



Persistent organic pollutants (POPs) in the topsoil of typical urban renewal area in Beijing, China: Status, sources and potential risk

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ABSTRACT

In order to assess the health risk of persistent organic pollutants (POPs) in the topsoil of a typical urban renewal area, a comprehensive study was conducted to determine their spatial distribution, possible sources and potential carcinogenic risk. Topsoil samples were collected from former chemical industrial areas in south-east Beijing and tested for concentrations of POPs, including polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). The concentration of PAHs ranged from 126.68 to 365926.17 ng/g, OCPs ranged from 2.38 to 933.12 ng/g, and PCBs ranged from 47.04 to 3883.77 ng/g. The spatial distribution of POPs was mapped using a geographic information system (GIS) to identify hotspots. Although PAHs, OCPs and PCBs varied in terms of their concentration and spatial distribution, the sources of each type of POPs were identified using multivariate statistical analysis and the diagnostic ratios method. Total lifetime carcinogenic risk (TLCR) for PAHs, OCPs and PCBs exposure was evaluated quantitatively for each sampling site using the Risk Assessment Guidance for Superfund (RAGS) methodology, and a risk distribution map was created. The TLCR values of 76% sites for the PAHs were higher than the target level for individual excess lifetime cancer risk (10^{-6}) and with 12% sites were higher than the acceptable levels (10^{-4}) for residential cancer risk. There are 28% sites that have TLCR above 10^{-6} for recreational exposure to PAHs.

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1. Introduction

Persistent organic pollutants (POPs) represent a diverse group of toxic substances that are semi-volatile, mobile in the environment, and prone to long-range transport, and bioaccumulation. Soil acts as a natural sink for these toxic chemicals (Čupr et al., 2010; Hassanin et al., 2005; Meijer et al., 2002, 2003).

Under the framework of the Stockholm Convention on POPs signed in 2001, a list of chemicals whose production, use and storage must be eliminated or severely restricted was produced. After the 2008 Olympic Games, Beijing implemented a series of measures to improve urban environmental quality. Nevertheless, Beijing remains a rapidly urbanizing and densely populated city that consumes over 84,000 t of coal and 20,300 t of petroleum fuel per day (Peng et al., 2011).

Data on the distribution of POPs in urban soil can be used for assessing levels of pollution, identifying emission sources and evaluating the environmental health risks associated with POPs exposure (Peng et al., 2011; Wu et al., 2011; Yang et al., 2012). A large number of previous studies have reported the presence of POPs contaminants in the topsoils of urban Beijing, including polycyclic aromatic hydrocarbons

(PAHs) (Li et al., 2006; Liu et al., 2010; Peng et al., 2011, 2012; Tang et al., 2005; K.Y. Wang et al., 2009; Wang et al., 2010), organochlorine pesticides (OCPs) (Cheng et al., 2011; Li et al., 2005, 2008; Yang et al., 2010, 2012) and polychlorinated biphenyls (PCBs) (Fu et al., 2008b; Wu et al., 2011). However, few studies have systematically considered at the same time of the behavior of the three groups of POPs within an urban specific functional section, such as a renewal area developed on an old industrial place.

The south-east chemical industrial area is located in south-east Beijing between the 4th Ring Road and 5th Ring Road. This chemical industrial area was founded in the 1950s, and there are more than ten chemical plants in this area associated with chemical raw material processing and the chemical production of chemicals. In preparation for the 2008 Olympic Games, some plants were dismissed and partly, moved to other areas. While in the process of Beijing urbanization, the former south-east chemical industrial area was gradually developed as a residential or recreational district.

Chemical industries have been identified as important sources of emissions for a wide range of chemical substances, including POPs (Kaisarevic et al., 2007; G. Wang et al., 2009). Recently, studies and risk assessments of POPs in topsoil of chemical industrial areas have received many attentions from researchers (Li et al., 2011; Nadal et al., 2011; Syed and Malik, 2011). For a former chemical industrial area like the south-east chemical industrial area of Beijing, POPs

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contamination of the topsoil has resulted not only from past local chemical emissions but also from inputs from air deposition. The contribution of air deposition cannot be ignored, especially in the Beijing area (W.T. Wang et al., 2011).

In this study, we implemented a systematic study of legacy POPs in the topsoil of the south-east chemical industrial area in Beijing. The specific objectives were to: (1) systematically determine the concentration and distribution of POPs, including PAHs, OCPs and PCBs, in the topsoil of the study area; (2) identify the respective possible sources of PAHs, OCPs and PCBs using the diagnostic ratios of congeners and a multivariate statistical analysis; and (3) comprehensively evaluate the human health risks due to the exposure to POPs in the topsoil.

2. Methods

2.1. Sampling

The total area of the south-east Beijing chemical district is 30 km². In July 2011, 25 soil samples were collected from the top soil layer (0–20 cm) in the study area using a 1 × 1 km² grid (Fig. 1). To minimize sampling errors, each sample was a compilation of five mixed sub-samples that were collected with a stainless steel spade within a 10 × 10 m area. The soil samples were stored in a clean black box (New Landmark Soil Equipment Co., China), transported to the lab and stored in frozen form until extraction.

2.2. Chemicals

The 16 USEPA PAHs standard solution (1000 µg/mL), including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno [1,2,3-cd]pyrene (InP), dibenz[a, h]anthracene (DBA) and benzo [g, h, i]perylene (BghiP), was purchased from Sigma-Aldrich, St. Louis, MO (USA). In addition, 2-fluorobiphenyl (2-FBP) was used as a surrogate standard (Supelco, Bellefonte, PA, USA).

