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Distribution of Organochlorine Pesticides in Urban Soil from Beijing, People's Republic of China

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Organochlorine pesticides (OCPs) are a group of compounds of great environmental concern because of their high toxicity and persistence, bioaccumulation to non-target organism in the ecosystem (Jones et al., 1999). In China, OCPs used to be the most important pesticides, produced to enhance agricultural yields, forestry and public health from the 1960s to 1980s (Li et al., 1998). In 1983, the Chinese government banned the production and usage of technical HCH, but lindane (about 99% ɣ-HCH) is still allowable to use in a restricted way (Li, et al., 2001). DDT has been officially restricted to campaigns for vector control or as the intermediate of dicofol. HCB was used as an industrial chemical and was also by-product of some industrial chlorination processes.

The rapid development of Beijing, as the capital with a population of 13 819 000, has resulted in significant stress to Beijng environments. The city area occupies a surface of 16807 km^2, with more than 400 km^2 is classed as urban areas. As urban areas are densely populated, the environmental quality of urban soil is closely related to human health. Recently some studies revealed that the atmosphere in the urban area of Beijing contained HCHs and DDTs (Wu et al., 2003; Xu et al., 2003). Zhang et al. (2004) reported that the water in Tonghui River, which is a main urban drainage river for Beijing, was moderately polluted by organochlorine pesticides. Generally, the soil was considered as the ultimate sink for OCPs. OCPs in soil can enter into the atmosphere by evaporation and migrate into water by rain et al, thus causing direct or indirect exposure of humans to the organic pollutants (Finizion et al., 1998; Waite et al., 1995). The above prompted us to carry out the monitoring of such pollutants in the urban soil, especially for Beijing, which had ever produced and used large amount of HCHs and DDTs.

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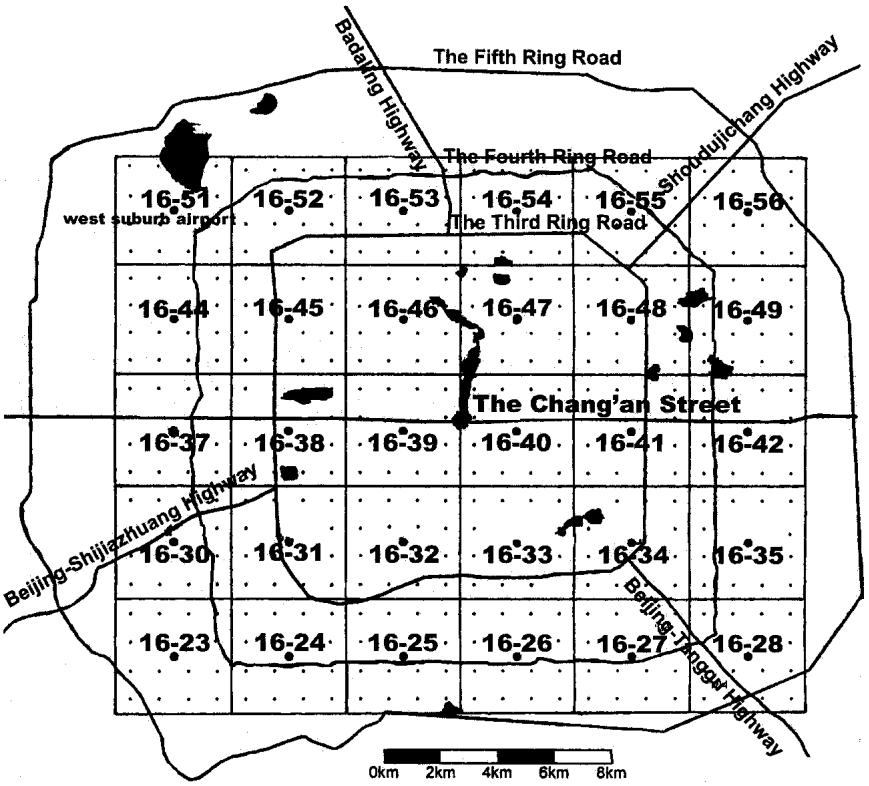

Figure 1. Geographic location of samples sites

The aim of the present study is to explore the current pollution status and accumulation feature of organochlorine pesticides in the topsoil of urban area of Beijing, to investigate the previous and current possible inputs of the OCPs pollutants. The information will be useful for evaluating the soil environmental quality of the metropolis, for the management and remediation of urban soil.

