Classification and ordination of DDT and HCH in soil samples from the Guanting Reservoir, China

Zhang Hong a,b,c, Lu Yonglong a,b,*, R.W. Dawson d, Shi Yajuan a,b, Wang Tieyu a,b

a Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
b Graduate School of Chinese Academy of Sciences, Beijing 100039, China
c School of Environmental Science and Resources, Shanxi University, Taiyuan 030006, China
d Center for Land Study, China Agricultural University, Beijing 100083, China

Available online 4 June 2005

Abstract

Organochlorine pesticides (OCPs) have been a major environmental issue, drawing much scientific and public attention due to their bioaccumulation potential, persistence and toxicity. Soil samples from three villages around the Guanting Reservoir, one of Beijing’s five major water systems located to the northwest of the city, were collected in 2003 and analyzed to determine DDT and HCH-concentrations. The samples were also analyzed for soil texture, pH, and concentrations of total carbon, nitrogen and phosphorus to investigate their possible relationship to current OCP-concentrations. Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA) were used to study the distribution and contamination levels of OCPs within the study area. Classification splits were made to divide the 30 samples into three groups. The first group contained samples in soils from village C; the second group contained all of the samples in village B and most of the samples in village A; and the third group contained just three samples from village A, and the three samples had a relatively high concentration of OCPs. Ordination plots of the first two axes from PCA (cumulative percentage 80.91%) were constructed to explore the HCH and DDT-distribution patterns as well as the degradation ratios between the parent substances and their isomers.

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Keywords: Organochlorine pesticides; DDT; HCH; Guanting reservoir; China; Hierarchical Cluster Analysis; Principal Component Analysis

1. Introduction

Persistent organic pollutants (POPs) continue to be a major environmental issue due to their high bioaccumulation potential, persistence in the environment, and high toxicity to non-target organisms (Jones and de Voogt, 1999; Loganathan and Kannan, 1994). With mounting evidence indicating the long-range transport potential of these substances to regions where they have never been used or produced and the consequent threats they pose to the environment, the international community has called for urgent global actions to reduce and eliminate their release into the environment (Bruce, 2002).
In China, as elsewhere, organochlorine pesticides (OCPs) were used to control pests and thus improve crop yields during the 1970s. Included in the group of OCP-pesticides were DDT, HCH, heptachlor, aldrin, dieldrin and endrin, among which DDT and HCH were the most extensively used. Although their use had been discontinued in China since 1982, their persistence has left residual amounts in the soil in many areas (Zhao Ling and Ma Yongjun, 2001; Gong and Gao, 2003; Ma et al., 2003). At present, the use of DDT is still allowed to control mosquitoes, particularly in the malarial transmission zones in China. Accordingly, China still produces a small amount of DDT and China is also allowed to export DDT to other countries for the same purpose, based on Prior Informed Consent (PIC) procedures established under the UNEP (2002). In addition to these original sources of DDT, the use of Dicofol, which contains DDT as impurities, is still allowed.

The Guanting Reservoir, one of the five major water systems in Beijing, is located to the northwest of the city. Prior to 1997 water from the reservoir was used as a source of drinking water for Beijing. Since then, however, industrial pollution and farming contamination have substantially degraded the quality of water in the reservoir (Ma et al., 2001; Wang et al., 2003). The purpose of this research was to determine the current state of pollution in the area due to OCPs, to analyze their distribution, and to distinguish between the previous and current inputs of formerly used organochlorine pesticides.

2. Material and methods

2.1. Sampling

Guanting Reservoir farmland soils from three different series were sampled at the village A (Beixinbu), village B (Langshan) and village C (Xiaogucheng). The three villages were located within a 1 km² area around Guanting Reservoir. The soils selected for sampling were known to have had OCP-usage in the past, and Dicofol was still found to be used till now based on our investigation and interview. The sites differed in physical and chemical soil properties and land use type. Thirty soil samples were collected from 10 farms in village A, 10 farms in village B and 10 farms in village C in the Guanting reservoir area during the summer of 2003 to investigate the degree of OCP content in the soils (Fig. 1). Samples were collected from the surface soil layer (10–20 cm) and the ploughed horizon (20–40 cm), where each sample was a composite of soil sub-samples that were mixed, sieved (1 mm) and freeze-dried prior to analysis. Each sample was divided into two parts, one for soil OCP-analysis and the other for soil geochemical factor analysis. Site descriptions were registered at the time of sampling to record the sample locations (e.g. A2 is the second site of village A, A2-1 is the surface soil of A2, A2-2 is the ploughed horizon soil of A2, etc.).

