Environmental Pollution 159 (2011) 287–293

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Spatial distribution and seasonal variation of atmospheric bulk deposition of polycyclic aromatic hydrocarbons in Beijing–Tianjin region, North China

Wentao Wang[a,b], Staci L. Massey Simonich[c], Basant Giri[c], Miao Xue[a], Jingyu Zhao[a], Shejun Chen[d], Huizhong Shen[a], Guofeng Shen[a], Rong Wang[a], Jun Cao[a], Shu Tao[a,*]

[a] Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China
[b] The Administrative Center for China's Agenda 21 (ACCA21), Ministry of Science and Technology, Beijing, 100038, China
[c] Department of Environmental and Molecular Toxicology and Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA
[d] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

The spatial distribution and seasonal variation of PAHs deposition in Beijing–Tianjin region were studied and quantitatively related to PAHs emission density and ambient air concentration.

ARTICLE INFO

Article history:
Received 1 March 2010
Received in revised form
19 August 2010
Accepted 19 August 2010

Keywords:
PAHs
Bulk deposition
Flux
Seasonal variation
Beijing
Tianjin

ABSTRACT

Bulk deposition samples were collected in remote, rural village and urban areas of Beijing–Tianjin region, North China in spring, summer, fall and winter from 2007 to 2008. The annually averaged PAHs concentration and deposition flux were 11.81 ± 4.61 μg/g and 5.2 ± 3.89 μg/m^2/day respectively. PHE and FLA had the highest deposition flux, accounting for 35.3% and 20.7% of total deposition flux, respectively. More exposure risk from deposition existed in the fall for the local inhabitants. In addition, the PAHs deposition flux in rural villages (3.91 μg/m^2/day) and urban areas (8.28 μg/m^2/day) was 3.8 and 9.1 times higher than in background area (0.82 μg/m^2/day), respectively. This spatial variation of deposition fluxes of PAHs was related to the PAHs emission sources, local population density and air concentration of PAHs, and the PAHs emission sources alone can explain 36%, 49%, 21% and 30% of the spatial variation in spring, summer, fall and winter, respectively.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants that are formed during the incomplete combustion of fossil and biofuels, and are serious health concern in the world (Zhang et al., 2009). Once enter into the atmosphere, PAHs are distributed between gas and particle phases and subject to removal mechanisms, such as oxidative and photolytic reactions, wet and dry deposition. It has been demonstrated that wet and dry deposition events are the major processes that remove PAHs from the atmosphere (Bidleman, 1988; Cousins et al., 1999). Researches on atmospheric PAHs deposition have been carried out widely in different parts of world (Halsall et al., 1997; Franz et al., 1998; Golomb et al., 2001; Park et al., 2001; Bae et al., 2002; Garban et al., 2002; Gigliotti et al., 2005; Terzi and Samara, 2005; Gocht et al., 2007; Tasdemir and Esen, 2007). In China, however, limited studies have been systematically performed on atmospheric PAHs deposition (Wu et al., 2005; Zhang et al., 2008).

There are two widely used methods to estimate PAH deposition. The first one uses gas and particulate phase PAHs concentration, and the deposition flux is calculated by multiplying the concentration and deposition velocity (Fang et al., 2004; Gigliotti et al., 2005). However, there are many uncertainties for determining the deposition velocity, which is influenced by particle size, meteorological conditions, properties of the receptor surface, and physical and chemical properties of the particle (Cousins et al., 1999). In the second method gaseous and particulate phase PAHs are collected directly on an artificial surface, such as metal pans, coated or uncoated glass fiber filter (GFF), plates filled fluid, greased surfaces, and water surface (Odabasi et al., 1999; Garban et al., 2002; Ollivon et al., 2002; Wu et al., 2005; Gocht et al., 2007; Pekey et al., 2007; Su et al., 2007; Tasdemir and Esen, 2007; Zhang et al., 2008), and the deposition flux can be calculated by PAHs concentration and sampling period. But the second method also has some drawbacks, which are PAHs re-volatilization from the collection surface and photo-degradation during sampling.

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* Corresponding author.
E-mail address: taos@urban.pku.edu.cn (S. Tao).

