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Distribution and sources of DDTs in urban soils with six types of land use in Beijing, China

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ABSTRACT

The concentrations of dichlorodiphenyltrichloroethanes (DDTs) were investigated for urban soil samples collected from business area (BU), classical garden (CL), culture and educational area (CU), large public green space (LA), residential area (RE), and roadside area (RO) in Beijing. The DDTs concentrations ranged from 0.03 to 1282.58 ng/g, with an average of 68.14 ± 189.46 ng/g. The DDTs concentration in CL was much higher than that in the other five types of land use, which was due to the usage of DDTs to protect vegetation in CL, and the DDTs concentration was affected by both the usage history of DDTs and the age of the CL. Only 22% of the samples, mainly located in RO, manifested the application of technical DDTs recently. DDTs concentration showed a decreasing trend from the city center to the suburb, and it increased with the age of the urban area. DDTs were positively correlated with total organic carbon and black carbon in soils. About 81.7% of the samples met the grade I standard (50 ng/g soil) of the Chinese Environmental Quality Standard for Soils, and only 1.5% of the samples exceeded the grade III standard (1000 ng/g soil).

1. Introduction

Urban soil is known to have unique characteristics such as unpredictable layering, poor structure, and considerable concentrations of trace pollutants [1]. As pollutants in urban soils can be easily transferred into humans through ingestion, inhalation, or dermal routes, etc., they have a direct impact on the health of human beings, especially children and elderly people who are physiologically more vulnerable to environmental pollution [2–7]. Urban soils play an important role in citizens' living, working and recreation, therefore, the study on the environmental quality of urban soils is necessary.

Due to the environmental persistence, dichlorodiphenyltrichloroethanes (DDTs) can be easily accumulated in soil, eventually resulting in human exposure directly or indirectly. Recently DDTs have been identified as hormone disrupters which are capable of affecting the normal function of endocrine and reproductive systems of humans [8,9]. Therefore, a need exists to better understand the distribution and fate of DDTs in the environment. Until now, only few researches have been done on the DDTs in urban soils. Falandysz et al. found that the values of DDTs in the center of Krakow city were even three orders of magnitude higher than elsewhere of the city [10]. Covaci et al. reported that the DDTs concentrations in urban soil of Romania did not exceed the official Romanian norms for DDTs of 500 ng/g soil [11]. Fu et al. found that DDTs were the predominant compounds of OCPs in urban soil of Taiyuan of China [12]. However, all of these studies did not concern about the DDTs levels in different types of land use of urban soils, and the pollutants in soils with different types of land use may exert different impacts on public health [13,14], so the study regarding to the DDTs levels in different types of land use of urban soils is desired.

Beijing is the political, economic and cultural center of China, with a history of over 1000 years and the residents of more than 10 million. Several studies indicated that Beijing soils are contaminated with persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) [15], polycyclic aromatic hydrocarbons (PAHs) [16], and organochlorine pesticides (OCPs) [17]. Zhu et al. and Zhang et al. have studied the distribution of DDTs in the outskirt and rural soils of Beijing [18,19]. Although Li et al. and Wang et al. have studied the distribution of DDTs in urban soil of Beijing, they only regarded to two types of land use: the urban parks and the urban schools [17,20]. So far the difference of DDTs in urban soils with different types of land use in Beijing has not been studied. With the rapid expansion and development of urbanization, the intensity of public activity in different types of land use is distinct; therefore, the research on DDTs levels in different types of land use as well as the possible sources and the impact factors for DDTs distribution in Beijing is necessary.

The aim of this study was to reveal the distribution characteristics of DDTs in urban soils with six types of land use in Beijing, including residential area (RE), business area (BU), large public

