52±0.77	1.40±2.07	0.69±1.34
∑DDT (ng/g)	6.58±10.62	20.75±29.03	1.62±3.47

Geostatistics has shown to be a robust tool for studies of spatial variability, even when there are only a few sample points. However, the application of semi-variogram analysis demands that the data have a normal or approximately normal distribution. Based on the HCH and DDT data obtained in the current research, the frequency histograms of the log-transformed data produced the same general unimodal distribution suggesting they were normally distributed. The abscissa of an experimental variogram point represents the mean of all distances included in a corresponding class, where the maximum distance component equals half of the largest dimension in the area as suggested by Journel and Huijbregts (1978). Clark (1982) recommended that the optimum distance class

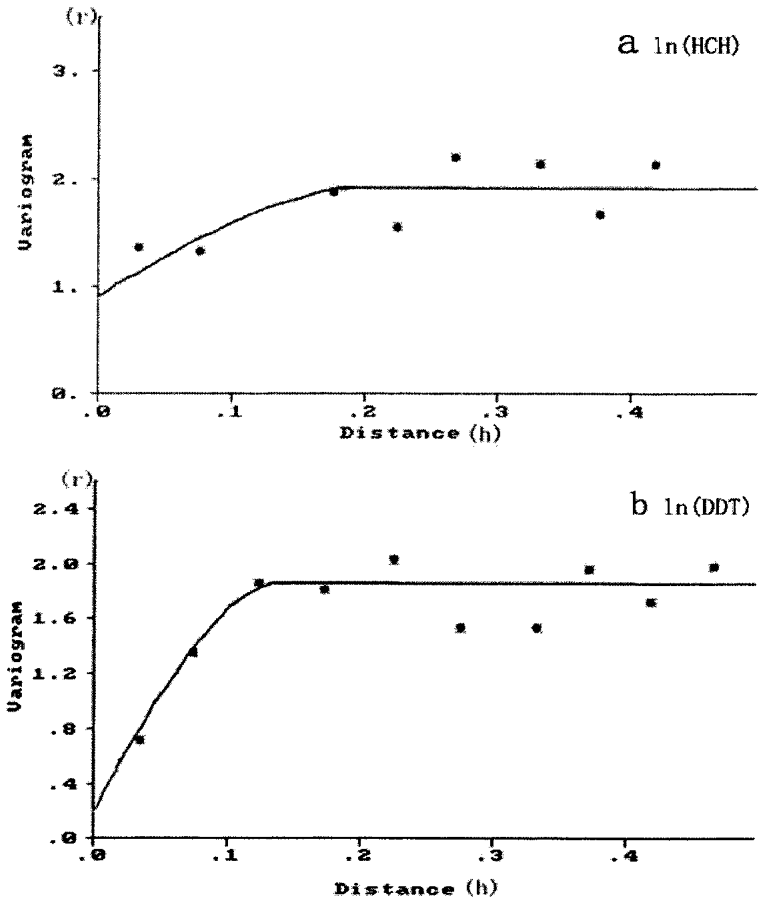

Figure 2. Semi-variogram of HCH (a), DDT (b) and spherical model fitness.

width should have a value of 10% of the mean distance calculated on the basis of all possible distances between pair of points. On this basis, a 0.1 class width was selected for both variograms developed here (Table 2).

Table 2. The theory models of soil OCPs contents and relevant parameters.

OCPs	Theory model	Nugget	Sill	Nugget/Sill	Range(°)	Trans.
HCH	Sphericity	0.9	1.00	90%	0.20	Ln
DDT	Sphericity	0.2	1.65	12%	0.14	Ln

HCH had a relative high nugget value (0.9) compared to DDT, with a moderate increase. Nugget constant usually represents variations caused by experimentation or scale affects. The results of the current work indicated that diversity in small-scale characteristics should be taken into account when examining the spatial variation of HCH - HCH has a lower characteristic temperature than DDT, which allows it to remain in a gas phase longer and thus be transported on a macro-scale (Wania and Mackay, 1996; Rodan, 2002). The Nugget/Sill value can also reflect the degree of the spatial correlation. A Nugget/Sill value less than 25% is typically associated with strong spatial correlation, between 25% and 75% there is medium correlation, and when the value is greater than 75% the spatial correlation is usually quite poor. Based on this criterion, the HCH content in the Guanting area (Nugget/Sill of 90% value) had poor spatial correlation, suggesting that the spatial variation of HCH was mainly induced by stochastic factors such as fertilizer application, cultivation and planting modes, etc. On the other hand, the Nugget/Sill value for DDT (12%) indicates a strong degree of spatial correlation; suggesting that the spatial variation was predominantly affected by structural factors, e.g. soil type, texture, parent materials and topographical factors.

Kriging is a flexible and convenient geostatistical technique used to investigate graphs of spatial autocorrelation that can be exact or smoothed depending on the measurement error model (Krige, 1951). Results of semi-variogram models of the probability maps of HCH and DDT developed here were plotted with ArcGis using ordinary Kriging are shown in Figure 3.

