



## Atmospheric concentrations and air–soil gas exchange of polycyclic aromatic hydrocarbons (PAHs) in remote, rural village and urban areas of Beijing–Tianjin region, North China

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### ARTICLE INFO

#### Article history:

Received 3 September 2010

Received in revised form 13 February 2011

Accepted 11 April 2011

#### Keywords:

Atmospheric PAHs  
Passive air sampling  
Air–soil exchange  
Beijing  
Tianjin

### ABSTRACT

Forty passive air samplers were deployed to study the occurrence of gas and particulate phase PAHs in remote, rural village and urban areas of Beijing–Tianjin region, North China for four seasons (spring, summer, fall and winter) from 2007 to 2008. The influence of emissions on the spatial distribution pattern of air PAH concentrations was addressed. In addition, the air–soil gas exchange of PAHs was studied using fugacity calculations. The median gaseous and particulate phase PAH concentrations were 222 ng/m<sup>3</sup> and 114 ng/m<sup>3</sup>, respectively, with a median total PAH concentration of 349 ng/m<sup>3</sup>. Higher PAH concentrations were measured in winter than in other seasons. Air PAH concentrations measured at the rural villages and urban sites in the northern mountain region were significantly lower than those measured at sites in the southern plain during all seasons. However, there was no significant difference in PAH concentrations between the rural villages and urban sites in the northern and southern areas. This urban–rural PAH distribution pattern was related to the location of PAH emission sources and the population distribution. The location of PAH emission sources explained 56%–77% of the spatial variation in ambient air PAH concentrations. The annual median air–soil gas exchange flux of PAHs was 42.2 ng/m<sup>2</sup>/day from soil to air. Among the 15 PAHs measured, acenaphthylene (ACY) and acenaphthene (ACE) contributed to more than half of the total exchange flux. Furthermore, the air–soil gas exchange fluxes of PAHs at the urban sites were higher than those at the remote and rural sites. In summer, more gaseous PAHs volatilized from soil to air because of higher temperatures and increased rainfall. However, in winter, more gaseous PAHs deposited from air to soil due to higher PAH emissions and lower temperatures. The soil TOC concentration had no significant influence on the air–soil gas exchange of PAHs.

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants that are formed mainly during incomplete combustion of fossil fuels and biomass. Chinese PAH emissions contributed to over 20% of the total global PAH emissions in 2004 (Zhang and Tao, 2008). As a result, PAH emissions in excess of 116,000 tons/year have resulted in the contamination of various environmental media in China, especially ambient air (Zhang et al., 2007). In addition, it was reported by Zhang et al. (2009) that 1.6% of the lung cancer morbidity in China was due to inhalation exposure to ambient air PAHs.

Air–soil exchange is one of the most important processes governing the fate of persistent organic pollutants (POPs), including PAHs, in the environment (Cousins et al., 1999) and understanding their air–soil exchange is important for evaluating the risk associated with environmental contamination and human exposure. Previous studies have focused on the air–soil exchange of organochlorine pesticides (OCPs) (Harner et al., 2001; Meijer et al., 2003a,b; Bidleman and Leone, 2004; Kurt-Karakus et al., 2006; Růžičková et al., 2008; Tao et al., 2008; Bozlaker et al., 2009; Kobližková et al., 2009; Wong et al., 2010), polychlorinated biphenyls (PCBs) (Harner et al., 1995; Cousins and Jones, 1998; Backea et al., 2004; Bozlaker et al., 2008a; Růžičková et al., 2008; Kobližková et al., 2009; Li et al., 2010), polychlorinated dibenzo-p-dioxins (PCDDs) (Cousins et al., 1998), and polybrominated diphenyl ethers (PBDEs) (Cetin and Odabasi, 2007). However, there is a limited number of studies on the air–soil exchange of PAHs

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(Bozlaker et al., 2008b; Wang et al., 2008a). Multimedia fugacity and atmospheric dispersion models predict that air–soil exchange of PAHs may be one of the most significant processes for removing PAHs from the atmosphere, as well as the most important process for contaminating soils with PAHs (Lang et al., 2007).

Beijing and Tianjin are two of the largest cities in northern China and the rapid population growth, industrialization and urbanization of this area during the last decade have resulted in high PAH emissions (Zhang et al., 2007) and high atmospheric concentrations (Zhou et al., 2005; Okuda et al., 2006; Wu et al., 2006, 2007; Wang et al., 2008b; Zhang et al., 2009). Recently, Liu et al. (2007, 2008) reported that atmospheric PAH concentrations in rural Chinese villages are similar to, or even higher than, those in urban areas due to the extensive use of biomass and coal as fuels for cooking and heating. Given this, it is important to further investigate this finding and assess the air–soil exchange of PAHs in rural villages and urban areas in the Beijing–Tianjin area.

The objectives of this study were to (1) investigate the seasonal variation and spatial distribution of the atmospheric PAH concentrations in this region, (2) determine the magnitude and direction of air–soil gas exchange of PAHs in remote, rural village and urban areas, (3) investigate the seasonal variation and spatial distribution of the air–soil gas exchange fluxes of PAHs, and (4) assess the influence of PAH emission density, total organic carbon (TOC) concentration in soil, and temperature, on the air–soil gas exchange of PAHs.