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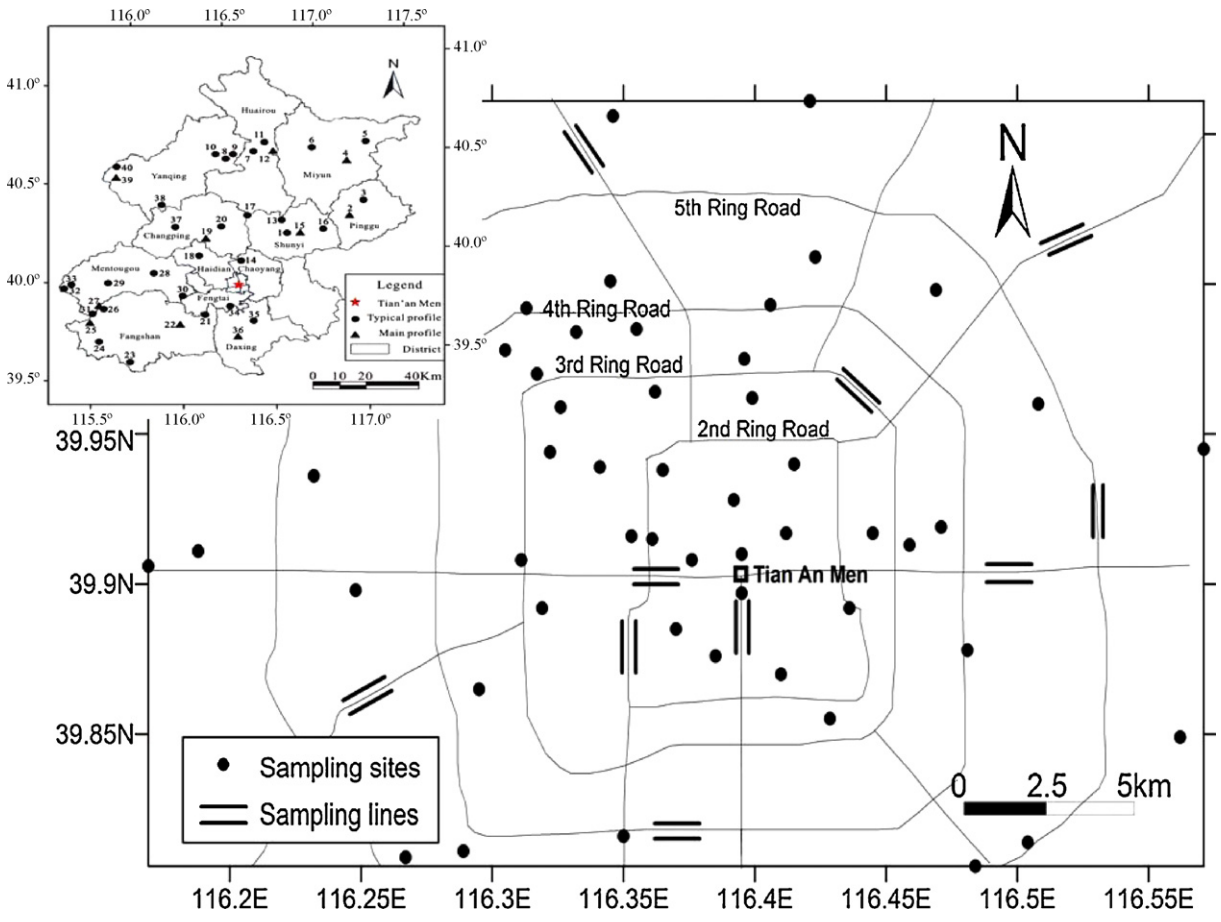

Fig. 1. Sample location of urban soil and rural soil in Beijing.

green space (LA), classical garden (CL), culture and educational area (CU) and roadside area (RO). The possible sources of DDTs were analyzed. The map of DDTs concentration was made to identify its spatial distribution, and the difference of DDTs among the six types of land use was investigated. The relationships between DDTs concentration and physiochemical properties, such as pH, clay content, total organic carbon (TOC) and black carbon (BC) were studied. In addition, the assessment of DDTs pollution in urban soils of Beijing was also conducted.

2. Materials and methods

2.1. Study area

Beijing (39°54′N, 116°23′E), the capital of China, is one of the biggest cities in China. Beijing spans an area of over 16,800 km^2, with urban area of 1040 km^2. Beijing city is surrounded by mountains in its west, north and northeast, its southwest is plain opening toward the lower reach of the Bohai Sea. The annual temperature is about 11.5 °C and the annual precipitation is about 650 mm, with a temperate semi-wet monsoon climate. The main soil texture of the studied area in this research is light loam with a pH from 7.8 to 9.1. The hypsography of Beijing is higher in the northwest direction and lower in the southeast direction so that the rivers flow from the northwest to the southeast areas.

2.2. Sample collection and pretreatment

In this research, the studied area located within the 5th Ring Road of the 9 districts, including Xicheng, Dongcheng, Chongwen, Xuanwu, Haidian, Chaoyang, Fengtai, Shi Jingshan and Changping districts (Fig. 1). Each type of land use contained at least 8 sampling sites, with each site having a consistent land use. We make sure that the layout of all the sampling sites was as even as possible in the urban area of Beijing. A total of 127 topsoil samples (0–20 cm) were collected from urban area of Beijing during April–May in 2008 with a stainless steel shovel, to avoid contamination, only the soil that did not contact with the stainless steel shovel was collected during the sampling. The coordinates of the sample location were recorded with a GPS, and the sampling location is shown in Fig. 1. A total of 8 samples were collected in BU, 9 samples were collected in CL, 9 samples were collected in CU, 12 samples were collected in LA, and 12 samples were collected in RE. In RO, 77 samples were collected from both sides of 10 roads, which are expressed by sampling lines in Fig. 1. Each road contained at least 4 sampling sites, which were within 30 m distant from the road. To make the samples be representative for each type of land use, the number of sub-samples was determined based on the area of sampling site. For RO and BU, each sample was the mixture of 5 sub-samples taken from the sample site; for RE, each sample was the mixture of at least 8 sub-samples taken from the sample site; for LA, CL and CU, each sample was the mixture of at least 10 sub-samples taken from the sample site. All the samples collected were kept in sealed Kraft packages respectively to avoid contamination and transported to the laboratory immediately.

In order to better understand the effect of anthropogenic activities on the environmental quality of urban soils, 40 samples were simultaneously collected from rural soils locating far away from the 5th Ring Road in 12 administrative regions in Beijing (Fig. 1). The concentrations of DDTs between urban soil and rural soil were compared.

For soil pretreatment, the soil samples were air-dried, slightly crushed and sieved through a 10 mesh stainless steel sieve to remove large debris, stones, and pebbles. The samples were then ground by an agate mortar to pass through a 18 mesh stainless steel sieve, sealed into a Kraft paper envelope and kept at room temperature until analysis.