0269-7491/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envpol.2010.08.029

Compared with the first method, the second one is more accurate and widely used in other studies.

Beijing and Tianjin are two of the largest cities in northern China. The high population growth and rapid industrialization and urbanization during the last decades have resulted in significant environmental problems, including severe PAH contamination (Tao et al., 2004). In addition, the PAH emission density in the North China Plain is among the highest in China and domestic coal combustion, biomass burning, and coking industry are the major contributors to PAH emissions in this area (Zhang et al., 2007).

The objectives of this study were to (1) measure bulk deposition concentration and fluxes (dry + wet deposition) of PAHs in remote, rural village and urban areas in Beijing–Tianjin region; (2) investigate the spatial and seasonal variations of the bulk deposition fluxes of PAHs in this region; (3) assess the influence of PAH emission sources, local population distribution, and atmospheric PAH concentration on the deposition fluxes of PAHs.

2. Materials and methods

2.1. Sampling

There were 40 background, rural village and urban sampling locations in Beijing–Tianjin region (Fig. 1). All sampling sites were selected far from industrial areas and roadsides, and located in open areas without trees, buildings or any other sheltering objects near them. Detailed sampling information about sampling height, longitude, latitude and sampling periods were presented in Table S1 in Supplementary material.

Stainless steel buckets (i.d. 32 ± 0.5 cm, height 50 cm, flat-bottom) were used to collect bulk deposition (dry and wet depositions were mixed together) from June 2007 to May 2008, and two identical buckets were deployed at each site (1.5–20 m heights). The spring, summer, fall and winter campaigns were conducted in March 2008–May 2008, June 2007–August 2007, September 2007–November 2007 and December 2007–February 2008, respectively, and the sampling period in winter covers the residential heating time. Since the contribution of wet deposition was small for the whole year in the studied area (Tao et al., 2003; Cao et al., 2004), no wet deposition samples were collected separately in this study, and all samples were treated as bulk deposition or dustfall. Similar methodology was used elsewhere (Garban et al., 2002; Wu et al., 2005; Gocht et al., 2007; Zhang et al., 2008).

Distilled water was added into the buckets before sampling, and the amount of distilled water was determined according to the evaporation and precipitation situation, generally 50 mL in summer and winter, and 100 mL in other seasons. About 60 mL glycol was also added into each bucket to avoid the freezing of water in winter and reduce the effects of biodegradation. Pilot experiment was conducted to investigate the impact of glycol on deposition through the comparison of two buckets, of which one bucket was added with glycol and water, and the other one was added with water only. Results showed that the impact of glycol is negligible. Since some of the buckets were dried out during the sampling period, possible spilling out of particles could not be totally avoided, which may lead to some uncertainty in the sample collection. Leaves and insects were picked out using forceps before sample preparation, and the samples were kept in a refrigerator (−18 °C) before analysis. The sites with sampling failure in different seasons were shown in Table S1.

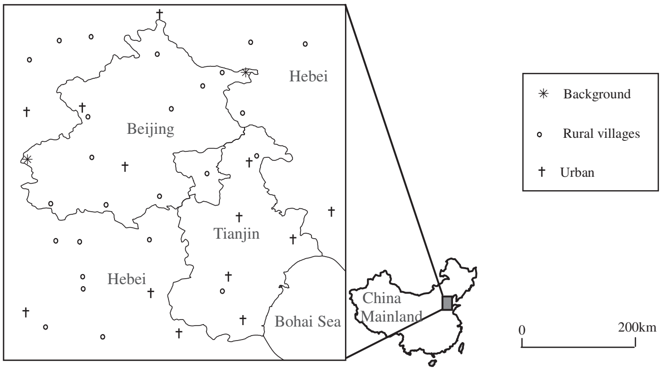

Fig. 1. Map of sampling locations in Beijing, Tianjin and surrounding areas.

2.2. Sample extraction and cleanup

Water in dustfall samples was removed using a freeze drying machine (FD-1A, Beijing Boyikang Apparatus Company, China) before analysis, and the weight of each sample was measured in order to calculate the dustfall and PAHs deposition fluxes.

