Occurrence, characteristics and sources of polycyclic aromatic hydrocarbons in arable soils of Beijing, China

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ABSTRACT

This study investigated the occurrence and sources of polycyclic aromatic hydrocarbons (PAHs) from arable soils in Beijing and compared them with 4 other types of soils: soil from uncultivated land, an incineration plant, a suburb and a woodland. The total concentrations of PAHs ranged from 189.3 to 888.7 µg/kg (mean: 518.2 µg/kg for greenhouses and 455.2 µg/kg for fields). The seven carcinogenic PAHs accounted for 11.2–81.3% of Σ15PAHs in arable soils. Benzo[a]pyrene toxic equivalent (BaP$_{eq}$) concentrations were 82.8 µg/kg and 85.4 µg/kg in greenhouses and fields, respectively. Greenhouses and fields were both dominated by PAHs with 3 and 4 rings. Acenaphthene (ACE), indeno[1,2,3-cd] pyrene (IcdP) and benzo[ghi]perylene (BghiP) were the major compounds. These results showed that there was insignificant difference between the soil from greenhouses and fields and both had low carcinogenic potential risk. The diagnostic ratios suggested that the arable soils were mainly contaminated by coal/biomass combustion. Based on a positive matrix factorization (PMF) model, six sources were identified including coal combustion, waste incineration, tar, diesel combustion, biomass burning and gasoline combustion. Coal and gasoline combustion contributed over 40% of the measured PAHs in arable soils. Diesel combustion, tar and waste incineration were the main sources of pollution for soil from the uncultivated land, woodland and incineration plant/suburban. It was concluded that PMF was effective in determining the source apportionment. Urbanization and the evolution of human activities have caused PAH sources to become more complicated in industrial areas compared to regions with little human disturbance. Because of this, various factors need to be considered to control the PAH contamination in arable soils.

1. Introduction

Sixteen polycyclic aromatic hydrocarbons (PAHs) were identified as priority controlled organic pollutants by the Unite States Environmental Protection Agency (USEPA) in 1983, seven of which were classified as carcinogens. Exposure to PAHs has been implicated in cancer and other diseases including reproductive disorders (Bolden et al., 2017). Research has also found that China has higher pollution levels and that higher cancer risks can be tied to elevated PAH levels (Hong et al., 2016).

Soil is the most important sink for PAHs in the environment with wet-dry deposition as the common source. It is reported that PAHs can stay in the soil matrix for a long time because of the strong absorption between soil particles and organic matter (Chen et al., 2017). The concentrations of PAHs in soils can be an indicator of the pollution degree of the environment (Yuan et al., 2015). PAHs in soils have been reported in multi-industrial cities in South Korea (Kwon and Choi, 2014), urban traffic soils in India (Suman et al., 2016), a large steel-smelting manufacturer in northern China (Liu et al., 2017), and urban soils in Shanghai (Wang et al., 2013). Because of their presence in largely populated areas and their carcinogenic toxicity to human health, verifying the sources of PAHs is important in minimizing their risks to human health.

PAHs mainly originate from the incomplete combustion of fossil fuels and organic materials, the most significant being anthropogenic sources such as vehicle exhaust, agricultural fires and other industrial sources. At present, various methods have been used to identify source characteristics and estimate the contributions of specific sources. Diagnostic ratio is a relatively simple method used but may cause some errors due to the various physicochemical behaviors of PAHs in the environment (Jautzy et al., 2013). To quantitatively identify the contributions of PAH sources, principal component analysis (PCA) and

positive matrix factorization (PMF) have been widely used. However, the occasional occurrence of negative factor loadings limits the application of PCA (Ma et al., 2010). Different from the traditional factor analysis method, the PMF method can integrate non-negativity constrained factor analysis for each factor score. Furthermore, source fingerprinting and non-negative decomposition matrix were dispensable (Jaeckels et al., 2007). Because of this, it is widely applied in source apportionment of organic compounds as a receptor model. The model has been used to identify PAH sources in both agricultural and industrial soils (Okuda et al., 2010; Liu et al., 2016), both of which were found to be reasonably stable to explore the source apportionment of PAHs.

In recent years, urbanization and industrialization have both developed rapidly, to the point that industry is now supporting agriculture. Characteristics of PAHs in agricultural soils at a coke production base in Shanxi (Duan et al., 2015) and coal production area in Xinzhou (Zhao et al., 2014) showed that the PAH pollution was affected by the nearby industrial production. The emissions of solid fuels (i.e., straw and firewood) from rural areas and other agricultural activities also contributed significantly to PAHs in soils (Wang et al., 2015a). These studies showcase how pollution degree and sources of PAHs in arable soils are becoming more and more complicated due to the influence of urbanization.