2.2. Organochlorine analysis

A 100 mg l⁻¹ standard organochlorine pesticide solution, including Aldrin, Heptachlor, Dicofol, α-, β-, γ- and δ-HCH and p,p’-DDT, o,p’-DDT, p,p’-DDE, p,p’-DDD, was purchased from the National Research Center for Certified Reference Materials in China and diluted to the desired concentration. All solvents were of analytical grade and redistilled to remove impurities prior to use.

Analytical procedures were adapted from the standard operating procedures specified in the State Environmental Protection Administration of China methodology guidelines (SEPA, 1993). Ten grams of freeze-dried soil samples were extracted twice with a 50 ml hexane–dichloromethane mixture (1:1 v/v) for 1 h in an ultrasonic bath. The extract was removed using a separating funnel and 10 ml concentrated sulfuric acid added to remove impurities. The procedure was repeated 2–3 times. The organic phase was washed twice with 50 ml 5% sodium chloride solution, and the extract concentrated to about 1 ml using a rotary evaporator as above, then further purified with 2 g silica gel and a 2 g Florisil column (ID 12 mm). Before the extract was loaded, 2 g of anhydrous sodium sulfate was added at the top. The elution was done using 20 ml n-hexane followed by 20 ml n-hexane containing 10% dichloromethane. The solution was evaporated down to 0.5 ml for GC analysis using a gentle stream of clean dry nitrogen. Both matrix blanks and method blanks were analyzed with every batch of 10 samples.

The GC-system was operated in splitless mode, and 1 µl of the extract injected into the GC-system to separate the OCPs. The oven heating regimen consisted of
Table 1

| Pesticide | Limit of detection | Recovery (%) | RSD (%) |
|-----------|--------------------|-------------|---------|
| α-HCH    | 0.46062            | 67.15       | 1.46-8.01 |
| β-HCH    | 0.81954            | 72.95       | 2.33-7.69 |
| γ-HCH    | 0.42246            | 70.56       | 1.30-14.73 |
| δ-HCH    | 0.43290            | 71.20       | 1.86-9.91 |
| p,p′-DDE | 0.47412            | 99.51       | 5.09-16.97 |
| p,p′-DDD | 0.52128            | 90.49       | 4.04-13.0 |
| α,p′-DDT | 1.14696            | 62.51       | 1.79-11.30 |
| p,p′-DDT | 1.24632            | 60.08       | 5.76-18.66 |
| Heptachlor| 0.77922            | 93.53       | 1.34-14.71 |
| Aldrin   | 0.21096            | 80.75       | 2.06-14.0 |
| Dicofol  | 3.65832            | 61.40       | 7.25-15.76 |

*a Values as mean of three determination.

raising the temperature from 150 °C to 200 °C at 5 °C min⁻¹, held for 2 min, then programmed to 270 °C at 8 °C min⁻¹, before holding for 5 min. The injector and detector were maintained at 220 °C and 300 °C, respectively. High-purity nitrogen was used as a carrier gas at a rate of 1.0 ml min⁻¹ and the make-up gas at 49 ml min⁻¹. GC-peaks were identified by accurate assignment of retention times for each standard (±1%).

The OCP-residues were quantitatively determined by comparing the area under each peak with the area under the standard peak. For each sample, a procedural blank and a spiked sample containing all chemicals were run to check for interference and cross-contamination. The resulting correlation coefficients for the calibration curves of the OCPs were all greater than 0.995. The limits of detection (LDS) for OCPs were based on a signal-to-noise ratio (S/N) of 3. The detection limits and recoveries of OCPs are shown in Table 1, with a relative standard deviation variance from 1.30% to 18.66%.

2.3. Soil geochemical factor analysis

The hydrometer method was used to determine texture and soil particle size. Soil pH was obtained from a 1:1 water–soil slurry and determined by pH meter (Jackson, 1964). Organic matter content and total N of soils was determined by high temperature combustion using a CHNOS-element autoanalyzer system. Total P was determined according to the colorimetric method with molybdenum vanadate as the color reagent (Jackson, 1964).