2.3. Reagents

Acetone, n-hexane, and dichloromethane, obtained from Fisher Scientific International Inc., USA were of High Performance Liquid Chromatography (HPLC) grade. Standard solutions of four DDTs including p,p′-DDT, o,p′-DDT, p,p′-DDE and p,p′-DDD were obtained from Labor Dr. Ehrenstorfer, Germany at concentrations of 10 mg L^{-1}. Dilutions were made in n-hexane in order to cover the entire range of DDTs expected in the samples. All solutions were stored at −20°C. Pentachloronitrobenzene (PCNB), obtained from Labor Dr. Ehrenstorfer, Germany, was used as internal standard. Silica gel 80–100 mesh was purchased from Qingdao Haiyang Chemical Co., Ltd. (Qingdao, China). It was activated at 180°C for 12 h in a muffle and then deactivated with 3–5% distilled water before use. Alumina 100–200 mesh, purchased from China National Medicines Corporation Ltd., Shanghai, China, was activated at 250 °C for 12 h and then deactivated with 3–5% distilled water. Diatomite (chemical purity), obtained from Beijing Chemical Factory, China, was used after being heated at 400 °C for 6 h. Anhydrous sodium sulfate, obtained from Beijing Chemical Factory, China, was first washed with hexane, and then heated at 650 °C for 12 h prior to use. Hydrochloric acid (A.R. grade) was purchased from Beijing Chemical Factory, China. Powdered copper (high purity), obtained from China National Medicines Corporation Ltd., China, was used as the desulfurizing agent and was treated with 1 mol/L HCl before use. All glassware for experiment was soaked in a prepared nitric acid lotion for above 6 h and then washed with distilled water and oven-dried; then the glassware was washed again with acetone for 3 times before use.

2.4. DDTs analysis

2.4.1. Extraction and cleanup

DDTs in all samples were extracted by accelerated solvent extraction method (ASE300, Dionex, America). The soil samples were first ground with agate mortar to pass through a 100 mesh stainless steel sieve. 14 g soil sample and 5 g active copper powder were mixed together; the copper was used to remove organic sulfide which can interfere with the peak of p,p′-DDE [12]. One piece of cellulose filter paper, 1 g of diatomite and the mixed sample described above were sequentially layered from the bottom of the ASE cell (66 ml volume). In addition, an appropriate amount of diatomite was packed on the top of the sample to fill the space of the ASE cell. The extraction was then carried out with n-hexane/acetone (1:1, V:V) at a temperature of 100 °C and a pressure of 1500 psi. The extraction was repeated twice for each sample. The combined extracts were solvent exchanged with 10 ml of hexane and evaporated to approximately 2 ml by rotary evaporator (RE-52, Shanghai Yarong Company, China) in a water bath at 40–45 °C. The concentrated extract was transferred to the top of a prepared SPE column (30 cm × 10 mm I.D.). Prior to use, the SPE column was successively filled with 12 cm of activated silica gel, 6 cm of activated alumina and 1 cm of anhydrous sodium sulfate, which were all pre-soaked in hexane. Then the column was eluted first by 15 ml of hexane. After that, the column was eluted by 70 ml of hexane/dichloromethane (7:3, V:V) and this part of the elution was collected for DDTs determination. The collected elution was concentrated by a rotary evaporator and then the solvent was exchanged with 10 ml of hexane twice in order to remove dichloromethane, and then blown to 2 ml under gentle nitrogen stream. Twenty microlitres of PCNB (10 μg ml^{-1}) as internal standard was added to the 2 ml concentrated extract prior to GC analysis.

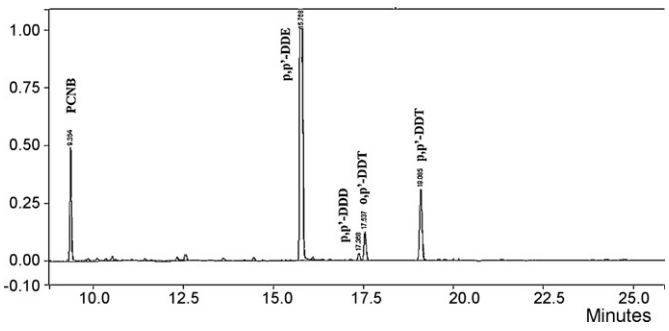

Fig. 2. Chromatogram of real sample.

2.4.2. Chromatographic analysis

The concentrations of DDTs in the extracts were analyzed with a Varian CP-3800 gas chromatograph equipped with a ^{63}Ni electron capture detector (GC-^{63}Ni ECD) and a DB-5 fused silica capillary column (30 m × 0.25 mm I.D., and 0.25 μm film thickness). The carrier gas was high-purity nitrogen with a flow of 0.8 ml min^{-1}. The temperature of injector and detector were kept at 250 and 330 °C, respectively. The temperature program of column oven was set to 100 °C, then with 20 °C min^{-1} to 190 °C, kept for 1 min, and further by 4 °C min^{-1} to 235 °C, kept for 10 min. One microlitre of sample was injected in pulse splitless mode with the split outlet opened after 1 min. GC peaks were identified with the accurate assignment of retention times of each standard (±1%). The chromatogram of a real sample was shown in Fig. 2. The residues of DDTs were determined by comparing the peak areas of the samples adjusted by internal standard and the calibration curves of the standards.

