Profile of Organochlorine Pesticides in Soil Cores from Some Hotspot Areas of Beijing, China

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Abstract For the valid use of urban land and the safety of public health, an extensive contamination survey of organochlorine pesticides from five soil cores was conducted in the highly urbanized areas of Beijing in China. For topsoils in five soil cores, level of $\sum$ HCHs and $\sum$ DDTs varied from 0.174 to 4,783 ng g⁻¹ and 0.62 to 57,849 ng g⁻¹, respectively. The profile in topsoil of cores displayed that levels of pollutants in four soil cores from the urban areas with dense population are higher than that from outskirts. The depth characteristics of pollutants indicated that the level of $\sum$ HCHs and $\sum$ DDTs in BY and WU was close to/below the background value of soil in China (50 ng g⁻¹), but those in some soil samples from A, B and ZX core, especially A and B, was above the threshold value for the soil safety (1,000 ng g⁻¹). In views of the usage history of the land and profiles of contaminants, the source in A and B probably came from the dumped waste chemical materials in the old chemical factories. The study of soil cores sampled revealed the existence of chemical “time bomb”

in urban regions of Beijing. Also, the finding indicated the absolute necessity of assessing the soil quality with the unprecedented land use changes in the big city community.

Keywords OCPs · Soil cores · Time bomb · Hotspot areas

HCHs (Hexachlorocyclohexane) and DDTs (Dichlorodiphenyltrichloroethane) are two groups 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). Considering their harm to public health and ecological system, the Chinese government banned the production and usage of technical HCH in 1983, but lindane (about 99% γ -HCH) is still allowable to use in a restricted way (Li et al. 2001), and DDT has been officially restricted to campaigns for vector control or as the intermediate of dicofol.

Beijing is situated in Northern China plain between latitudes 39°26'N and 41°03'N, and the longitudes 115°25'E and 117°30'E and has an area of about 16,800 km². It was well known that Beijing had ever been a heavy industrial city, with great emphasis on coal mining, thermal energy development, metallurgical industry, and industries producing machinery, chemicals, and iron and steel etc., which resulted directly that Beijing was ranked in one of the top ten most polluted cities in the world. With the rapid expansion of urban, the city function regions and land uses of Beijing have been experiencing great alteration. Beijing's government is currently attempting to help a “black list” of more than 200 highly polluting factories or enterprises transform, shut down or move out of the city center. Since these idle land was generally reused to be housing or business, some waste pollutants/hazardous

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materials abandoned to soils by those polluting factories would result in the indirect/direct exposure of human, further caused various social problems. For both of matching the unprecedented land use changes and avoiding the occurring of soil pollution accident as Love canal in America again, the assessing of soil sanitation appeared to be so essential for Beijing. On the basis, this study was carried out for investigating the residue levels of HCHs and DDTs in the soil cores sampled in the hotspot areas in the urban community of Beijing.

Materials and Methods

Stock solutions of eight organochlorine pesticides including α -HCH, β -HCH, γ -HCH, δ -HCH, p,p'-DDT, p,p'-DDE, o,p'-DDT and p,p'-DDD were obtained from National Research Center for Certified Reference Materials of China at a concentration of 100 mg L^{-1} and further diluted to obtain the desired concentration. 2,4,5,6-tetrachloro-m-xylene (TCMX) from Supelco (Bellefonte, PA) was used as surrogates. All solvents were of analytical purity (Beijing Chemical Factory, China) and were redistilled in an all-glass system before use. Florisil (60–100 mesh) was purchased from Supelco and was activated in drying oven at 130°C for 16 h. Anhydrous sodium sulfate (Beijing Chemical Factory, China) was heated at 600°C for 12 h before use.

