Characterization of HCHs and DDTs in urban dustfall and prediction of soil burden in a metropolis-Beijing, China

Hangxin Cheng^{a,*}, Lingling Ma^{b,*}, Chuandong Zhao^a, Xinghong Li^c, Xiaofei Wang^c, Yinghan Liu^a, Ke Yang^a

^a Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences, Langfang 065000, China

^b Key Laboratory of Nuclear Analytical Techniques, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

^c State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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ABSTRACT

The concentrations, spatial distribution and compositional patterns of extensively used hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) in urban dustfall in a metropolis-Beijing are presented in this paper. The potential sources are discussed and soil burdens are predicted based on the fluxes. The hotspots in commercial areas are identified by spatial distribution maps and the fractional value isomers indicates that dustfall in urban Beijing are affected by both current and historical usage of DDTs. It is worth noticing that there is possible application “dicofol-type of DDTs” in Beijing. The measured atmospheric deposition flux is $1.14 \times 10^5 \text{ ng h}^{-1} \text{ m}^{-2}$ for HCHs and $1.47 \times 10^5 \text{ ng h}^{-1} \text{ m}^{-2}$ for DDTs, respectively. However, when compared with atmospheric deposition flux, the volatilization flux estimated from concentrations in soils by fugacity model is significantly lower for HCHs ($2.41 \text{ ng h}^{-1} \text{ m}^{-2}$) and DDTs ($0.07 \text{ ng h}^{-1} \text{ m}^{-2}$). The net atmospheric flux to the soil suggests that the levels of HCHs and DDTs in soil are dominated by atmospheric deposition and the urban soil in Beijing would be a sink for HCHs and DDTs in the long term.

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1. Introduction

Organochlorine pesticides (OCPs) are receiving continuous concerns due to the persistently negative impacts on the environment and human health (Li et al., 2009; Liu et al., 2009; Tao et al., 2009; Roosens et al., 2010). China is known for intensive production and consumption of hexachlorocyclohexane isomers (HCHs) and dichlorodiphenyltrichloroethane with metabolites (DDTs) for more than three decades (MCI, 1992). Although the usage of DDTs and technical HCHs was banned by the government in 1983, technical DDTs is still being produced and used for non-agricultural purposes such as malaria control (Li et al., 2001). The quality of the urban environment is of growing concern as its human population continues to dramatically increase. Beijing, the capital with a population up to 13 million, is the second largest city in northern China. The rapid industrialization during the last decades had resulted in a lot of environmental problems. There was a long history of heavy production/usage of HCHs and DDTs in Beijing (Li et al., 1998). For the valid use of urban land and the safety of public health, a systematic project was carried out in 2000 to

assess the soil contamination in Beijing. The high concentrations of HCHs and DDTs together with other semi-volatile persistent organic pollutants were observed (Ma et al., 2005; Zhu et al., 2005; Li et al., 2006). Contaminated soil could still continue to be a source of current atmospheric contamination and result in ongoing exposure for the public health. As a continuous study of the previous “2000 project”, atmospheric particulate matter (PM) was characterized in urban city in 2005 and Beijing was categorized as a city that is highly contaminated with OCPs (Wang et al., 2008).

Atmospheric deposition has been of a considerable environmental interest due to its important role in OCPs transportation (Pozo et al., 2006). A few recent studies further revealed the increasing concentrations of HCHs and DDTs in various environmental media in Beijing (Xu et al., 2004, 2005, 2009; Li et al., 2009). The concentrations of OCPs in atmosphere decreased with boundary layer height, which indicated the potential of Beijing as a local source of OCPs (Li et al., 2009). The observed high levels of OCPs in the atmosphere may be due to the ongoing usage as well as emission of old residues from surface soil, which have a huge retention capacity of organic pollutants and is considered as the ultimate sink for OCPs (MCI, 1992; Wong et al., 2008). Airborne dust may be delivered to surfaces by bulk deposition and has been a notable atmospheric feature of China since ancient times (Derbyshire et al., 1998). As an important source of urban

* Corresponding authors. Tel.: +86 316 2267630; fax: +86 316 2014156.

