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Characterization of HCHs and DDTs in urban dustfall and prediction of soil burden in a metropolis-Beijing, 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 1.14×10^5 ng h^{-1} m^{-2} for HCHs and 1.47×10^5 ng h^{-1} 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 ng h^{-1} m^{-2}) and DDTs (0.07 ng h^{-1} 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.

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

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atmospheric particulate matter and house dust, dustfall ($d > 10$ μm) 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-tetrachloromxylene (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 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 wipes 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 $km^2 \times 7$ 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 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 cm × 10 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 m × 0.25 mm i.d.) coated with a 0.25 μm 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 °C min^{-1}, then to 230 °C at 4 °C min^{-1} for 5 min, and to 280 °C at 10 °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

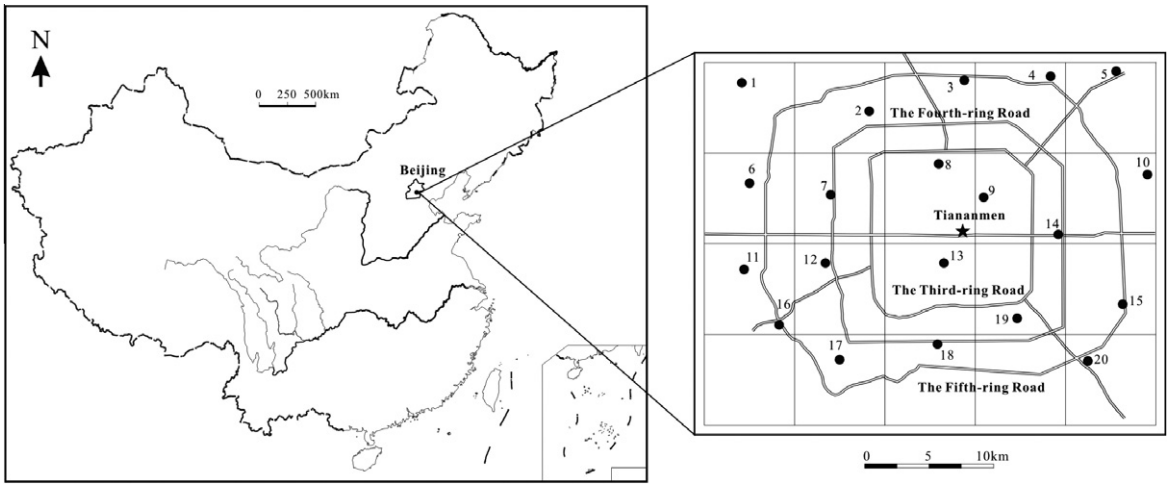

Fig. 1. Map of sampling site of urban dustfall in urban Beijing.