MATERIALS AND METHODS

Stock solutions of eight organochlorine pesticides including α-HCH, β-HCH, γ-HCH, δ-HCH, p,p′-DDT, p,p′-DDE, p,p′-DDD, HCB were obtained from National Research Center for Certified Reference Materials of China at a concentration of 100 mg/L and further diluted to obtain the desired concentration. 2,4,5,6-tetrachloro-*m*-xylene was used as surrogate. All solvents were of analytical purity (Beijing Chemical Factory, China) and were redistilled in all-glass system before use. Florisil (60-100 mesh) were purchased from Supelco (Bellfonte, USA) and was activated in drying oven at 130 ℃ for 16 h.

Anhydrous sodium sulfate (Beijing Chemical Factory, China) was heated at 600 ℃ for 12 h.

The urban area of the whole Beijing city was surrounded by five ring roads. 30 sites at different locations within the five Ring Roads of Beijing city were sampled in the fall in 2003. The study area was divided into regular grids of 4×4 km^2, within which the topsoil samples (5-30 cm) were collected. Each of the composite soil samples was made of 16 sub-samples obtained in a 1×1 km^2 grid using a stainless steel hand auger. The detailed sampling locations are shown in Figure 1. The soil was air-dried at room temperature, thoroughly mixed, sieved to 30 mesh and stored in glass bottles at -4 ℃ until further processing. The remaining water content in the soil was determined gravimetrically after drying individual sample in an oven at 105 ℃ for 12 h. All the results were reported as dried weight.

5 g of soil was ground with anhydrous sodium sulfate into free flowing powder. The sample was ultrasonically extracted in centrifuge tube with 30 mL of 1/1 (v/v) acetone/hexane for 5 min and then the extact was separated by centrifugation. The process was repeated for three times. The solvents were combined and were evaporated by rotary evaporator with a reduce pressure at 35 ℃ water bath, then hexane was added as solvent. The concentrated extract was transferred to chromatograph column (30 cm $\times$10 mm I.D.) containig 5 g activated Florisil and 1 g of anhydrous sodium sulfate on the column top. The Florisil was soaked in hexane and was filled in the column. The concentrated extract was transferred to the column top and was eluted by 50 mL n-hexane/diethyl-ether (9/1). The washing solvent was evaporated by rotary evaporator, then was adjusted to 0.2 mL for GC analysis.

The identification and quantification of organochlorine pesticides were carried out with an Agilent 6890 gas chromatograph equipped with micro-cell ^{63}Ni electron capture detector (μ-ECD). The separation was performed on a fused silica capillary column (HP-5, 30 m$\times$0.25 mm I.D., and 0.25 μm film thickness). The carrier gas was nitrogen with a flow of 0.7 mL/min. The injector and detector temperature were 225 ℃ and 310 ℃, respectively. The GC oven temperature was programmed as follows: initial temperature 100 ℃ held for 2 min, increased to 160 ℃ at a rate of 10 ℃/min, then increased to 230 ℃ at a rate of 4 ℃/min, followed by 10 ℃/min ascent to 280 ℃, maintained for 10 min. 1 μL of sample was injected in splitless mode. Peak identification of organochlorine pesticide was made by comparison of retention times with corresponding standards(see Figure 2).