E-mail addresses: hangxin@vip.sina.com (H. Cheng), malingling@ihep.ac.cn (L. Ma).

atmospheric particulate matter and house dust, dustfall ($d > 10 \mu\text{m}$) is scavenged mainly by gravity and thus tends to reflect potentially non-point sources near the sampling sites (Wu et al., 2005). As the carrier of pollutants, dustfall not only affects urban air quality but also directly threatens public health. However, limited reports on OCPs are currently available, despite the fact that atmospheric pesticide pollution has been well documented worldwide. Since precipitation is rare in Beijing, the dry deposition of airborne OCPs has a high likelihood of being the predominant mode of atmospheric OCPs input into underlying surfaces.

To get an understanding of atmospheric OCPs level and its contribution to the soil burden, bulk deposition (dry and wet deposition together) were collected in a municipal scale during 1 year period by passive sampling method in this study. HCHs and DDTs will be characterized and the hot-spots will be recognized according to the spatial maps. Furthermore, modeling will be conducted on the soil burdens in Beijing based on the fluxes and reported levels of pesticide on surface soil.

2. Materials and methods

2.1. Materials and reagents

A mixed stock standard solution was 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. The surrogate of 2,4,5,6-tetrachloromxylylene (TCMX) was bought from Supelco (Bellfonte, USA). Florisil (Dikma Co. USA) was activated at 600°C for 6 h and then at 130°C for 16 h. All solvents were of analytical grade and redistilled in all-glass system prior to use.

2.2. Dustfall sampling

The Beijing city occupies a surface area of $16\,807 \text{ km}^2$, with 748 km^2 classified as urban area. Twenty flat bottom ceramic buckets (32 cm i.d., height of 40 cm) for collecting bulk deposition on 6–10 m high stands situated throughout the urban area of the city from December 2005 to November 2006. The buckets were thoroughly washed with distilled water and acetone/hexane before setting. Dustfall particles were wiped off from the bottom of buckets with a brush and then washed twice with distilled water and freeze-drying. The dustfall samples were weighted and then stored in glass jars and kept in a refrigerator at -18°C before

analysis. The climate of the country as a whole is dominated by temperate semi-wetness monsoons, and the annual temperature during the sampling period was from -4°C to 27°C with a mean value of 13°C . The study area was divided into regular grids of $7 \text{ km}^2 \times 7 \text{ km}^2$ based on approximately equal longitude and latitude. The detailed sampling locations are shown in Fig. 1. The sample numbered 19 was lost due to the housebreaking and no data was shown with regards to this site. Five different functional zones (industrial: sample of 3, 4, 6, 10, 11, 15 and 20; commercial area: sample of 2, 8, 9 and 12; residential area: sample of 1, 7 and 14; farm: sample of 5 and 18; park: sample of 13 and 17) were divided according to the surrounding environment of the sampling sites. The sample of 16 was collected in a desertification area beside Yongding River.

2.3. Sample extraction and cleanup

The cleanup and analytical procedures were carried out according to the previous reports (Li et al., 2006; Wang et al., 2008). Briefly, after 1 mL of TCMX added, the dustfall was ultrasonically extracted in 30 mL acetone/hexane (1/1) thrice and centrifuged for separation. Then the solvent was rotary evaporated and then reduced to 1 mL under the gentle stream of nitrogen. The concentrated extract was further cleaned up with a Florisil column ($30 \text{ cm} \times 10 \text{ mm i.d.}$) packed with 5 g of florisil (in hexane). It was eluted with 40 mL of hexane/ethyl ether (7/1, v/v). The solvent was reduced to 0.1 mL under a gentle nitrogen stream before analysis.

2.4. Instrumental analysis

The measurement was performed on a 6890 gas chromatograph (GC, Agilent J&W Co., USA) coupled to an electron capture detector (ECD) with a fused silica capillary ($30 \text{ m} \times 0.25 \text{ mm i.d.}$) coated with a $0.25 \mu\text{m}$ thick film of DB5 column (5% phenylmethylpolysiloxane, Agilent J&W Co., USA). Inlet and detector temperature were 225°C and 310°C , respectively. The oven temperature program was as follows: initial temperature 100°C held for 2 min, increased to 160°C at $10^\circ\text{C min}^{-1}$, then to 230°C at 4°C min^{-1} for 5 min, and to 280°C at $10^\circ\text{C min}^{-1}$, then held for 10 min. Identification of the compounds was based on the retention time with corresponding standards and confirmed on a GC coupled to a 5973 mass selective detector (Agilent J&W Co., USA). The inlet and detector temperature together with the temperature program were the same as those for the GC-ECD.