2.5. Physicochemical parameter analysis

Parameters such as pH, clay content, total organic carbon (TOC) and black carbon (BC) were determined for general characters of these urban soil samples. Soil pH was measured by potential method, with 2.5:1 ratio of water and soil. Particle size distribution was analyzed by the hydrometer method (LY/T 1225-1999). For TOC and BC, the soil samples were first ground with agate mortar to pass through a 100 mesh stainless steel sieve. An elemental analyzer (Vario El, Elementar Analysensysteme GmbH, Germany) was used for the TOC analysis after the samples were treated with HCl (1:1, volume). BC content in soil samples was determined with the chemo-thermal oxidation method [21]. Inorganic carbon in soil samples was firstly removed by HCl (1:1, volume); amorphous organic carbon (OC) was subsequently removed in a thermal oxidation procedure at 375 °C in a tube furnace for 24 h in the presence of excess oxygen (air) [22]. Then BC content in soils was determined with an elemental analyzer (Vario El, Elementar Analysensysteme GmbH, Germany).

2.6. Quality assurance and quality control

The method detection limits (MDLs, ng/g) of each DDT were determined as the lowest concentration giving a response of 3 times the standard deviation of the baseline noise defined from the analysis of three control (untreated) samples [23]. For every 10 field samples, a method blank (diatomite), a spiked blank (diatomite spiked with standards), a matrix spike (pre-extracted soil spiked with standards) and control sample (uncontaminated soil) were

Table 1
The range, mean, median and geometric mean of DDTs (ng/g) and selected soil properties in urban soils.

Compounds	Min[a]	Max[a]	Mean ± S.D.[a]	Median[a]	Geometric[a]
pH	7.8	9.1	8.3 ± 0.2	8.3	8.3
Clay (%)	14.5	43.3	29.1 ± 5.5	28.8	16.8
TOC (%)	2.2	6.9	1.5 ± 1.0	1.3	1.3
BC (%)	0.0	2.7	0.5 ± 0.5	0.4	0.4
p,p′-DDE	0.005	600.35	29.19 ± 80.99	1.80	2.63
p,p′-DDD	0.005	185.96	3.19 ± 16.32	1.00	0.73
o,p′-DDT	0.010	322.31	13.68 ± 46.27	0.83	1.03
p,p′-DDT	0.010	521.24	22.07 ± 67.52	3.30	5.26
ΣDDTs	0.030	1282.58	68.14 ± 189.46	9.96	13.72

[a] Minimum, maximum, geometric mean, arithmetic mean, median were calculated assuming non-detect (ND) measurements were equal to one-half of MDLs.

processed; and duplicated samples were performed simultaneously. The method blank contained no detectable amount of the target analytes. The MDLs of p,p′-DDE, p,p′-DDD, o,p′-DDT and p,p′-DDT were 0.01, 0.01, 0.01 and 0.02 ng/g-dry weight, respectively; the recoveries of p,p′-DDE, p,p′-DDD, o,p′-DDT and p,p′-DDT in spiked blanks and matrix spikes were 71.9–95.5%, 81.5–95.1%, 96.7–113.2% and 90.0–104.2%, respectively. The calibration curves of DDTs were determined before each batch of samples being analyzed, with the correlation coefficients (r) all greater than 0.99. All of the calibration curves were adjusted by internal standard to remove the change of instrument response signal caused by matrix effect and instrument instability. A degradation check solution obtained from Labor Dr. Ehrenstorfer, Germany was analyzed daily, and the extent of degradation must be less than 15% before the analysis of DDTs could proceed.

2.7. Statistical analysis

A global position system (GPS) was employed to precisely record each location of soil sampling. Conventional statistical analyses, correlation analysis between the residues of DDTs and TOC, BC, pH as well as clay content in the study area, and t-tests were carried out using SPSS 17.0 statistical software. In addition, the concentrations of DDT and its metabolites at each sampling site were used to construct contour maps using the program SURFER v.8.0 (Golden Software Inc., Colorado, USA), with the method of kriging interpolation technique.

3. Results and discussion

3.1. Concentrations of DDTs in urban soils of Beijing

The concentrations of DDT and its metabolites in the soil samples followed the lognormal distribution. As shown in Table 1, the total DDTs concentrations (sum of p,p′-DDE, p,p′-DDD, o,p′-DDT and p,p′-DDT) in the soils varied from 0.03 to 1282.58 ng/g, with an average of 68.14 ± 189.46 ng/g. p,p′-DDE and p,p′-DDT were the principal contaminants of DDTs, with a mean concentration of 29.19 ± 80.99 and 22.07 ± 67.52 ng/g, respectively. The percentage of individual compounds in soils followed the sequence: p,p′-DDE > p,p′-DDT > o,p′-DDT > p,p′-DDD. p,p′-DDE was the main metabolite of p,p′-DDT, accounting for 42.8% of the total DDTs. Similar results have been reported by other researchers [17,24,25]. As DDT would be dechlorinated to DDE in aerobic conditions and DDE is more persistent than the parent compound DDT [26], the higher concentration of DDE was found in urban soils of Beijing.