3. Results and discussion

3.1. Concentrations of organochlorine pesticides

The major organochlorine pesticides in the soil samples were from the HCH and DDT-families. Aldrin, heptachlor and Dicofol were not detected in the samples. Although the use of some OCPs ceased in China in 1982, the results described in this paper indicate that residues still persist in the upper soil layers at various concentrations after 20 years (Table 2). The concentration of ∑HCH ranged from non-detectable to 8.96 ng g⁻¹, with a median of 0.56 ng g⁻¹, while that for ∑DDT ranged from non-detectable to 94.07 ng g⁻¹, with a median of 5.11 ng g⁻¹. DDT was also more abundant than HCH. In comparing current levels in the soil with those determined in earlier studies (Zhang et al., 2004), the concentration in 2003 was slightly lower than that in 2002, supporting the principle that OCP-degradation does occur in the soil, although the process may be slow.

Commercial HCH contains 55–80% α-HCH, 5–14% β-HCH, 12–15% γ-HCH, 2–10% δ-HCH and other chloroorganic compounds (Kim et al., 2002). In soils, the average half-life of δ-HCH is 20–50 days while that for α-HCH is 20 weeks (FAO, 2000). Because the ratio of α-HCH/γ-HCH (4–7 in commercial grade HCH) is relatively stable, it can be used as an indicator of the level of degradation or use of HCHs (Kim et al., 2002). In this study, the ratio of α- to γ-HCH (ratio1) was between 0 and 1.92 (with 0.56 as median); lower than that for the HCH mixture and lower than in the previous year’s analysis (1.73) (Zhang et al., 2004). The results indicate that γ-HCH decomposes or biotransforms into other HCH isomers in agricultural soils with time.

Commercial grade DDT generally contains 75% p,p′-DDT, 15% α,p′-DDT, 5% p,p′-DDE, <0.5% p,p′-DDD, <0.5% α,p′-DDD, <0.5% α,p′-DDE and <0.5% unidentified compounds (WHO, 1979). DDT-isomers have a long persistence in the environment, gradually degrading to DDE and DDD under both aerobic and anaerobic conditions. Changes in the ratio of DDE and DDD to DDT has been regarded as an indication of either no or decreasing inputs to the environment (Aguilar, 1982). In this work, the ratio of DDE plus DDD to DDT (ratio 2) was between 0.17 and 3.93, compared to last year’s analysis while ratio 2 is 0.24–4.06 (Zhang et al., 2004), the ratio in this study was lower than that in 2002, indicating that DDT-degradation occurred in the soil, and where the predominance of the DDE-isomer suggests that extensive DDT contamination occurred in the past.

3.2. Cluster analysis

Cluster analysis has proven useful in solving classification problems (Livingstone, 1995) where the object is to sort cases or variables into groups, or clusters, such that the degree of association is strong between members of the same cluster and weak between members of different clusters. Both Q- and R-cluster analyses were performed here using the square of the mean Euclidian distance matrix and the correlation matrix. The samples
were arranged in a series of groups based on relative similarity as shown in Fig. 2 (R cluster) and Fig. 3 (Q cluster).

An R-cluster multivariate analysis was conducted to examine the distribution of geochemical indicators in soils in the Guanting area and any relationships that might exist between them. The results of that analysis produced a dendrogram of indicator connections having similar distribution and behavior (Fig. 2). The first group of elements (OCPs) contained \( \alpha \)-HCH, \( \beta \)-HCH, \( \gamma \)-HCH, and \( \delta \)-HCH, all of which accumulated because of their persistence. This group was further subdivided into two groups as the DDT-group and HCH-group. The second group of elements contained total C, total N and total P in their distributions and is connected with soil organic fertility. The third group is soil texture and the fourth group soil pH, both of which are controlled by soil formation and development processes.

All of the samples were again divided into 2 sets based on a Q-cluster analysis (Fig. 3). The first group (1 group) included 27 samples, which was further divided into 2 sub-groups, C and AB. Group C included all the samples from village C while group AB included most of the samples from village B and most of the samples from village A.