The recoveries were in the range of 75–115%, and relative standard deviation ($n = 5$) was less than 10%. The recoveries of

Fig. 1. Map of sampling site of urban dustfall in urban Beijing.

surrogate spiked in bland, matrix, samples were between 84% and 109%. The limits of detection (LODs), as three times response of signal-to-noise in matrix blanks ($n = 5$), ranged from 0.05 ng g⁻¹ for α -HCH to 0.15 ng g⁻¹ for p,p'-DDT.

2.5. Data analysis

A global position system was employed to precisely record each location. Principal component analysis (PCA) was performed with SPSS 13.0 for Windows (SPSS Inc., Chicago, IL). Surfer (Version 8.0, Golden software, CO. USA) was used to draw the spatial distribution maps.

3. Results and discussion

3.1. Levels and spatial distribution

The amount of dustfall varied from 9.00 g to 62.00 g with a median of 21.30 g in this study. Despite the restricted usage, HCHs and DDTs were still in detectable levels in the dustfall in urban Beijing. The maximum, 90th, 75th, 50th (median), 25th, and 10th percentiles and minimum of HCHs and DDTs in dustfall are shown in Fig. 2. A much wider ranges of Σ HCHs (sum of α -, β -, δ -, γ -HCH) and Σ DDTs (sum of p,p'-DDT, dichlorodiphenyldichloroethane (p,p'-DDD), dichlorodiphenyldichloroethylene (p,p'-DDE) and o,p'-DDT) were found with the coefficient of variation of 95.14 and 104.00, respectively. Σ DDTs (1.75–63.29 ng g⁻¹ with a median of 9.46 ng g⁻¹) was higher than Σ HCHs (1.80–

36.19 ng g⁻¹ with a median of 5.77 ng g⁻¹). The average concentration of Σ HCHs (6.87 ng g⁻¹ $\pm$ 10.62 ng g⁻¹) and Σ DDTs (12.99 ng g⁻¹ $\pm$ 13.51 ng g⁻¹) were obviously lower than those in Tianjin, a large industrial city 120 km southeast of Beijing, whereas the average concentrations were 519.00 ng g⁻¹ for Σ HCHs and 266.00 ng g⁻¹ for Σ DDTs, respectively (Wu et al., 2005).

The spatial distributions of HCHs and DDTs are shown in Fig. 3 by counter plots. The hotspots (sites 8 and 9) were located in the northern commercial center around the 3rd Ring Road and the 4th Ring Road for both HCHs and DDTs. For HCHs, another hotspot (site 20) was in the southeast city, which was consistent with the previous finding that the southeast city was highly polluted by OCPs in both topsoil and particulate matter (Li et al., 2006; Wang et al., 2008). Since dustfall would reflect the potential non-point sources nearby, the finding indicates that there are possible sources of OCPs in the commercial area. In order to probe the clue of sources, Σ HCHs and Σ DDTs in five functional zones are checked. The levels of HCHs and DDTs were comparable in four zones except for the park with a much higher Σ DDTs than Σ HCHs. The average concentration of OCPs was in the order of commercial (23.18 ng g⁻¹ for HCHs; 27.76 ng g⁻¹) > park (8.97 ng g⁻¹ for HCHs; 20.88 ng g⁻¹ for DDTs) > industrial center (8.05 ng g⁻¹ for HCHs; 10.56 ng g⁻¹ for DDTs) > farm (9.41 ng g⁻¹ for HCHs; 8.76 ng g⁻¹ for DDTs) > residential area (4.94 ng g⁻¹ for HCHs; 3.72 ng g⁻¹ for DDTs). The results indicate the reliability of layout for residential areas in Beijing. However, the management of commercial areas and park should be strengthened for protecting public health.

3.2. Composition of HCHs and DDTs

Principal component analysis (PCA) was conducted and is provided by Table 1. Three factors were extracted and accounted for 83.94%. The first principal component explained 51.55% of total variance, was highly associated with α -HCH, β -HCH, p,p'-DDT, o,p'-DDT and p,p'-DDD. γ -HCH and δ -HCH were related to the second component, indicating their similar origin. The third component explained 14.10% of the variance and with only p,p'-DDE was significantly loaded on. The composition patterns are deserved to be discussed separately in order to get more information.