As shown in Table 2, the mean concentration of DDTs in urban soils was 3 times higher than that in rural soils of Beijing, and also higher than that in Guanting Reservoir of Beijing, with fewer anthropogenic activities [19]. Similarly, the level of DDTs in this study was much higher than that in Tibet, which was considered as an area of pristine [27], suggesting that the DDTs levels in urban soils were affected by anthropogenic activities. The concentration of DDTs in this study was much lower than that in the industrial site soil of Beijing, which was occupied by a OCPs (HCH and DDT) pesticides plant until 1983 [28]. In comparison with other cities in China, the mean concentration of DDTs in Beijing urban soils was lower than that in surface soils of Hong Kong and Yinchuan [29,30]; and close to that in Taiyuan urban soils [12] and that in Tianjin urban soils [25]. Compared with regions outside China, the average concentration of DDTs in Beijing was considerably lower than that found in the urban soils of Romania [11], and that in the urban and rural soils of Katowice and Krakow [10] in Poland.

3.2. Sources of DDTs in urban soils

Technical DDT is typically composed of 77.1% p,p′-DDT, 14.9% o,p′-DDT, 4% p,p′-DDE, and some other trace impurities. The ratio of parent compounds to metabolites was used to infer sources and qualitatively judge the age of contaminant residues in soil. The ratio of (p,p′-DDE + p,p′-DDD) to p,p′-DDT can be used to indicate whether p,p′-DDT in soils is “aged (degraded)” or “new (input recently)” [31,32]. If the ratio is higher than 1, it means that DDTs in soils are aged mixtures and if the ratio is lower than 1, it indicates that the parent DDT is inputted to soils recently [33]. In this study, the ratios of the urban soils ranged from 0.00 to 1063.41, with a geometric mean of 1.20. The ratio was higher than 1 for 78% of the samples, indicating that most of the sampling sites had no DDTs input recently. The ratio was lower than 1 for only 22% of the samples, which were mainly collected from the RO. The results also showed that although high DDTs level was detected in CL, there was no recent application of DDT in CL except the Yuetan Park.

Recently, the ratio of o,p′-DDT to p,p′-DDT was used to distinguish whether DDT contamination was caused by the usage of technical DDT or dicofol. It is reported that dicofol contains about 3–7% of DDTs as impurities, in which the ratio of o,p′-DDT to p,p′-DDT ranges from 1.3 to 9.3, while in technical DDT the ratio only ranges from 0.2 to 0.3 [31]. In this study, the ratio of o,p′-DDT to p,p′-DDT varied from 0.00 to 1.73, with geometric mean of 0.06, it was higher than 0.3 for only 7.4% of the samples, indicating that the recent application of DDT is mainly introduced by the use of technical DDT.

3.3. Comparision of DDTs levels in six types of land use

As shown in Table 3, DDTs concentrations in urban soils among different types of land use followed the sequence: CL > LA > CU > BU > RE > RO. The mean concentration of DDTs in CL was 5 times higher than that in LA and CU, and was more than 10 times higher than that in RE, BU and RO. The highest DDTs level detected in CL was probably due to the fact that DDTs were used to protect vegetation in these areas [17]. For LA and CU, lawn and shrub are largely cultivated and protected routinely by

Table 2
Concentrations of DDTs in soils in this study and other areas (ng/g).

Area	Land use	ΣDDTs	Reference
Tibet, China	Soil in pristine areas	ND[a] –2.83	Fu et al. [27]
Beijing, China	Soils from Guanting Reservoir	ND[a] –94.07, 5.11 (median)	Zhang et al. [19]
Beijing, China	Industrial site soil	3020–67,430	Yang et al. [28]
Taiyuan, China	Urban soil (n = 15)	1.8–100, 12 (median)	Fu et al. [12]
Tianjin, China	Urban and rural soil (n = 188)	49.6 ± 126.8, 11.7 (geometric)	Gong et al. [25]
Hong Kong, China	Surface soil (n = 66)	0.13–1900, 520 (mean)	Zhang et al. [29]
Yinchuan, China	Urban soil (n = 16)	0.410–1068, 92.1 (mean)	Wang et al. [30]
Romania	Rural soil (n = 7) Urban soil (n = 13)	226.9 ± 157.2, 113.1 ± 151.8 (mean)	Covaci et al. [11]
Krakow, Poland	Urban and rural soil (n = 24)	4.3–2400, 260 ± 620 (mean)	Falandysz et al. [10]
Katowice, Poland	Urban and rural soil (n = 24)	23–260, 110 ± 89 (mean)	Falandysz et al. [10]
Beijing, China	Urban soil	0.03–1282.6 68.14 ± 189.46 (mean) 13.72(geometric) 9.96(median)	This study
Beijing, China	Rural soil	0.24–304.71 21.45 ± 54.15 (mean) 6.77 (geometric) 7.22 (median)	This study
Beijing, China	Urban and rural soil	0.03–1282.58 21.45 ± 168.87 (mean) 10.21 (geometric) 8.69 (median)	This study

[a] Not detected.

administrators using pesticide which contains DDTs, so higher DDTs levels were also observed in LA and CU. As little vegetation is cultivated in BU, RE and RO, and most of these places may be lack of special vegetation management, DDTs concentration was much lower in BU, RE and RO than in CL, LA and CU.

For soil samples in CL, excepting the Beijing Zoo and the Temple of Heaven Park, the longer history the garden was, the higher concentration of DDTs was. As shown in Fig. 3, for the classical gardens established after 1950s, when DDTs began to produce in China [34], the concentrations of DDTs have a rapid increasing trend with the

Table 3
Concentrations of DDTs in six types of land use of urban soils in Beijing (ng/g).