Based on investigating organochlorine pesticides in topsoil (Li et al. 2006), five soil cores were collected in the research area. The detailed sampling locations are shown in Fig. 1. ZX (26.5 m depth) is between the west Fourth Ring Road and the west Fifth Ring Road. Three of WU (18.0 m depth), A (4.6 m depth) and B (4.2 m depth) are located in the south area of Beijing, and between the south Fifth Ring Road and the south Third Ring Road. The sampling areas of ZX, WU, A and B were ever famous for the old industrial bases of Beijing. BY (15.5 m depth) is situated in the northeast direction outside of the Fifth Ring Road and there is not obviously industrial activities in its surrounding regions. The total 18, 26, 13, 23 and 21 samples were involved in ZX, WU, BY, A and B soil core, respectively. Individual depths of every soil cores are shown in Fig. 2 in detail.

The soil samples were air-dried at room temperature, thoroughly mixed, sieved to 30 mesh, and transferred to pre-cleaned amber glass, and was maintained at 4°C until further processing. The remaining water content in the soil was determined gravimetrically after drying individual composite soil sample in an oven at 105°C for 12 h. All the results were reported as dried weight.

Five grams of soil was ground with anhydrous sodium sulfate into free flowing powder. The sample was

Fig. 1 Geographic location of soil core samples

ultrasonically extracted in centrifuge tube with 30 mL of 1:1 (V:V) acetone: hexane for 5 min and then the extract 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°C water bathing, then hexane was added as solvent. The concentrated extract was transferred to a chromatograph column ($30 \text{ cm} \times 10 \text{ mm I.D.}$) containing 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 the appropriate volume 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 (DB-5, $30 \text{ m} \times 0.318 \text{ mm I.D.}$, and $0.25 \mu\text{m}$ film thickness). The carrier gas was nitrogen with a flow of 0.7 mL min^{-1} . The injector and detector temperature were 225 and 310°C , respectively. The GC oven temperature was programmed as followed: initial temperature 100°C held for 2 min, increased to 160°C at a rate of $10^\circ\text{C min}^{-1}$, then increased to 230°C at a rate of 4°C min^{-1} , followed by $10^\circ\text{C min}^{-1}$ ascent to 280°C , maintained for 10 min. Then, $1 \mu\text{L}$ of sample was injected in splitless mode.

Fig. 2 Depth characteristics of HCHs and DDTs in five soil cores (ng g⁻¹)

Quality control was based on the following procedures. Method blanks were first run. The matrix blanks, the recoveries of OCPs, and the limits of detection (LODs) were based on the measures of deep layer soil from the rural area of Beijing, which had little interference for the target analytes. The average recovery experiments in triple were done by spiked known concentration standards in matrix blank soil and were $87 \pm 7\%$ for DDTs and $82 \pm 4\%$ for HCHs. Before extraction, each of the soil samples was spiked with known amounts of TCMX as surrogate to compensate for the losses of compounds. Recoveries for TCMX surrogate were 72–108% (mean 85%) and the values were satisfactory so that no correction was applied to the samples. The limits of detection (LODs) as three times response of signal-to-noise in matrix blank sample ranged from 0.05 ng g^{-1} for α -HCH to 0.15 ng g^{-1} for p,p'-DDD. The method blank and matrix blank were measured for duplicate with each batch of ten samples. All data have been corrected by blank.

Results and Discussion

Based on the prediction maps for the concentration of pollutants in the topsoil (Li et al. 2006), usage history and future planning of land in Beijing, four soil cores (ZX, WU, A and B) in identified hotspot areas and a soil core (BY) located in the rural county as comparison were sampled for further research. The sampling sites of soil cores were displayed in Fig. 1.