3.2.1. HCHs

Technical HCH was once widely used in China with a mixture of 65–70% α -HCH, 5–6% β -HCH, 13% γ -HCH and 6% δ -HCH. Technical HCH was substituted by lindane in 1991 and approximately 3200 tons of lindane had been used until 2000, primarily concentrated in northern part of China (Hua and San, 1996). On average, the percentage of γ -HCH (36%) was comparable to those of β -HCH (31%) in the dustfall in Beijing. In comparison with those in particulate matter (18%) collected in the same studied areas, the percentages in dustfall were much comparable to those (~54%) in the topsoils (Li et al., 2006), which indicated the reemission of HCHs from topsoil to atmosphere. β -HCH is more stable than other isomers and ratio of β/γ -HCH from 0.38 to 0.46 indicates a lack of current technical HCHs application in the studied area (Kim and Smith, 2001; Qiu et al., 2004). In addition, the ratio of α/γ -HCH typically ranged from 4 to 7 for technical HCH mixture, while nearly zero for lindane (Iwata et al., 1995). Although there is photochemical isomerization of γ -HCH to α -HCH in atmosphere, the action is slow compared with regional atmospheric transportation and will not change the ratio greatly in dustfall (Oehme and Manø, 1984; Poissant and Koprivnjak, 1996; Garmouma and Poissant, 2004). As shown in Fig. 4, the ratio of γ/α -HCH (0.06–1.11 with a median of 0.32) was less than 4, which supports the conclusion that the sources of HCHs in dustfall of Beijing possibly come from both

Fig. 2. Concentration of HCHs and DDTs in dustfall samples (ng g⁻¹). The values of maximum, the 90th, 75th, 50th (median), 25th, and 10th percentiles, and minimum are illustrated by box-whisker symbols and the arithmetic means are present as "□".

Fig. 3. Spatial distribution of Σ HCHs (A) and Σ DDTs (B) in dustfall in urban Beijing.

Table 1
Factor loading (varimax rotated) for organochlorine compounds in dustfalls.

	PC1	PC2	PC3
α -HCH	0.89	0.00	−0.24
β -HCH	0.93	−0.22	−0.17
γ -HCH	0.22	0.81	0.07
δ -HCH	0.02	0.82	−0.23
p,p'-DDT	0.89	−0.15	−0.32
o,p'-DDT	0.92	−0.03	0.08
p,p'-DDD	0.80	0.23	0.30
p,p'-DDE	0.38	−0.03	0.89
Proportion of total variance (%)	51.55	18.29	14.10

historical usage of technical HCH and lindane. The relatively higher ratios were observed in samples out of the 4th Ring Road, indicating the effects of old sources of technical HCHs on the dustfalls. Generally, park and residential area were characterized with β -HCH as the major contributing compound and a high percentage of γ -HCH in farm dustfall indicated the possible agricultural application of lindane. One identified hotspot at site 8 (γ/α -HCH of 1.11 and β/γ -HCH of 8.77) was polluted by the technical HCHs, while the other hotspot at site 9 (γ/α -HCH of 0.06 and β/γ -HCH of 0.11) was possibly polluted by lindane.

3.2.2. DDTs

As shown in Fig. 4, the average percentages of individual compounds in dustfall were as follows: p,p'-DDT > p,p'-DDE > o,p'-DDT > p,p'-DDD, which was different from the order of p,p'-DDE > p,p'-DDT > p,p'-DDD > o,p'-DDT reported in topsoil in Beijing (Li et al., 2006). This suggested that the DDT compounds in dustfall was not merely from soil release, other sources possibly existed. Technical DDTs is typically composed of 77.1% p,p'-DDT, 14.9% o,p'-DDT, 4% p,p'-DDE and some other trace impurities. The relative amounts of DDT congeners were expressed as the fractional value of (p,p'-DDD + p,p'-DDE)/p,p'-DDT and the ratios are shown in Fig. 4. This ratio >1 is normally expected for aged mixtures in the environment and <1 indicates the relatively recent exposure to parent DDT (Jaga and Dharmani 2003). In this study, the ratio varied from 0.09 to 6.54 with a median of 0.69. Nearly half of dustfall samples (sites 1, 2, 3, 4, 5, 7, 13, 14 and 16) contained more DDE and DDD than DDT, which indicated that the levels

Fig. 4. Characterized ratio of HCHs and DDTs in dustfall in urban Beijing.

and proportions of DDTs in those suburban areas are affected by both old sources. While other sites, including the hotspots of sites 8 and 9, showed that p,p'-DDT had a large percentage of over 50%, indicating current application of DDT or input of dicofol since it contains about 3.5–10.8% DDT (Luo et al., 2000). In fact, the total input of dicofol was from 3 ton a^{−1} to 4 ton a^{−1} in 2000 in Beijing (Xu et al., 2005).