Land-uses categories	p,p′-DDE[a]	p,p′-DDD[a]	o,p′-DDT[a]	p,p′-DDT[a]	ΣDDTs[a]
RE (n = 12)					
Minimum	0.005	0.005	0.01	0.01	0.03
Maximum	91.72	1.02	9.52	49.78	205.72
Geometric mean	1.90	0.30	0.34	2.04	6.29
Mean ± S.D.	12.24 ± 7.41	0.50 ± 0.10	1.41 ± 0.75	9.00 ± 4.01	23.15 ± 12.12
CU (n = 9)					
Minimum	0.21	0.35	0.02	1.22	2.95
Maximum	327.59	4.59	38.23	126.28	496.68
Geometric mean	28.13	1.37	2.52	13.50	52.74
Mean ± S.D.	78.51 ± 26.92	1.73 ± 0.34	7.08 ± 2.89	31.01 ± 10.61	118.34 ± 39.14
CL (n = 9)					
Minimum	50.45	0.15	25.69	25.80	116.77
Maximum	339.02	185.96	322.31	391.00	1003.99
Geometric mean	167.96	5.13	121.34	129.97	403.01
Mean ± S.D.	201.75 ± 42.55	30.78 ± 25.90	166.75 ± 42.17	185.35 ± 48.12	584.63 ± 124.69
LA (n = 12)					
Minimum	0.28	0.15	0.01	0.43	1.02
Maximum	600.35	19.77	141.22	521.24	1282.58
Geometric mean	2.63	0.73	1.03	5.26	13.72
Mean ± S.D.	54.66 ± 45.65	2.27 ± 1.47	15.66 ± 10.80	49.64 ± 39.52	122.23 ± 97.00
BU (n = 8)					
Minimum	0.09	0.13	0.01	1.55	2.28
Maximum	136.52	3.50	60.83	56.73	174.26
Geometric mean	6.56	0.59	2.32	5.27	16.06
Mean ± S.D.	34.14 ± 15.41	0.87 ± 0.31	11.51 ± 6.04	10.14 ± 5.25	56.66 ± 24.22
RO (n = 77)					
Minimum	0.005	0.005	0.01	0.01	0.41
Maximum	59.39	13.96	66.10	62.19	130.52
Geometric mean	0.71	0.85	0.49	1.93	6.32
Mean ± S.D.	2.53 ± 0.81	1.79 ± 0.27	2.60 ± 0.94	4.423 ± 0.926	11.34 ± 2.12

[a] Minimum, maximum, geometric mean, arithmetic mean were calculated assuming non-detect (ND) measurements were equal to one-half MDLs.

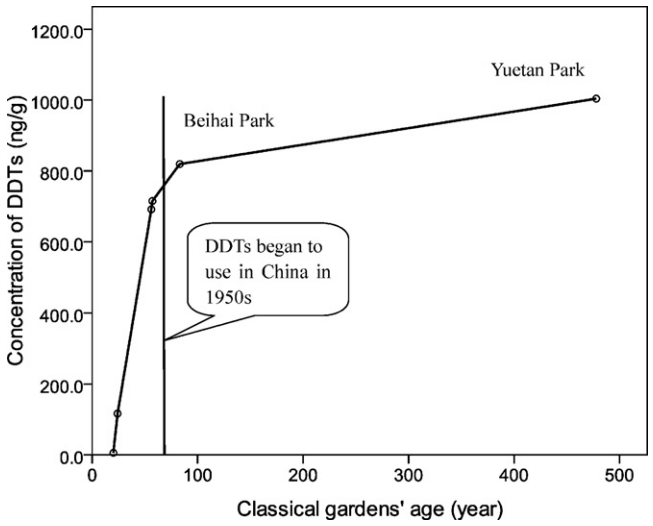

Fig. 3. Correlation between DDTs concentration and the age of classic garden.

age of classical gardens. For the classical gardens established before 1950s, the DDTs concentrations were similar. For example, both of the Yuetan Park and the Beihai Park were established before 1950s; although the former is almost 400 years older than the latter, the concentration of DDTs in the Yuetan Park was little higher than that in the Beihai Park. This suggests that the DDTs concentration in CL was affected by both the usage history of DDTs and the age of the classical gardens.

3.4. Spatial distribution of DDTs

In general, as shown in Fig. 4, the DDTs concentration in Beijing showed a decreasing trend from the center of the city to the suburb. The high values or hotspots existed in the center of Beijing, especially within the 3rd Ring Road. The district inside the 3rd Ring Road is an old urban area with the longest history in Beijing. DDTs also had a relatively high concentration in the northern part of the city, where some universities are located and most of them were built in 1950s. As mentioned in Section 3.3, the vegetation management in universities may contribute to the accumulation of DDTs in urban soils around. This spatial distribution trend of DDTs may result from the development process of Beijing. The urban area of Beijing was formerly within the confines of the 2nd Ring Road, and it did not make a big change until the middle of the 20th century. With 30 years rapid development since the economic reforms in 1978, the urban area of Beijing has expanded to the newly constructed 5th Ring Road. It was found that the DDTs concentration in newly built urban area, especially the area around the 5th Ring Road, was much lower than that in the center of the city. It inferred that DDTs concentration in urban soils of Beijing varied greatly with the history of the urban area; the longer history the urban area was, the higher the DDTs concentration was.