Sixteen USEPA priority PAHs were measured in this study, including naphthalene (NAP), 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). Detailed information on the dustfall sample extraction and cleanup can be found in Wang et al. (2007). One gram of sample was Soxhlet extracted using 100 ml portions of n-hexane and acetone (1:1,v/v) for 15 h. Twenty percent of the samples were spiked with a range of deuterated PAHs (NAP-d_8, ACE-d_{10}, ANT-d_{10}, CHR-d_{12} and Perelyne-d_{12}) before extraction in order to monitor the efficiency of the extraction and cleanup procedures. After extraction, the samples were purified using a silica gel column. The final volume was adjusted to 1 ml under a gentle stream of N_2, and an appropriate volume (125 μl) of 2-Fluoro-1,1′-biphenyl and p-terphenyl-d_{14} (J&K chemical Ltd. USA) were spiked into the vial as internal standards prior to analysis by GC/MS.

2.3. GC–MS analysis and quantification

The PAHs were quantified by GC/MS (Agilent GC6890/5973MSD) using the internal standards. An HP-5 MS column (Agilent, length 30 m, i.d. 0.25 mm, film thickness 0.25 μm) was used with the following temperature program: 60–280 °C at 6 °C/min, isothermal holding at 280 °C for 20 min using helium as the carrier gas. All PAH concentrations were determined using selected ion monitoring (SIM) (Wang et al., 2007).

2.4. Quality control and Quality assurance

Samples were analyzed in duplicate to check for reproducibility. The average coefficients of variation for the duplicate samples were 12% (5–24%) for 16 PAHs. The analytical procedural blanks (Table S2) were more than one order of magnitude lower in concentration than the dustfall samples. The PAH concentrations were blank corrected using the arithmetic mean of the procedural blanks. The method detection limits (MDLs) were defined as the mean blank values plus three standard deviations, and the MDLs for the 16 individual PAH compounds ranged from 0.29 ng/g (PHE) to 1.02 ng/g (BghiP). Method recoveries were determined by spiking dustfall with a working standard (the standard mixture of 16 PAHs from J&K chemical Ltd., USA). For the 16 spiked individual PAHs, the recoveries from NAP to BghiP were from 66% to 114%. The recoveries for the deuterated PAHs were from 76% to 108%. Because of high blank values and variation of the duplicate samples (15–39%) for NAP, only 15 PAHs without NAP are discussed in this paper.

3. Results and discussion

3.1. PAHs concentration in the deposition

All of 15 PAHs were detected in the deposition samples, and the concentrations of individual PAHs in the deposition samples in different seasons are presented in Table 1. The annually averaged concentrations of 15 PAHs ($\sum PAH_{15}$) varied from 4.22 to 24.81 μg/g, with an arithmetic mean of 11.81 μg/g for the whole study region. Higher proportions of individual PAHs with three rings (50.4%) and four rings (36.5%) were observed in the deposition samples, followed by five and six ring (10.8%), and two ring PAHs (2.3%). Generally, The PAH profile was characterized by 3–4 ring PAHs, and PHE, FLA, PYR and BbF were the PAHs in the highest concentrations in the deposition samples, accounting for 28.2%, 20.2%, 11.5% and 10.3% of $\sum PAH_{15}$, respectively (Fig. S1).

The $\sum PAH_{15}$ are 0.61–5.99 μg/g, 1.90–20.58 μg/g, 4.72–35.83 μg/g, and 2.46–59.54 μg/g, with an average of 2.73 ± 1.37 μg/g, 8.00 ± 4.35 μg/g, 13.74 ± 6.75 μg/g, and 22.63 ± 13.66 μg/g in the spring, summer, fall and winter respectively. The highest PAHs concentration (59.54 μg/g) was measured at Tianjin, a highly industrialized city, in winter, while the lowest PAHs concentration (0.61 μg/g) was measured in a national forest park in Yaoqiaoyu of Beijing City in spring. PAH concentrations of deposition samples in this study were comparable to previous results in northern China. For example, total concentration of 15 PAHs were 10.7 μg/g and 6.6 μg/g in Tianjin city, northern China for heating and non-heating seasons

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