A ratio of o,p'-DDT/p,p'-DDT can be used to distinguish technical DDT from "dicofol-type DDT", which was reported to be 0.20–0.26 in technical DDT and about 7.5 in dicofol product (Qiu et al., 2005). Due to the environmental processes such as evaporation and air-surface exchange, the ratios would change and these product ratios would result in a calculated of 0.74–0.96 for technical DDT and 28 for dicofol-type DDT, respectively, in the atmosphere (Kurt-karakus et al., 2006; Liu et al., 2009). As shown in Fig. 4, the ratio in dustfall varied from 0.06 to 3.44 with a median of 0.43, which suggests that technical DDT still dominate in the atmosphere in Beijing dustfall although possible "dicofol-type DDTs" was observed in dustfalls from a park (site 13: 3.44) and one residential area (site of 14: 1.24). It can be estimated that the current DDT sources in dustfall was composed of ~10% of dicofol-type DDTs, which was higher than the average level of ~5% in Chinese cities (Liu et al., 2009).

3.3. Prediction of soil burdens of HCHs and DDTs

The bulk depositions fluxes (F_D , $\text{ng h}^{-1} \text{m}^{-2}$) are presented in Table 1 and were calculated by

$$F_D = CW/A \quad (1)$$

where C is concentration (ng g^{-1}) of HCHs or DDTs in dustfall, W (g h^{-1}) is converted hourly dustfall dried weight according to total dustfall collected during 1 year, A is the bucket mouth area (m^2).

As shown in Table 2, the average deposition flux was $1.14 \times 10^5 \text{ ng h}^{-1} \text{m}^{-2}$ for HCHs and $1.47 \times 10^5 \text{ ng h}^{-1} \text{m}^{-2}$ for DDTs. Based on the unit area fluxes and the studied area of 784 km^2 , the annual atmospheric deposition flux in 2006 in Beijing urban soil was 783 g for HCHs and 1010 g for DDTs, respectively. The model estimated deposition flux of HCHs in Beijing was 37.72 g in 2005 (Cao et al., 2005), which was over 20 times lower than that in the present study. The differences between the modeling and experimental results may come from both fugacity model and experimental monitoring limitation such as the relatively small sampling site (Wu et al., 2005). Although there are some degree of uncertainties for all estimates of atmospheric deposition of HCHs and DDTs, the modeling calculations to some extent suggest the current input of OCPs in/nearby Beijing in 2006, which should be notable. The average concentrations of HCHs and DDTs in particulate matter collected in 2006 were significantly higher than those in 2002–2003, which further confirmed the increasing of atmospheric OCPs in 2006 (Xu et al., 2005; Wang et al., 2008).

The soil burdens of OCPs depend on the difference between input and output. Pesticides are delivered to the soil mainly by local usage, wastewater irrigation and atmospheric deposition.

However, in this study, the sampling areas were urban areas and the soil was not irrigated by wastewater. Therefore, atmospheric deposition is assumed as the only plausible source in this study. The dominant losses of OCPs from the soil in the studied area include soil-air volatilization, soil erosion, degradation, etc. The erosion and compounds degradation in soil are not considered in this study and then the changes of OCPs in per m^2 surface soil (0–20 cm) could be expressed by

$$\Delta C = \Delta F/W = (F_D - F_V)/W \quad (2)$$

where ΔC ($\text{ng g}^{-1} \text{h}^{-1} \text{m}^{-2}$) is the variation of soil burden for HCHs or DDTs ($\Delta C > 0$ indicating net atmospheric deposition to the soil, while $\Delta C < 0$ indicating net volatilization from the soil), ΔF ($\text{ng h}^{-1} \text{m}^{-2}$) is the net flux which is the driving force for OCPs volatilization due to the difference in fugacities between soil and air, W (g) is the weight of surface soil and is 300 kg for the surface soil (20 cm) assuming the solid density to be 1500 kg m^{-3} , F_V ($\text{ng h}^{-1} \text{m}^{-2}$) is the volatilization flux, and was calculated using the Mackay's fugacity model according to (Mackay, 1991; Kobližková et al., 2009)