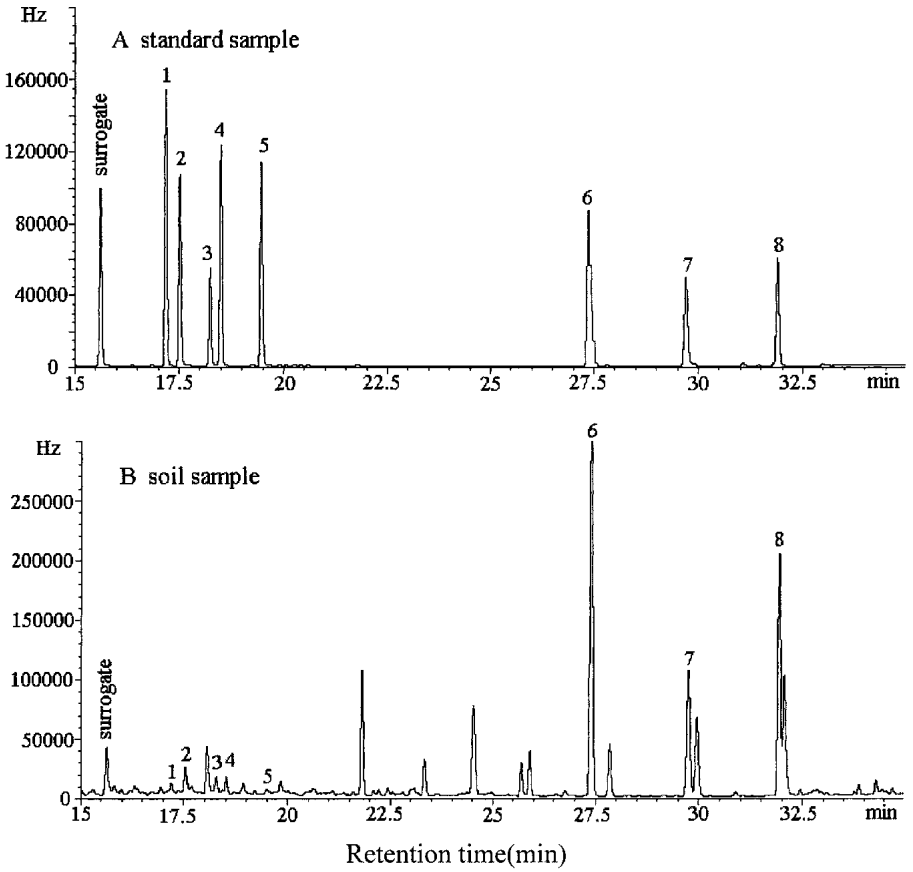

Figure 2. Chromatography of OCPs (A) standard sample; (B) soil sample; Peak numbers correspond to: (1) α-HCH, (2) HCB, (3) β-HCH, (4) γ-HCH, (5) δ -HCH, (6) p,p′-DDE, (7) p,p′-DDD, (8) p,p′-DDT.

Quality assurance criteria for these compound analyses were based on the measures of soil samples from underground about 20 m depth. The limit of detection (LOD) for OCPs as three times response of signal-to-noise in blank sample, ranged from 0.05 to 0.15 ng/g. The average recovery experiments in triple were done by spiked known concentration standards in soil and were 87±7% for DDTs, 82±4% for HCHs and 94±6% for HCB.

RESULTS AND DISCISSION

The concentrations of OCPs residues in each sample analyzed in this study are shown in Figure 3. The ∑DDT (equivalent sum of pp′-DDE, pp′-DDD and pp′-DDT) content had a mean of 56.78 ± 55.42 ng/g of the dry weight and ranged

