



## Seasonal and spatial occurrence and distribution of atmospheric polycyclic aromatic hydrocarbons (PAHs) in rural and urban areas of the North Chinese Plain

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*The seasonal and spatial features of atmospheric PAHs were both related to the emission in rural and urban areas of the North Chinese Plain.*

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### ABSTRACT

Passive air sampling (PAS) was employed to study the occurrence of gaseous and particle-bound PAHs in the North Chinese Plain. The averaged concentrations of gaseous and particle-bound PAHs were  $485 \pm 209 \text{ ng/m}^3$  and  $267 \pm 161 \text{ ng/m}^3$ , respectively. The PAHs concentrations at urban sites were generally higher than those at rural ones with ratios  $< 1.5$  in spring, summer and fall, but differences between them were not significant for the wintertime and annually averaged concentrations. This urban–rural distribution pattern was related to the PAHs emission sources. PAHs spatial variation can be partially (49%) explained by emission with a simple linear regression method. Both the gaseous and particle-bound PAHs were highest in winter and lowest in summer, with winter/summer ratios of 1.8 and 8, respectively. Emission strength was the most important factor for the seasonality.

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### 1. Introduction

In China, emissions of polycyclic aromatic hydrocarbons (PAHs) in excess of 27,000 tons/year have resulted in the contamination of various environmental media, especially ambient air (Zhang et al., 2007). High emission density was revealed in North Chinese Plain (300,000 km<sup>2</sup>, a region with 130 million inhabitants) in both urban and rural areas (Zhang et al., 2007), and it was previously validated for the wintertime by a pilot study of atmospheric PAHs (Liu et al., 2007a). For a more comprehensive understanding and further regulations of the PAHs contamination, seasonal atmospheric PAHs data were still necessary for urban and rural areas in this region. However, traditional active air sampling (AAS) technology is impractical for this kind of data collection in this region with 300,000 km<sup>2</sup>. Therefore, passive air sampling (PAS) technology was employed in this study to provide average seasonal concentrations of PAHs for the North Chinese Plain.

PAS has been extensively used to measure semi-volatile organic contaminants in a variety of field monitoring situations (Harner et al., 2006). Advantages over AAS include easy handling, low cost and no

power supply requirement. PAS was able to provide time-averaged data within a factor of 2–3 compared to routine AAS and especially suitable for developing regions (Harner et al., 2006). In developed countries most of the PAHs are distributed in the gas phase (Hafner et al., 2005; Sun et al., 2006), standard passive samplers, which only collect the gas phase, are appropriate (Motelay-Massei et al., 2005; Wania et al., 2003). However, the sampling of particle-bound PAHs was necessary in this area, especially in winter when particle-bound PAHs exceed those in the gaseous phase (Liu et al., 2007a,b). Therefore, a passive sampler that is able to separately collect gaseous and particulate phase PAHs was used (Tao et al., 2007).

Seasonal concentrations of gaseous and particle-bound PAHs were measured at 17 urban sites, 28 rural sites and 2 mountainous sites. The PAS results for Beijing and Tianjin were compared to AAS data as a validation. The levels of gaseous and particle-bound PAHs were provided. The seasonal and spatial occurrence and distribution of atmospheric PAHs were revealed and discussed against the emission.