The topsoil sample in five soil cores was recorded as B-1, A-1, ZX-1, WU-1, and BY-1, respectively. For $\sum$ HCHs, the content was in the order of A-1 > B-1 > ZX-1 > WU-1 > BY-1. For $\sum$ DDTs, it was in the order of B-1 > A-1 > ZX-1 > WU-1 > BY-1. The levels of pollutants in topsoil from four soil cores (A, B, ZX and WU) located in urban area are higher than that (BY) in rural county, suggesting the great anthropogenic effect on the sources of pollutants (Fig. 2). The levels of HCHs in A-land B-1 were much higher than that in the others, which were over the safe limit of soil usage ($1,000 \text{ ng g}^{-1}$). Additionally, the levels of DDTs in A-1, B-1 and ZX-1 were higher than in WU-1 and BY-1, and all exceed the safe limit of soil usage ($1,000 \text{ ng g}^{-1}$).

Depth characteristics of HCHs and DDTs in the five soil cores could be further seen in Fig. 2. For HCHs and DDTs in BY as well as WU, the levels of pollutants in the whole core were nearly the background value of soil in China. For ZX, the level of HCHs could be neglected in the whole core. However, the level of DDTs was dominant, which was over 100 ng g^{-1} in most samples in the depth of 0–650 cm. It was worth noticing especially that pollutant levels in A and B cores were with the extremely high

concentration of $\sum$ HCHs and $\sum$ DDTs from top to bottom. For A and B soil core, the highest concentrations of $\sum$ HCHs and $\sum$ DDTs ($1\text{--}100 \text{ mg kg}^{-1}$) exist in the surface/sub-surface depth (0–40 cm for A and 0–60 cm for B). And the lowest level was not yet less than several decades of ng g^{-1} .

To the composition, some difference existed in five soil cores. For HCHs, β -HCH was most dominant in the whole B core and its median of percentage in four components (α -HCH, β -HCH, γ -HCH and δ -HCH) was 0.70. However, γ -HCH was with the highest percent ratio in the whole ZX (percentage median: 0.39) and WU core (percentage median: 0.65). α -HCH was the most abundant in the whole A (percentage median: 0.54) and BY core (percentage median: 0.44). In general, high percentage and concentration of β -HCH meant that there was a significantly historical usage of HCHs in the soil. It seemed that the predominance of β -HCH (percentage median: 0.70) in B soil core indicated that the longer usage time of HCH elapsed than that in other four soil cores. Additionally, 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). The median of α -/ γ -HCH in the whole of A, B, ZX, WU and BY cores was 3.63, 5.04, 0.43, 0.44 and 8.91, respectively. The higher ratio of α -/ γ -HCH in the whole A (percentage median: 3.63), B (percentage median: 5.04) and BY (percentage median: 8.91) cores meant the source of technical HCHs, whereas the lower ratio in ZX (percentage median: 0.43) and WU (percentage median: 0.44) indicated the mixed source of technical HCHs and lindane.

For DDTs, p,p'-DDE was predominant in ZX (percentage median: 0.62) and BY (percentage median: 0.68). The parent compound of p,p'-DDT was the most dominant in B (percentage median: 0.67) and WU (percentage median: 0.46). It was notable that o,p'-DDT was the highest percentage in the total DDTs in A (percentage median: 0.70) and p,p'-DDT was the second highest percentage. The ratio of (p,p'-DDE + p,p'-DDD)/p,p'-DDT generally may be used as an indicator of resident time of p,p'-DDT in the environment (Qiu et al. 2004). The ratio >1 was normally expected for aged mixtures in the environment and <1 indicated the relatively recent exposure to parent DDT (Jaga and Dharmani 2003). In this study, the ratio of (p,p'-DDE + p,p'-DDD)/p,p'-DDT in A, B, ZX, WU and BY was 0.20, 0.22, 3.58, 0.71 and 5.55, respectively. The ratio (less than 1) indicated some new input of DDT recently in A, B and WU. Though there was higher level of DDTs in certain depth of ZX soil core, the ratio (median: 3.58) suggested the old source of DDTs.