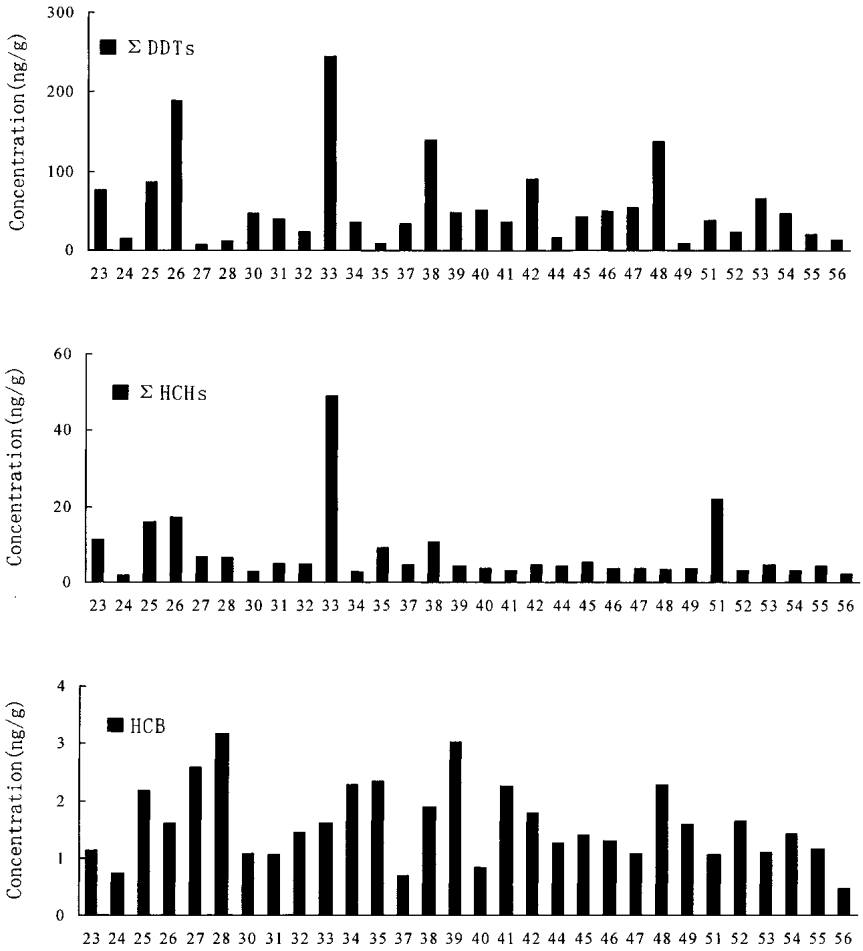

Figure 3. Concentration of DDTs, HCHs and HCB in urban soil from Beijing

from 7.24-244.37 ng/g with 41.31 ng/g as media. The concentrations of DDTs were in general in order pp′-DDE > pp′-DDT > pp′-DDD. The pp′-DDE was the major metabolite and it contributed about 61.0 % of the ∑DDT. The concentrations of DDTs were slightly more than that of DDE concentrations only in three samples (site 33, 26 and 42). Since level of DDT in the natural environment will decrease with time and the major metabolite is expected to be DDE and DDD (Cooke et al., 1982), the ratio of (pp′-DDE+ pp′-DDD) /pp′-DDT may be used to monitor the new input of DDT in the environment. In this study, the ratio of (pp′-DDE+ pp′-DDD)/pp′-DDT was found from 0.81-7.79 ng/g with 1.81 ng/g as median and the ratios of only three soil samples were less than 1. The predominance indicated extensive contamination of DDT occurred in the past.

However, high concentration of DDT in some sites might indicate that there seemed some new input of DDT recently. In comparison with the soil around Beijing, the ∑DDT level in this survey was slightly higher than that in soil around Beijing Guanting Reservoir (nd-176.01 ng/g, Hong et al., 2004), was lower than that in the greenhouse soils from Beijing suburbs (64.44±30.36 ng/g; Ma et al., 2003) and was comparable to soil in Tianjing area (Gong et al., 2004a). Compared the levels of ∑DDT with the other urban areas abroad, value of concentration was lower than that in Romanian (113.1±151.8 ng/g; Covaci et al., 2001), in Katowice (110±89 ng/g; Falandysz et al., 2001) and Kraków (260±620 ng/g; Falandysz et al., 2001). However, it was higher than that in India (3.4-190 ng/g; Kawano et al., 1992).