Urban agriculture is a practice widely spread in Beijing. One report about the distribution and sources of PAHs has shown that PAHs were widespread in urban soils in Beijing (Peng et al., 2011). However, knowledge about the PAH contamination in arable soils is less available. PAH contamination in arable soils may contribute to food chain contamination and presents a human health risk through the consumption of contaminated meat or vegetables (Wang et al., 2015b). So, it is important to investigate the sources of PAHs in arable soils to control arable soil quality and reduce human exposure to these toxic chemicals. The aims of this study were as follows: (1) to measure the concentrations of PAHs in arable soils in Beijing, (2) to identify the possible sources by PMF, (3) to compare the pollution degree and sources with different types of soils.

2. Material and methods

2.1. Soil sampling

A total of 41 arable soil samples were collected in June 2015 (Beijing). Another 4 types of soils were collected from uncultivated land, an incineration plant, a suburb and a woodland as comparison (Table S1). One sample was collected in the uncultivated land and woodland, respectively and two samples were collected in the incineration plant and suburb in two seasons, respectively. Arable soil samples were divided into greenhouse and field samples. The uncultivated land was an open space in a rural area. Samples from the incineration plant and suburb were collected 0.5 km and 3 km away from the chimney of the incineration plant, respectively. The woodland was located in Beijing Songshan National Nature Reserve. At each 10 m × 10 m sampling site, 5 subsamples were taken at a depth of 0–10 cm and bulked together to form one composite sample. All the samples were air-dried at room temperature for one week, sieved to 100-mesh size particles and stored in amber glass containers at − 4 °C until analysis.

2.2. Sample preparation

Each soil sample was weighed to 2.0 g and Soxhlet extracted for 24 h with 100 mL n-hexane/dichloromethane (V/V = 1:1). The extracts were concentrated by rotary vacuum evaporation and then solvent-exchanged with n-hexane for 2 mL. The concentrated extracts were cleaned using silica gel column chromatography (25 cm × 1 cm internal diameter). The glass chromatography column fitted with a

Teflon® stopcock was packed with glass wool from the bottom, then 5 g silica gel, followed by 2 cm anhydrous sodium sulfate. After adding the sample extract, the column was eluted with 15 mL n-hexane and then 30 mL n-hexane/dichloromethane (V/V = 3:2). The first fraction containing n- hexane was discarded and the second fraction containing PAHs was collected. Next, the collected PAH fraction was vacuum-evaporated and solvent-exchanged with n-hexane and then concentrated to 1 mL under a stream of nitrogen before analysis by gas chromatography/mass spectrometry (GC/MS).

2.3. Gas chromatography/mass spectrometry

The determination of PAHs was performed on an Agilent GC7890/ 5975 MSD equipped with HP5-MS column (30 m × 250 μm × 0.25 μm). The carrier gas was helium. The oven temperature program was as follows: the initial temperature of 50 °C was held for 2 min, increased at a rate of 20 °C min^{-1} to 200 °C and held for 2 min, and then increased at a rate of 6 °C min^{-1} to 240 °C and then held for 2 min. The temperature was finally increased at a rate of 3 °C min^{-1} to 290 °C then held for 3 min. A 10 μL sample extract was injected in splitless mode. The injector and ion source were maintained at 280 °C and 230 °C, respectively. Ionization was carried out using the electron impact (EI) mode and data was acquired using the selective ion monitoring (SIM) mode. Identification of PAHs was based on the selected ions and the relative retention time between samples (Table S2 and Fig. S1).

2.4. Quality control

The PAHs were quantified using the external standard method. The recoveries based on matrix-spiked samples (PAH standards spiked into 3 pre-extracted soil) were 52.1 − 124.1%. The detection limit was calculated as three times the noise level of the chromatogram for the blank sample. The detection limits and recoveries of the PAHs are listed in Table S3. The assay results of naphthalene are usually inaccurate because of the unstable nature and susceptibility to environmental and operational factors and so they were not used in the data analysis. Therefore, the data analysis included only 15 of the 16 PAHs.

2.5. Positive matrix factorization (PMF) model

In this study, PMF analysis was used to analyze the relationships among the 15 PAHs (excluding naphthalene) and was carried out using the US EPA PMF 3.0 model (USEPA, 2008). The PMF model was developed by Paatero and Tapper (1994) and utilized non-negativity constraints for obtaining physically realistic meanings. It defines a n × m data original matrix X, where n represented the number of samples and m represented the number of chemical species, could be factorized into two matrices, namely G (n × p) and F (p × m) with an unexplained part E (n × m).

$$X = G \cdot F + E \tag{1}$$

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{2}$$

where x_{ij} was the concentration of the jth chemical species measured in the ith sample, g_{ik} was the contribution of source k to the ith sample, f_{kj} was the concentration of the jth chemical species in source k, and e_{ij} was the residual for each sample and species.

The objective function (Q) related to the residual and uncertainty is minimized using weighted least-squares by PMF, which is defined as

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{u_{ij}} \right)^2 \tag{3}$$

where e_{ij} is the difference between the observations and the model and u_{ij} is the uncertainty for each observation. The robust Q value is selected to reduce the impact of outliers in the fitting of the model. The