$$F_V = 10^9 D_V f_s M \quad (3)$$

where M is the molecular weight of chemical, D_V , representing a molar flux between the soil and air compartments, is the transfer coefficient ($\text{mol h}^{-1} \text{Pa}^{-1} \text{m}^{-2}$) which is defined based on the three resistance model (Mackay, 1991). Fugacity in soil (f_s) was calculated from (Mackay, 1991; Harner et al., 2001)

$$f_s = C_s H / 0.411 \phi_{\text{om}} K_{\text{ow}} \quad (4)$$

where C_s as reported elsewhere (Li et al., 2006) is the concentration of the chemical in soil (mol m^{-3}) and was listed in Table 1 in this study for easily understanding, H is the Henry's law constant ($\text{Pa m}^3 \text{mol}^{-1}$), K_{ow} is the dimensionless octanol–water partition coefficient, the fraction of soil organic matter ϕ_{om} was 0.03 in this study.

Averagely, the model volatilization flux of HCHs was $2.41 \text{ ng h}^{-1} \text{m}^{-2}$ while that of DDTs was $0.07 \text{ ng h}^{-1} \text{m}^{-2}$. Basing on the deposition fluxes in the present study ($1.14 \times 10^5 \text{ ng h}^{-1} \text{m}^{-2}$ for HCHs and $1.47 \times 10^5 \text{ ng h}^{-1} \text{m}^{-2}$ for DDTs), the prediction of the soil burdens of HCHs and DDTs was carried out and were listed in Table 1. Thus, according to Eq. (2), $\Delta C > 0$ indicates the dominant deposition contributions to the soil burdens in urban Beijing and the net flux was $0.38 \text{ ng g}^{-1} \text{h}^{-1} \text{m}^{-2}$ for HCHs and $0.94 \text{ ng g}^{-1} \text{h}^{-1} \text{m}^{-2}$ for DDTs.

Table 2
Deposition flux in dustfall and predicted volatilization flux in urban Beijing.

	Flux (ng h ⁻¹ m ⁻²)				Soil burden (ng g ⁻¹ h ⁻¹ m ⁻²)
	Volatilization ^a		Deposition (×10 ⁵)		
	Range	Mean ± SD ^c	Range	Mean ± SD	
α-HCH	nd ^b –0.79	0.18 ± 0.08	0.02–0.32	0.10 ± 0.07	0.03
β-HCH	0.06–7.76	0.87 ± 0.45	0.06–2.54	0.35 ± 0.06	0.12
γ-HCH	nd–2.90	0.44 ± 0.32	0.08–2.48	0.38 ± 0.54	0.13
δ-HCH	nd–6.10	0.92 ± 0.21	0.02–2.25	0.30 ± 0.55	0.1
∑HCHs	0.06–17.44	2.41 ± 0.68	0.20–4.06	1.14 ± 1.07	0.38
p,p'-DDT	nd–2.01	0.05 ± 0.21	0.03–5.40	0.78 ± 1.20	0.26
o,p'-DDT	/	/	0.01–1.25	0.28 ± 0.33	0.09
p,p'-DDD	nd–0.18	0.01 ± 0.12	0.01–0.11	0.05 ± 0.03	0.09
p,p'-DDE	nd–0.30	0.01 ± 0.26	0.11–0.79	0.36 ± 0.17	0.12
∑DDTs	nd–0.06	0.07 ± 0.42	0.19–7.17	1.47 ± 1.53	0.94

^a Data from model prediction.

^b At or below the detection of limits.

^c Standard deviation.

4. Conclusions

Despite restrictions on the usage of HCHs and DDTs, these pesticides are still prevalent in urban dustfall in Beijing. The possible application of lindane and dicofol in Beijing should be notable. The polluted dustfall will eventually deposit on the surface soil, enter the food web, and impact on the human health. The surface soil will continue to be a sink of atmospheric HCHs and DDTs for a long time in Beijing, China. As one of 173 parties of the Stockholm Convention pledging to take sound management of the OCPs inventories, the identification of several hotspots would be very helpful for China to cut the application of HCHs and DDTs in Beijing and near-by areas.

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