All the samples had presented the residues of HCH. The ∑HCH content (equivalent sum of α- + β- + γ- + δ-HCH) had a mean of 7.53±9.15 ng/g and ranged from 1.83-48.83 ng/g with 4.43 ng/g as media. β-HCH was the major composition and contributed about 54 % of the ∑HCH. High concentrations of β-HCH meant that there was a significant historical usage of the technical HCH in the research area. The α-/γ-HCH has been used to monitor the source and use history of HCHs. The ratio of α/γ-HCH would be in the range of 4.64-5.83 for the technical HCH and nearly zero for lindane (Zhang et al., 2004). In this study, α-/γ-HCH ratios were in the range of 0-1.25 ng/g (0.36 ng/g as median) and most were less than 0.8, and α/γ-HCH > 1 was only observed in samples from site 38 (1.25) and site 32 (1.01). This result indicated that long time has elapsed since the use of HCHs in the area or/and implied the presence of a possible emission source of lindane, which was used in a restricted way in China. In comparison with the soil study around Beijing, HCHs level in this study was significantly higher than that in soil around Beijing Guanting Reservoir (nd-19.23 ng/g, Hong et al., 2004) and was lower than that in the greenhouse soils from Beijing suburbs (15.77±6.0 ng/g; Ma et al., 2003) and was much lower than that in Tianjing urban area (45.8 ng/g; Gong et al., 2004b). Compared with the other urban areas abroad, the value of concentration was lower than that in Romanian (29.17±27.14 ng/g; Covaci et al., 2001), and Kraków (11±29 ng/g; Falandysz et al., 2001). However, it was higher than urban soil in India (in the range of 0.55-27 ng/g; Kawano et al., 1992) and in Katowice (5.9±3.3 ng/g; Falandysz et al., 2001).

HCB has very strong environmental persistence and toxicity. It can be transported in a long range and be significant accumulated in biota (Muir et al., 1993). In our study, the concentration of HCB was in the range of 0.46-3.17 ng/g with a mean of 1.58±0.68 ng/g. HCB in all soil samples was detected out and the highest concentration appeared in site 28 (3.17 ng/g). The mean value of HCB level in this study was similar to that in Romanian (1.9±2.1 ng/g; Covaci et al., 2001) and

Kraków (1.7±2.6 ng/g; Falandysz et al., 2001), but was lower than that in Katowice (6.4±9.6 ng/g; Falandysz et al., 2001).

In the terms of data obtained, the total pesticides concentration in soil varied from 14.27 to 294.78 ng/g dry weight with a mean value of 50.08 ng/g. The highest concentration was found in site 33. The DDT was major pollutant in urban soil of Beijing and was obviously more abundant than HCHs and HCB reflecting the use of the former insecticide in relatively large amounts for vector control in Beijing. According to the guidelines of Chinese environmental quality standard for soil (GB 15618-1995), the maximum allowable concentration of class I soil was < 50 ng/g, and that of class II soil was < 500 ng/g and that of classIII soil was < 1000 ng/g for both ∑HCH and ∑DDT, respectively. The levels of ∑HCH here in all the soil samples were beneath the criteria of class I .The levels of ∑DDT in all soil samples was beneath the criteria of class II and twenty to thirty soil samples were beneath the criteria of class I . In short, our study showed that the levels of ∑HCH and ∑DDT in all soil samples of the urban area in Beijing were fitted with the national criteria of class II . However, the high concentrations residues of ∑DDT and ∑HCH were found in sites 33 and 26 and this might contribute to this fact that some pesticide and/or chemical industry factories had ever been located in the areas in the past. These sites should be paid close attention.

This work revealed the soil contamination information by DDTs, HCHs and HCB residues in urban area of Beijing. It extends ours understanding of the current OCPs contamination status in the metropolis of China. Concentrations of OCPs at all sites did not exceed the Chinese guideline values for soil. Although the contamination levels detected here weren't high enough to cause acute effects, they could have negative impacts on the local atmosphere, aquatic ecosystems in a long term, especially for several sites with higher concentrations of OCPs.

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