The OCPs standard solutions were the products of Sigma-Aldrich, St. Louis, MO (USA) and contained α -HCH, β -HCH, γ -HCH, δ -HCH, HCB, Heptachlor, Aldrin, Oxychlordane, *cis*-Heptachlor Epoxide, *trans*-

Heptachlor Epoxide, *trans*-Chlordane, *cis*-Chlordane, *trans*-Nonachlor, *cis*-Nonachlor, Dieldrin, Endrin, 2,4'-DDE, 4,4'-DDE, 2,4'-DDD, 4,4'-DDD, 2,4'-DDT, 4,4'-DDT and Mirex. 2,4,5,6-tetrachloro-m-xylene (TCMX) was used as a surrogate standard (Supelco, Bellefonte, PA, USA).

The four PCBs standard solutions were purchased from AccuStandard Inc. (New Haven, CT, USA). The PCBs calibration mixtures were diluted, which contained 125 congeners (Listed in Table S1 Supplementary Materials (SM)), with *iso*-octane to 20 ng/mL for each congener. The 125 PCB congeners represent the commercial mixtures of PCBs most widely used, such as Aroclor 1016, 1242, 1254, 1260 (Ahlborg et al., 1994). TCMX was also used as a surrogate standard. Standard reference material GBW08307 (reference soil for PCBs congeners analysis, including CB-28, 52, 77, 81, 101, 118, 114, 105, 138, 153, 167, 156, 157 and 180) was obtained from the National Research Center for Certified Reference Materials of China.

Silica gel (100–200 mesh) (Qingdao Haiyang Chemical Co., Qindao, China) was activated in a drying oven at 550 °C for 6 h. Anhydrous sodium sulfate (Beijing Chemical Factory, China) was heated at 600 °C for 12 h and then used to eliminate organic contamination. Methanol, dichloromethane and acetone were the products of Beijing Chemical Factory, China (analytical grade). The other solvents were of pesticide grade and were purchased from J. T. Baker (Phillipsburg, NJ, USA).

2.3. Extraction and cleanup

Five gram of each soil sample containing one of the surrogate standards was ground with anhydrous sodium sulfate into a free-flowing powder. Each sample was extracted with 30 mL of hexane/dichloromethane (1:1, vol/vol) by ultrasonication for 4 min and then centrifuged the samples at 3000 ×g, this process was repeated three times and extracts were combined. The concentrated extracts were evaporated to 1 mL in a Kuderna–Danish concentrator under a gentle N₂ stream for cleanup. Each sample was separately extracted three times for cleanup and analysis of PAHs, OCPs and PCBs. Before extraction, 2-FBP, TCMX and TCMX were added to the accurately weighed soil samples as surrogate standards for PAHs, OCPs and PCBs individually, and balanced at desiccator for 2 h. Cleanup of PAHs, OCPs and PCBs individually followed the modified methods of our previous reports (Fu et al., 2008a,b, 2009), and the detailed processes are described in the SM.

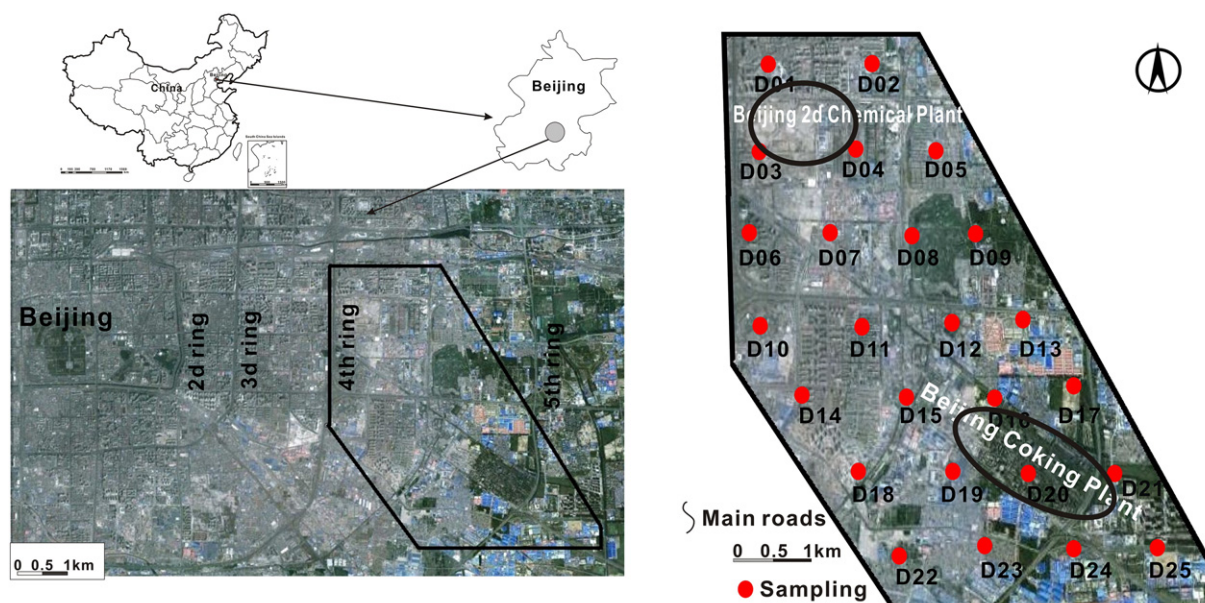


Fig. 1. Soil sampling sites in the Beijing south-east chemical industrial area.

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