The results show a clear spatial pattern surrounding the Guanting Reservoir for both HCH and DDT, with significantly higher concentrations in the central area as compared to other regions. There was also a strong association between HCH and DDT indicated for areas in the center of the study area. The region is quite mountainous and a great amount of HCH and DDT was used here during the 1970s to protect the forests (Beijing Environment Protection Agency, unpublished). As a result, the effects of DDT usage were far higher than in other areas. Also, because much of the area has been converted to orchards, abundant pesticides (include dicofol) are still being used to control pests and diseases.

In Figure 3a, the areas with highest risk are located around the town of Beixinpu. Except for the highest region in center of the study area, the general spatial trend extended in an approximately NE-SW direction. In areas upstream of the Guanting Reservoir (the northeast corner of the map), the HCH concentration was relatively low. Areas with low probabilities (<40%) may be regarded as "safe" areas where HCH concentrations are unlikely to pose an ecological risk. On the other hand, areas with high probabilities (>70%) may be regarded as "dangerous" areas where HCH concentrations are very likely to induce contamination and affect human health. The general trend of DDT is presented in Figure 3b. The highest value occurred in the center of the plot (the area surrounding Beixinpu town), but relatively high DDT content is also noticeable at the left and right margins of the research area. The study shows that the spatial patterns of HCH and DDT concentrations in soils surrounding Guanting Reservoir are very similar.

It also strongly suggests that the occurrence and formation of OCPs was dependent on historical application and contemporary anthropogenic activities. Given these initial findings, more studies are needed to elucidate the relationship between the OCPs status and various driving force factors, e.g. soil physicochemical properties, climate parameters and biological factors.

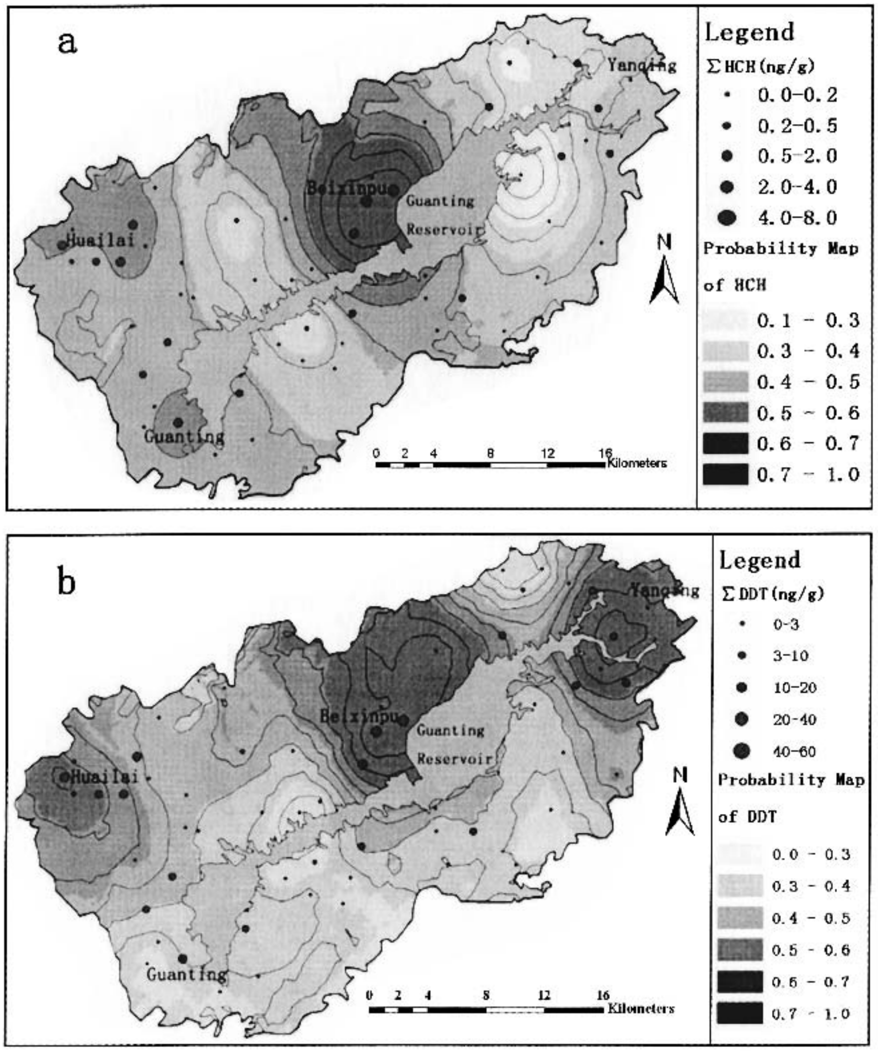

Figure 3. Kriged maps of HCH and DDT contents in soils around Guanting Reservoir.

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