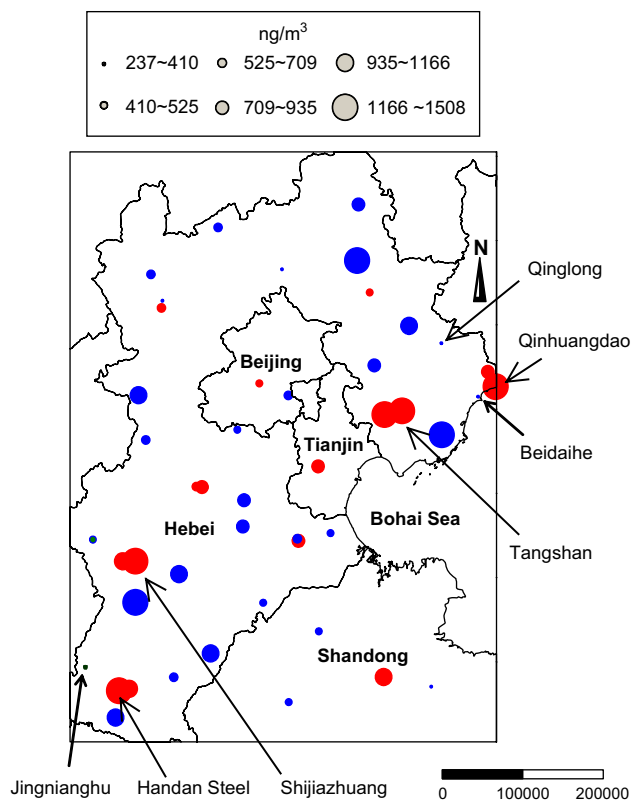
### 2. Materials and methods

#### 2.1. Sampling

Passive air sampling data were collected at 47 urban, rural and background sites between 2005 and 2006 (Fig. 1). The study area covers Beijing, Tianjin, Hebei and part

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**Fig. 1.** The spatial distribution of annually averaged TP concentrations in North Chinese Plain measured using PAS. The sizes of the symbols are proportional to the concentrations and the urban, rural and background sites were represented by red, blue and green colors, respectively (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

of Shandong Province. Two identical samplers were deployed at each site on rooftops or open areas to avoid air flow obstruction (1.5–18 m heights, Table S1, Supplementary material). The spring, summer, fall and winter campaigns were conducted in March–June, June–September, September–November and November–March, respectively (Table S1, Supplementary material). Two control sites were initially chosen; however, PAHs concentrations at one control site (Gangnan,  $\sim 500 \text{ ng/m}^3$ ) were higher than the other (Jingnianghu,  $\sim 250 \text{ ng/m}^3$ ) because of the widespread human activity and contamination, thus only the latter served as the control.

## 2.2. The passive sampling device

Passive air samplers with PUF disk and glass fiber filter (GFF) in a stainless steel cylinder were used to collect PAHs in the gas and particulate phases, respectively (Tao et al., 2007). The sampler was designed to restrict air circulation, to dampen the effect of wind and to, ultimately, minimize the collection of particles on the PUF disks. Although the uptake rates of the samplers were very low ( $\sim 0.10 \text{ m}^3/\text{d}$ ), it appears high enough for a seasonal study of heavily contaminated areas. Depuration compounds (DCs) have been used to obtain site-specific sampling rates of PAS (Gouin et al., 2005). However, the accuracy of DCs-correction was still under question (Gioia et al., 2006). DCs were not employed in this study, and volume concentrations were calculated based on calibration equations derived previously,

$$P7L = 10^{1.02 \log P + 0.969}$$

$$P8M = 10^{0.992 \log P + 2.175}$$

where P7L is the concentration of the sum of seven low molecular weight PAHs including acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA) and pyrene (PYR), P8M is the concentration of the sum of eight median molecular weight PAHs including FLO, PHE, ANT, FLA, PYR, benz(a)anthracene (BaA), chrysene (CHR) and benzo(b)fluoranthene (BbF), and  $P$  is the corresponding PAHs measured in PUF (or GFF) in  $\text{ng/sampler/day}$  (Tao et al., 2007). Note that the PAS results were semi-quantitative due to the complex influence factors during sampling. P7L represents total gaseous PAHs. However, ratios of P8M to total particle-bound PAHs were 64–76% and 74–77% in summer and winter, respectively, according to various reports (Liu et al., 2007a,b;

Okuda et al., 2006; Zhou et al., 2005). Ratios of P8M to total particle-bound PAHs at rural and urban sites in Tianjin were both 69% in winter (Wu et al., 2007). Otherwise, no relevant data were available on the ratios of P8M to total particle-bound PAHs at other sites in this study. As such, a ratio of 0.7 was applied to P8M to estimate the total particle-bound PAHs, and the total of gaseous and particle-bound PAHs were estimated as  $\text{TP} (\text{ng/m}^3) = \text{P7L} + \text{P8M}/0.7$ .

## 2.3. Extraction and analysis

PUF disks were Soxhlet extracted in a 1:1 mixture of *n*-hexane and cyclohexane for 4 h and GFFs were Soxhlet extracted in the same solvent for 10 h. These extracts were concentrated to 1 mL by rotary evaporation at a temperature below  $38^\circ\text{C}$ .