### Table 2

| Variable | Samples | Median | Minimum | Maximum | Kurtosis | Skewness | Std. deviation |
|----------|---------|--------|---------|---------|----------|----------|---------------|
| \( \alpha \)-HCH | 30 | 0.000* | 0.00 | 1.10 | 2.80 | 1.78 | 0.30 |
| \( \beta \)-HCH | 30 | 0.00 | 0.00 | 2.67 | 9.31 | 3.12 | 0.66 |
| \( \gamma \)-HCH | 30 | 0.00 | 0.00 | 1.37 | 2.48 | 1.82 | 0.38 |
| \( \delta \)-HCH | 30 | 0.00 | 0.00 | 3.93 | 18.95 | 4.04 | 0.75 |
| Total HCH | 30 | 0.56 | 0.00 | 8.96 | 10.33 | 2.95 | 1.87 |
| \( p,p' \)-DDE | 30 | 1.24 | 0.00 | 44.82 | 2.93 | 1.98 | 12.37 |
| \( p,p' \)-DDD | 30 | 0.30 | 0.00 | 7.54 | 7.81 | 2.52 | 1.64 |
| \( o,o' \)-DDT | 30 | 0.00 | 0.00 | 5.84 | 5.01 | 2.25 | 1.56 |
| \( p,p' \)-DDT | 30 | 2.69 | 0.00 | 39.80 | 13.02 | 3.36 | 7.91 |
| Total DDT | 30 | 5.11 | 0.00 | 94.07 | 5.46 | 2.31 | 21.97 |
| Total P | 30 | 0.46 | 0.31 | 0.83 | 0.01 | 0.83 | 0.13 |
| Total N | 30 | 0.94 | 0.48 | 1.58 | −0.17 | 0.53 | 0.29 |
| Total C | 30 | 7.60 | 7.00 | 7.90 | 0.72 | −0.77 | 8.15 |
| pH | 30 | 7.00 | 0.00 | 8.15 | 0.13 | 0.29 | 1.30 |

* Values below detection limit indicated as 0.00.
* Median as the average of the concentration of OCPs for non-normality distribution of the data.

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Fig. 2. Dendrogram of Hierarchical Cluster Analysis for variables (R-cluster).
from village A (samples A3-2, A4-1 and A4-2 excluded). The smaller group (2 group) consisted of samples A3-2, A4-1 and A4-2. There were logical reasons for the groupings: (1) different OCP-usage levels in the three villages during the 1980s resulted in different OCP-residues in the soil. Dicofol-usage are also different in the three village; (2) the soil geochemical indicators in village A were more similar to those in village B than to those in village C. Soils of village A and B were mostly loamy and had relatively high organic matter content, soils of village C were sandy and had lower organic matter content; and (3) land use type is a most important factor which influenced the OCP-residuals, for the concentrations of OCPs in farm soils were lower than those in orchard soils.

3.3. Principal Component Analysis

The use of Hierarchical Cluster Analysis and Principal Component Analysis provides a clear overview of the degradation behavior of OCPs (Manz et al., 2001). PCA is one of the simplest and oldest eigenvalue analysis-based ordination methods for quantitative community data. It was performed here to determine the degradation behavior of DDX and HCHs. Ordination reduces the dimensionality of a complex multivariate data set and extracts a set of uncorrelated components from a series of correlated ones. These factors, or axes, are orthogonal linear combinations of the measurement variables and can be useful when examining or comparing the structure of biological communities. When the

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![Dendrogram of Hierarchical Cluster Analysis for cases (Q-cluster).](image-url)
The first two axes of the ordination function are plotted, data from an experimental system with similar characteristics lie close together, while those with dissimilar characteristics are plotted far apart (van Wijngaarden et al., 1995).

PCA was applied here to examine the patterns of OCP-distribution among the sampling sites. The numerical results of the efficiency of the ordination are indicated in Table 3. It can be seen that manipulations along the first three axes (or factors) explain over 80% of the total variation. This is really quite a good result. Normally, one considers that an ordination result is good if this value is 75% or better. Table 3 shows the correlation between PCA axes (or factors) and soil chemical data. The axes for which significant differences ($P < 0.10$) were detected were then examined to determine which chemicals contributed the most to factor loadings. We can see that DDX accounted for the greatest loading for factor 1 and that HCHs accounted for the greatest loading for factor 2, while, pH, TOC, total N and total P accounted for the greatest loading for factor 3.