## 2. Materials and methods

### 2.1. Sampling

Passive air samplers with PUF (polyurethane foam) disks and glass fiber filter (GFF) were used to collect PAHs in the gas and particulate phase, respectively. The sampler has been tested in field conditions at different meteorological conditions with satisfaction and detailed calibration and uptake rates of this sampler were described previously (Tao et al., 2009). It is important to note that this passive air sampler samples the particle-bound PAHs less efficiently than gas-phase PAHs. Therefore, higher uncertainties are associated with the measured particle-phase PAH concentrations in this study. Passive air sampling data were collected at 40 remote, rural village and urban sites between 2007 and 2008 covering four seasons, and the sampling period in winter included the residential heating time. Two identical samplers were deployed at each site on rooftops or in open areas at each site at 1.5 to 20 m high off the ground in order to avoid airflow obstruction. The passive air samplers were mounted at different heights because of logistical constraints. PAH concentrations may change over height, the effect of sampling height on the result could be a constrain of the method and the results should be interpolated with care.

Soil samples were collected from the same sampling sites in September 2007 (Wang et al., 2010). Briefly, surface soils (0–5 cm in depth) were collected using a stainless steel soil corer after the upper organic vegetative material was removed. Five soil samples were collected over a 100 m<sup>2</sup> area, pooled and homogenized to obtain a composite soil sample. Detailed sampling information, including the sampling height, longitude, latitude and sampling periods are given in Table S1.

The study area covers Beijing, Tianjin and part of the Hebei province (50,000 km<sup>2</sup>, with 70 million inhabitants) (Fig. S1) and all of the sampling sites were located far from industrial areas and roadsides. The northern and southern rural villages and northern and southern urban areas were divided based on a boundary line between the mountain area and the plain area of the Beijing–Tianjin region (Fig. S1). This separation between the northern and southern sites is demonstrated by a scatter plot of gross domestic product (GDP) and population density for northern rural villages, southern rural villages, northern urban areas and southern urban areas (Fig. S2).

After sampling, all PUF disks were stored at –18 °C. The GFFs were equilibrated in a desiccator (25 °C) for 24 h and weighed before and after the sampling, in accordance with USEPA Method 5 of 40 CFR Part 60 (<http://www.epa.gov/ttn/emc/methods/method5.html>). It is likely that the particles will adjust to a new equilibrium with the air inside the desiccators, which brings uncertainties to the following sample extraction and analysis. Before sampling, the PUF disks were pre-cleaned in a Soxhlet extractor with dichloromethane for 24 h and the GFFs were prebaked in a furnace at 450 °C for 4 h.

### 2.2. Extraction and analysis

PUF disks and GFFs were Soxhlet extracted with 100 mL dichloromethane for 12 h (Liu et al., 2007; Tao et al., 2009), and the extracts were concentrated by rotary evaporation to about 1.0 mL, solvent exchanged to *n*-hexane, and purified on an alumina silica packed column (10 cm, 3% deactivated silica gel, 6 cm, 3% deactivated alumina, and 1 cm anhydrous sodium sulfate). The silica gel, alumina and anhydrous sodium sulfate were baked at 450 °C for 4 h prior to use. The column was eluted with 50 mL of dichloromethane/hexane (2:3) at a rate of 2 mL/min to yield the PAHs fraction. The eluant was concentrated on the rotary evaporator at below 38 °C to approximate 1 mL.

Fifteen PAHs, including acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CHR), benzo(b)-fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA), indeno(1,2,3-cd)pyrene (IcdP), and benzo(ghi)perylene (BghiP), were analyzed on a gas chromatograph (Agilent 6890) coupled to a mass selective detector (MSD, Agilent 5973). Twenty percent of the samples were spiked with deuterated PAHs (NAP-*d*<sub>8</sub>, ANE-*d*<sub>10</sub>, ACE-*d*<sub>10</sub>, ANT-*d*<sub>10</sub>, CHR-*d*<sub>12</sub> and Perelyne-*d*<sub>12</sub>) before extraction to monitor the loss of PAHs during extraction and cleanup procedures. 2-fluoro-1,1'-biphenyl and *p*-terphenyl-*d*<sub>14</sub> (2.0 µg/mL, J&K Chem, USA) were spiked onto the samples and used as internal standards for quantification of the 15 PAHs in each sample. Details of the analysis and quantification methods have been described previously (Liu et al., 2007). All solvents were of analytical grade and redistilled. All glassware was cleaned using an ultrasonic cleaner (Kunshan KQ-500B, China) and baked at 400 °C for 6 h.

### 2.3. Quality control and quality assurance

Thirty-two field blanks, including a PUF and GFF, were analyzed. The instrumental detection limits and the concentration range of PAHs in the field blank samples are shown in Table S2. The PAH concentrations in blank samples were at least one order of magnitude lower than the actual samples. The reported sample PAH concentrations were blank subtracted using the mean of all blanks. Method recoveries were determined by spiking the standard mixture of 15 PAHs onto the PUF disks and GFFs and performing the entire analytical methods. The recoveries were 79–114% for the PUF disks and 72–102% for the GFFs. The recoveries for the deuterated PAHs were 79–96% for the PUF disks and 73–91% for the GFFs. The average coefficients of variation for PAH concentrations measured in duplicate samples were 3–18% for the PUF disks and 4–28% for the GFFs. The same quality control steps are also used in other studies (Liu et al., 2007, 2008; Tao et al., 2009; Wang et al., 2010).

## 3. Results and discussion

### 3.1. PAHs concentration in air

The annual median air PAH concentration for the entire study region was 222 ng/m<sup>3</sup> for the gaseous PAHs, 114 ng/m<sup>3</sup> for the particulate PAHs, and 349 ng/m<sup>3</sup> for the total 15 PAHs (sum of gaseous

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