The analysis and quantification methods were described previously (Tao et al., 2007). Briefly, all samples were analyzed on a GC-MSD (Agilent GC6890/MSD 5973), using a HP-5MS capillary column in selective ion monitoring mode. The PAHs were quantified with an internal standard, 2-fluoro-1,1'-biphenyl and *p*-terphenyl- $d_{14}$  (J&K Chemical, USA,  $2.0 \mu\text{g/mL}$ ). The PAHs quantified for PUF disks were ACY, ACE, FLO, PHE, ANT, FLA and PYR, while for GFFs were FLO, PHE, ANT, FLA, PYR, BaA, CHR and BbF. PAHs with heavier molecular weights were detected in few samples (such as CHR in PUF disks, and BkF, BaP in GFFs) but not quantified. Statistical methods employed in this study were performed using SPSS v.10.0.

## 2.4. Quality control

Laboratory blanks were analyzed with every extraction. Four field blanks (samplers brought to and back from the field with no significant exposure) were analyzed with the true samples in every seasonal campaign. The concentration of target PAHs in the field blanks were higher than laboratory blanks and more than one order of magnitude lower than real samples for both PUF disks and GFFs. The only exception was GFFs in summer campaign with a ratio of  $\sim 6$ . We performed a method recovery procedure with a spiked, working standard of the target PAHs ( $100 \mu\text{L} \times 10 \mu\text{g/mL}$ ). Method recoveries were between 79–114% and 72–102% for PUF disks and GFFs, respectively. All field measurements were field blank and method recovery corrected. The detection limits, field blanks, and method recoveries of target PAHs are listed in Table S2, Supplementary material.

The average coefficients of variation of the duplicate samples for target PAHs in the PUF disks were 18% (spring), 11% (summer), 13% (fall), and 16% (winter), while in the GFFs were 25% (spring), 50% (summer), 22% (fall) and 17% (winter). Prior to extraction, deuterated PAHs were spiked in samples as surrogates ( $250 \mu\text{L} \times 4 \mu\text{g/mL}$ ). The average recoveries of ACE- $d_{10}$ , ANT- $d_{10}$  and CHR- $d_{12}$  were 84.2%, 93.5% and 79.6% for PUF disks and 72.3%, 79.0% and 79.1% for GFFs, respectively.

All solvents were analytical grade and redistilled. The standard mixture of PAHs was diluted with *n*-hexane (PPH-10JM, Chem Service Inc., U.S.). All glassware was cleaned using an ultrasonic cleaner (Kunshan KQ-500B, China) and heated to  $400^\circ\text{C}$  for 6 h. The detection limits, field blanks and method recoveries are tabulated in the Supplementary material.

## 3. Result and discussion

### 3.1. Comparison of PAS vs. reported AAS results

The passively measured PAH concentrations in  $\text{ng/device}\cdot\text{day}$  were converted into volume concentrations presented as P7L and P8M for gaseous and particle-bound PAHs, respectively (Tao et al., 2007). Due to limited air circulation, particles collected by the passive sampler were primarily the fine fraction (Tao et al., 2007); however, the majority of particle-bound PAHs are associated with the fine particle phase (Allen et al., 1996; Wu et al., 2006). As a result, P7Ls measured by passive sampler in Beijing in 2006 ( $230 \text{ ng/m}^3$  in summer and  $700 \text{ ng/m}^3$  in winter) were consistent with AAS data at the same location in 2004, ( $266 \text{ ng/m}^3$  in summer and  $472 \text{ ng/m}^3$  in winter) (Liu et al., 2007b,c). The estimated particle-bound PAHs concentrations also agreed well with AAS data in the literature by a factor of less than 3 or 2 (Table 1).

Gouin et al. compared AAS and PAS technique by using PUF passive samplers in the Great Lakes basin and found that the two sampling methods were consistent within a factor of 2 or 3 for organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers (Gouin et al., 2005). Harner et al. reached similar conclusion and also found agreement within a factor of 2 or 3 (Harner et al., 2006). The AAS campaigns cited here were performed 2–4 years ago. However, according to the leveling-off of atmospheric BaP in Beijing in recent 5 years (Beijing Environment Protection Bureau, 2007), insignificant variations of

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