Fig. 4 shows a plot of the fourteen chemical variables against their values for axes $X$ and $Y$, where 47.74% and 19.88% of the variance are accounted for by the first (axis $X$) and second (axis $Y$) principal components, respectively. The DDX-group and the HCH-group dominated the $X$- and $Y$-axis of the PCA-ordination. In interpreting the diagram the following points should be noted: (1) the distance between the chemical variables shows the degree of similarity and dissimilarity, (2) the distance between the chemical variables from axes is representative of the relationship power in the explanation of variations, and (3) as the length of vector loading increased, the angle between vectors and axes got smaller. The result is that the four isomers of DDX and HCHs have different correlations with different axes, i.e., $p,p'$-DDT has more loading on the $X$-axis with an inverse relationship to the $Y$-axis.

The ordination results of samples sites on the PCA-plot (calculated by regression) are shown in Fig. 5, with most of the sites located near the origin. Because the origin represents the mean concentration of all samples, the results reflect the relatively low concentration of OCPs in the samples (van Wijngaarden et al., 1995). The concentration of OCPs and the degradation behavior of DDT and HCH-isomers for the 30 samples sites are presented in Fig. 5. Fig. 5a shows that the concentration of HCH was highest at A4-1, with $\delta$-HCH dominant among the four HCH isomers. A3-2 also had a high concentration of HCH, but with both $\alpha$-HCH and $\beta$-HCH as dominant isomers compared to A4-1. Fig. 5b shows that the concentration of DDT was much higher in A4-2 and A3-2 than in the other samples. Sample A4-2 had a higher proportion of $p,p'$-DDT compared to the degradation products $p,p$-DDE and $p,p'$-DDD. Sample A3-2, on the other hand, had a high proportion of DDE within the DDX group, clearly indicating the presence of old inputs.

3.4. Correlation analysis

The intensity of OCP-degradation depends upon several environmental factors, temperature, soil type and pH, redox potential, moisture and organic carbon content (Hitch and Day, 1992; Cousins et al., 1999), although substance specific parameters, such as water solubility, vapor pressure and Henry’s law often play a dominant role (Senesi and Miano, 1995). These parameters affect both the current concentration in the soil.
system as well as possible adsorption onto various soil components. In order to get a rough estimate of OCP-behavior in the Guanting soil system, we calculated correlations between several soil geochemical factors and soil OCP-concentration (Table 4). The results indicated a significant correlation between HCHs and soil organic factors, and a poor correlation between the concentration of DDX and soil geochemical levels. Because the degradation of OCPs in soil is a very complicated reaction, this finding suggests that the use of the soil geochemical factors alone is insufficient to assess the soil’s ability to sorb the pesticide.

4. Conclusion

The concentrations of DDT and HCH in soils samples collected in 2003 around Guanting Reservoir were detected and assessed. The investigations illustrate the continued presence of POPs in the area’s soils. In com-
paring the current levels in the soil with those determined in earlier studies, the concentration in 2003 was slightly lower than that in 2002. Only rarely do the concentrations of OCPs found in soils show a large input of these substances in the past and a slow degradation processes in soil.

Hierarchical Cluster Analysis and Principal Component Analysis were used to provide an overview of OCP-degradation behavior in Guanting area in China. Classification splits of the 30 samples into three groups were used to prepare the data for ordination analysis (PCA) to provide an overview of OCP-degradation behavior. Most sample sites were located near the origin of the PCA plot, reflecting a low concentration of OCPs.

In terms of the impact on the environment, the presence of pesticides at the concentrations reported in this work is relatively small. However, the fact that harmful chemicals still persist in the soil 20 years after cessation of use emphasizes the need to ensure that sufficient environmental risk assessments are carried out on such chemicals prior to their release for general use (Kim and Smith, 2001). While progress continues to be made in understanding issues related to OCPs, further exploration is needed to better understand the degradation behavior of OCPs under various conditions.

Acknowledgements

Colleagues at the key lab of Environmental Chemistry and Ecological Toxicology, Research Center for Eco-environmental Science, Dean Jiang Guibing and Dr. Yang Ruiqiang assisted in chemical analyses. This work was supported by the Knowledge Innovation Program of the Chinese Academy of Sciences, with Grant No. KZCX2-414.

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