Moreover, decreasing trend of DDTs concentration in each type of land use was discovered from the area inside the 2nd Ring Road to the area of the 5th Ring Road. Taking the CU for example, the averages of DDTs between the 2nd and 3rd Ring Road was 170.50 ng/g, between the 3rd and 4th Ring Road was 88.80 ng/g, and between the 4th and 5th Ring Road was 35.68 ng/g, respectively. In addition, the spatial distribution of p,p′-DDE, p,p′-DDT and o,p′-DDT was the same as that of the total DDTs.

3.5. Relationship between DDTs levels and physicochemical properties of soil samples

The physicochemical properties of soil, such as pH, clay content, total organic carbon (TOC) and black carbon (BC) can affect the distribution of DDTs in soils [35–37]. In this study, pH and clay content in the soil samples followed normal distribution; TOC and BC followed lognormal distribution. No significant correlations between DDTs concentrations (log transformed) and pH and clay content were found. Significant positive correlations of TOC (log transformed) with p,p′-DDE ($p = 0.006$), p,p′-DDD ($p = 0.036$), p,p′-DDT ($p = 0.005$) and total DDTs ($p = 0.002$) (log transformed) were observed. Other researchers have reported similar positive correlations between TOC and organic contaminants in soils [35,36,38,39]. Significant positive correlations of BC (log transformed) with p,p′-DDE ($p = 0.000$), o,p′-DDT ($p = 0.000$), p,p′-DDT ($p = 0.000$) and total DDTs ($p = 0.000$) (log transformed) were also observed (Fig. 5), and DDTs concentrations were better correlated to BC ($r^2 = 0.182$) than to TOC ($r^2 = 0.076$). Similar results were also found by Oen et al. [40]. BC may dominate hydrophobic organic compounds (HOCs) sorption by soils because of its special structure and reduce the bioavailability of HOCs in soils [41,42]. In this study, the DDTs residue levels based on rigorous extraction and analysis might overestimate the risk to organisms, it is necessary to make further researches on the bioavailability of DDT levels in these areas.

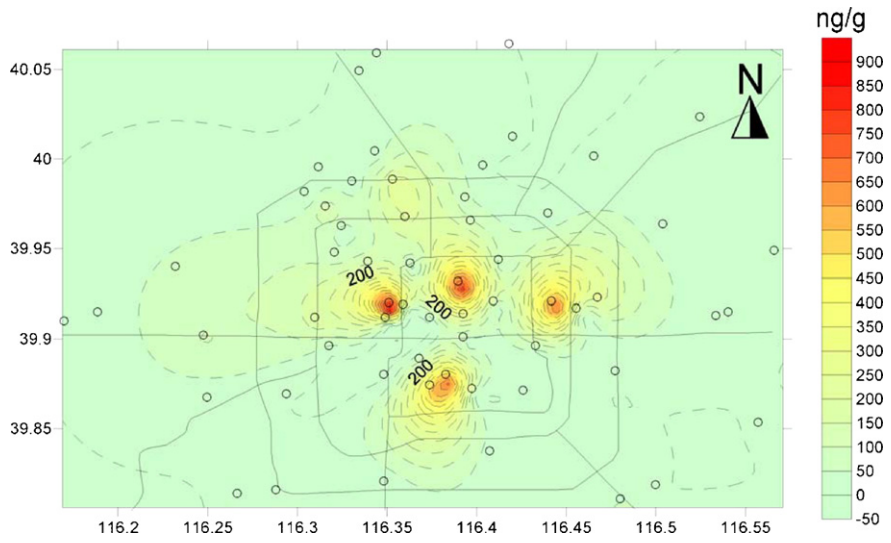

Fig. 4. Map of DDTs distribution in urban soils of Beijing.

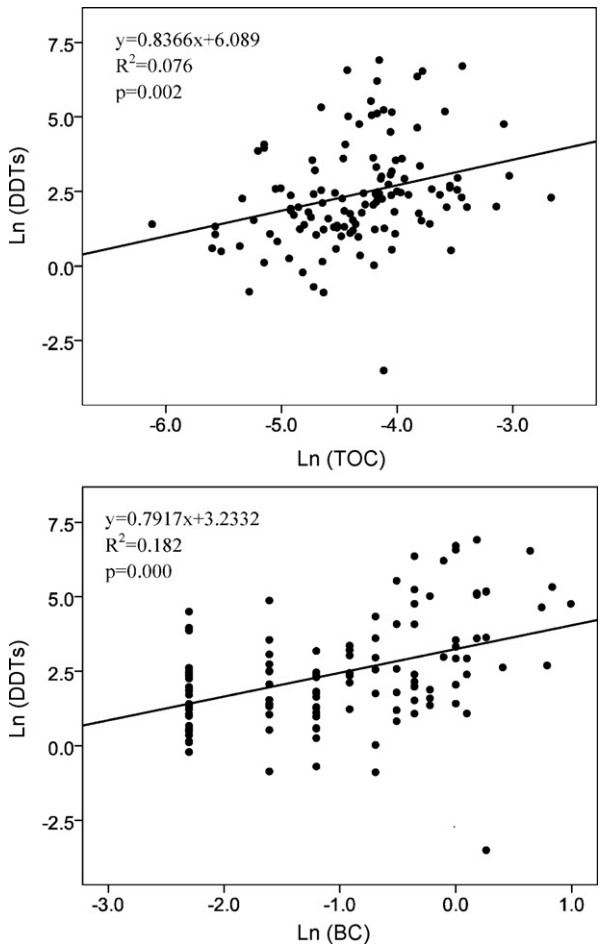

Fig. 5. Correlations of DDTs with soil TOC and BC.