Though extremely high level of pollutants existed in A and B soil cores, it seemed that their characteristics were different. As be discussed above, HCHs was the major compounds with the predominance of α -HCH in A soil

core and DDTs was the major compounds with the predominance of p,p'-DDT in B soil core, suggesting the different sources of pollutants in A and B soil core. To our knowledge, the areas of B and A were typical industrial zones in the old Beijing about two decades ago. Beijing chemical factories and Beijing pesticides factory were located around. For more importance, technical HCHs were ever produced more than 10 year in Beijing pesticide factory until its shutdowns at the end of the 1980's. However, it was surprised that there were few archives about how to deal with the rest of chemical materials and pesticides produce in the pesticides factory. Now, both HCHs and DDTs were detected with so large amount and so high fraction of parent compounds (α -HCH and p,p'-DDT) in the soil cores from the zones, probably meaning the existence of some terrible "time-bomb" in the soil surrounding environment, which are probably from the disposal of waste chemical material such as technical HCHs and DDTs. In addition, though the sampling site of A were close to B, it seemed that the compounds profiles and depth characteristics of pollutants were so different, maybe reflecting the disposal different product from the same company or disposal product from different company.

According to the guidelines of Chinese environmental quality standard for soil (GB 15618-1995), the maximum allowable concentration of grade I soil was $<50 \text{ ng g}^{-1}$, and that of grade II soil was $<500 \text{ ng g}^{-1}$ and that of grade III soil was $<1,000 \text{ ng g}^{-1}$ for both $\sum \text{HCH}$ and $\sum \text{DDT}$, respectively. By comparison with the guidelines, the quality of soil was classified as no pollution, low pollution, middle pollution and high pollution. If the pollution level was below grade I, it was defined as no pollution; if the pollution level was between grade I and grade II, it was defined as low pollution; if the pollution level was between grade II and grade III, it was defined as moderate pollution; and if the pollution level exceeded grade III, it was defined as high pollution. For the BY soil core, which located in the rural area, whatever HCHs or DDTs in any depth, both of HCHs and DDTs were beneath the criteria of class I. Though both of the levels of HCHs and DDTs in WU were higher than that in BY, they were still less than the criteria of class I. Therefore, they could be categorized as no pollution for BY and WU soil cores, showing the good quality of soil in BY and WU areas. For ZX, all of HCHs and DDTs were beneath the criteria of class II except for samples from 0 to 50 cm, 600–650 cm ($>$ class III) and 50–100 cm ($>$ class II), therefore they can be categorized as the low pollution in the main. However, for A soil core, the levels of HCHs in most samples were over grade III and might be considered as high pollution of HCHs. The levels of DDTs were nearly in the range of grade I and grade II except for samples in the depth of 0–40 cm and

300–340 cm over grade III. Therefore, they might be mainly categorized as low pollution and those in the depth of 0–40 cm and 300–340 cm might be considered as high pollution of DDTs. For B soil core, the level of HCHs and DDTs were 2–22 fold over the criteria of class III from 0 to 60 cm and might be categorized as high pollution of both HCHs and DDTs. Then, levels in most samples below 80 cm were between class I and class II and might be categorized as low pollution. It was worth noticing that extremely high concentration of HCHs and DDTs appeared in the upper soils in both A and B soil cores. Since pollutants in upper soils easily evaporated to atmosphere, there were great potential for exposure to HCHs and DDTs for nearby residents in the urban environment with dense population. Additionally, in A and B soil cores, the existence of large amount of pollutants in the deep layer soil meant the possibility of underground water polluted. Therefore, some measures about keeping environmental safety must be taken urgently in those regions.

On the basis of the survey of the surface soil in Beijing, China, extreme serious contamination of HCHs and DDTs were found in soil cores from some hotspot areas. Combined with the history usage of land in the serious polluted areas, the contamination source was predicted probably from the disposal of waste chemical material. The results indicated the importance and urgency of assessment of soil quality, which was beneficial to help the development of strategies for the planning and validity of land use with the unprecedented urbanization in big city region.

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