3.6. Pollution assessment

According to the Chinese Environmental Quality Standard for Soils (GB 15618-1995), the soil quality is categorized to three grades in which grade I is best and grade III is worst. The maximum allowable concentrations for DDTs of grade I, grade II and grade III are 50, 500 and 1000 ng/g, respectively. In this study, accordingly, the quality of soils was classified into no contamination with DDTs concentration less than 50 ng/g; low contamination with DDTs concentration between 50 and 500 ng/g; moderate contamination with DDTs concentration between 500 and 1000 ng/g, and high contamination with DDTs concentration more than 1000 ng/g. It was found that the concentrations of DDTs were less than 50 ng/g in 81.7% of the samples; and those were between 50 and 500 ng/g in 13.7% of the samples. Only 1.5% of the samples contained high DDTs levels which exceeded 1000 ng/g. Therefore, the levels of DDTs in most samples from the urban area of Beijing could be considered as no contamination. However, the DDTs levels in several samples from CL, including the Beihai Park, the Temple of Heaven Park, the Tao Ranting Park, and the Ritan Park, were between 500 and 1000 ng/g, which can be regarded as moderate contamination; and those in the Yuetan Park and in the Agricultural Tourism Park in Haidian (1282.58 ng/g,) were higher than 1000 ng/g, which can be regarded as high contamination. Although DDTs levels in most samples of Beijing urban soil were considered as no contamination, the mean concentration of DDTs in urban soils was indeed higher than that in rural soils of Beijing.

Furthermore, the DDTs contamination in RE and CU was assessed with the standard of Canadian Soils Quality Guidelines for residential areas (700 ng/g). One sample *t*-test showed that the means of DDTs in RE and CU are significantly lower than the guidelines ($p < 0.01$), and the concentrations of DDTs in all the samples of RE and CU were less than the guidelines, suggesting that DDTs levels in these two types of land use soils might be categorized as no contamination. The DDTs levels in BU were assessed with the soil standard of Maryland in America (17,000 ng/g). One sample *t*-test showed that the mean of DDTs in BU is significantly lower than the standard ($p < 0.01$), and the concentration of DDTs did not exceed the standard, indicating that the DDTs levels in BU may do no harm to humans. Using the standard of Canadian Soils Quality Guidelines for park areas (700 ng/g) to assess the DDTs levels in CL and LA, one sample *t*-test showed that the mean of DDTs in LA is significantly ($p < 0.01$) lower than the standard, and the concentrations of DDTs in all the samples of LA were less than the standard except the sample from the Agricultural Tourism Park in Haidian with the DDTs concentration of 1282.58 ng/g. For CL, except the samples of the Beihai, the Yuetan and the Ritan Park, the concentrations of DDTs in other samples were lower than the standard of Canadian Soils Quality Guidelines.

In general, according to GB 15618-1995, the Canadian Soils Quality Guidelines and the soil standard of Maryland in America, the DDTs levels in the samples of RE, CU, BU, LA and RO could be categorized as no contamination, and high contamination of DDTs occurred in some samples from CL.

4. Conclusions

This work revealed the levels, spatial distribution and sources of DDTs in urban soils of Beijing as well as DDTs variations in different types of land; the main conclusions were drawn as follows:

(1) DDT and its metabolites were detected in urban soils of Beijing, with their concentrations sequence as p,p′-DDE > p,p′-DDT > o,p′-DDT > p,p′-DDD. The total DDTs concentrations varied from 0.03 to 1282.58 ng/g, which were moderately compared to other areas around the world. p,p′-DDE and p,p′-DDT were the major contaminant compounds in the soil samples.
(2) Source identification indicated that only 22% of the samples, which mainly located in RO, had the application of technical DDTs recently. Although high DDTs level was detected in CL, the ratio of (p,p′-DDE + p,p′-DDD) to p,p′-DDT showed that there was no application of DDT in CL recently except the Yuetan Park.
(3) Among the six types of land use, the mean concentration of DDTs in CL was 5 times higher than that in LA and CU, and was more than 10 times higher than that in RE, BU and RO, which was due to the use of DDTs to protect vegetation in CL. Furthermore, for soil samples in CL, the longer history the garden was, the higher concentration of DDTs was, suggesting that the DDTs concentration in CL was affected by both the usage history of DDTs and the age of the classical gardens.
(4) Spatial distribution revealed that DDTs concentration in Beijing showed a decreasing trend from the center to the suburb. This was due to the development process of Beijing. The longer history the urban area was, the higher the DDTs concentration was.
(5) For all of the samples, no significant correlations between the residue levels of DDTs with soil pH and clay content were found; positive correlations of DDTs with TOC and BC were found, and DDTs concentrations were better correlated to BC ($r^2 = 0.182$) than to TOC ($r^2 = 0.076$).
(6) On the basis of GB 15618-1995, the Canadian Soils Quality Guidelines and the soil standard of Maryland in America, the DDTs levels in the samples of RE, CU, BU, LA and RO could be

considered as no contamination, and high contamination of DDTs occurred in some samples from CL.

As high contamination of DDTs was found in CL, attention should be paid to the environmental quality of the CL for the sake of human health safety. In addition, some measures should be implemented to avoid the application of technical DDTs in RO.

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