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

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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 $11.81 \pm 4.61 \mu\text{g/g}$ and $5.2 \pm 3.89 \mu\text{g/m}^2/\text{day}$ 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 ($3.91 \mu\text{g/m}^2/\text{day}$) and urban areas ($8.28 \mu\text{g/m}^2/\text{day}$) was 3.8 and 9.1 times higher than in background area ($0.82 \mu\text{g/m}^2/\text{day}$), 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.

Keywords

PAHs; Bulk deposition; Flux; Seasonal variation; Beijing; Tianjin

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

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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.

Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version at doi:10.1016/j.envpol.2010.08.029.

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. 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.

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-d₈, ACE-d₁₀, ANT-d₁₀, CHR-d₁₂ and Perelyne-d₁₂) 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 N₂, and an appropriate volume (125 μl) of 2-Fluoro-1,1'-biphenyl and p-terphenyl-d₁₄ (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 $^{\circ}\text{C}$ at 6 $^{\circ}\text{C}/\text{min}$, isothermal holding at 280 $^{\circ}\text{C}$ 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 (ΣPAH_{15}) varied from 4.22 to 24.81 $\mu\text{g/g}$, with an arithmetic mean of 11.81 $\mu\text{g/g}$ 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 ΣPAH_{15} , respectively (Fig. S1).

The ΣPAH_{15} are 0.61–5.99 $\mu\text{g/g}$, 1.90–20.58 $\mu\text{g/g}$, 4.72–35.83 $\mu\text{g/g}$, and 2.46–59.54 $\mu\text{g/g}$, with an average of 2.73 ± 1.37 $\mu\text{g/g}$, 8.00 ± 4.35 $\mu\text{g/g}$, 13.74 ± 6.75 $\mu\text{g/g}$, and 22.63 ± 13.66 $\mu\text{g/g}$ in the spring, summer, fall and winter respectively. The highest PAHs concentration (59.54 $\mu\text{g/g}$) was measured at Tianjin, a highly industrialized city, in winter, while the lowest PAHs concentration (0.61 $\mu\text{g/g}$) 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 $\mu\text{g/g}$ and 6.6 $\mu\text{g/g}$ in Tianjin city, northern China for heating and non-heating seasons respectively (Wu et al., 2005), and 1.62–9.64 $\mu\text{g/g}$ in the rural area of Beijing (Zhang et al., 2008). The differences among the seasons for ΣPAH_{15} concentrations in the studied areas were significant ($p < 0.01$, one-way ANOVA), concentrations in winter were 7.3, 1.8, and 0.7 times higher than those in spring, summer and fall, respectively.

Some PAHs, especially the light molecular weight compounds, tend to stay in gas phase due to the high air temperature in summer based on gas-particle partitioning theory (Bidleman, 1988). Furthermore, photolysis and rain washout effects are also strong in summer, which can result in lower particle-bound PAHs concentration (Liu et al., 2008). Because PAHs deposition mainly comes from the dry deposition of particle-bound PAHs, lower PAHs concentration in particle phase can result in lower PAHs concentration in deposition in summer (Cousins et al., 1999). However, in winter the large amount of coals and biofuel burning for residential heating, as well as the prevailing meteorology (i.e. lower inversions) accounted for the higher PAHs concentrations of deposition. In addition, the particle deposition flux in spring was 0.63 ± 0.24 $\text{g/m}^2/\text{day}$ (Table 2, Table S3), higher than that in summer (0.21 ± 0.13 $\text{g/m}^2/\text{day}$) and in fall (0.24 ± 0.14 $\text{g/m}^2/\text{day}$), and comparable with that in winter (0.62 ± 0.29 $\text{g/m}^2/\text{day}$) because of several Asian dust storms in spring of 2008 (March 2, March 17–19, May 19–21, May 28). The PAHs concentration in deposition samples was low but dustfall flux was high in spring, which may be explained by dilution of high particle concentration in spring and small amount of PAHs in most coarse particles in the dust storm samples (Hou et al., 2006).

The different emission sources can be qualitatively identified on the basis of PAHs composition profiles represented by diagnostic ratios (Yunker et al., 2002; Motelay-Massei et al., 2007). Fig. S2 in Supplementary material illustrates a plot of FLA/(FLA + PYR)

against IcdP/(IcdP + BghiP) for deposition samples. An FLA/(PYR + FLA) ratio <0.4 implies petroleum, $0.4\text{--}0.5$ implies petroleum (liquid fossil fuel, vehicle and crude oil) combustion, and >0.5 implies combustion of coal, grass and wood (Yunker et al., 2002). The judgment rule for IcdP/(IcdP + BghiP) is the same with that for FLA/(PYR + FLA). Most samples from the studied area had ratios >0.5 , indicating a predominant influence of coal/biofuel combustion in Beijing–Tianjin region. In addition, there is a significant difference for these ratios between winter and other three seasons, and it looks like more coal and biomass (straw, firewood) combustion is prevalent in winter (Fig. S2). Actually, in Beijing–Tianjin region, the wintertime consumption of these fuels was 1.5–2 times higher than in summer due to residential heating, and the difference of the total emission was estimated to be 1.5 times higher (Zhang and Tao, 2008). The results from diagnostic ratios were consistent with the seasonal variation of PAHs concentration aforementioned.

In addition, the BaP-equivalent concentrations (BaP_{eq}) were calculated based on toxic equivalent factors from Nisbet and LaGoy (1992). The average BaP_{eq} in Beijing–Tianjin region were $0.27 \pm 0.14 \mu\text{g/g}$, $0.65 \pm 0.34 \mu\text{g/g}$, $1.03 \pm 0.58 \mu\text{g/g}$, and $0.76 \pm 0.38 \mu\text{g/g}$ in the spring, summer, fall and winter respectively, and the seven carcinogenic PAHs contribute the most to the total carcinogenic potency of the dustfall. Furthermore, the accumulative probabilistic risk frequency of BaP_{eq} is shown in Fig. S3, and 100%, 78%, 60% and 81% of this study area for exposure risk was less than $1 \mu\text{g/g-BaP}_{\text{eq}}$ in the spring, summer, fall and winter, respectively. According to the result of a one-way ANOVA, exposure risk of local inhabitants to PAHs from deposition in the fall was significantly higher than those in other three seasons ($p < 0.05$).

3.2. Bulk deposition fluxes of PAHs

The annually averaged deposition flux of PAH_{15} was $5.22 \pm 3.89 \mu\text{g/m}^2/\text{day}$, and varied from 0.69 to $18.17 \mu\text{g/m}^2/\text{day}$ (Table 2). It is estimated that there is 95 ton PAH_{15} deposition every year in Beijing–Tianjin region ($50,000 \text{ km}^2$) based on the PAHs deposition flux in this study, equivalent to 4.5 ton deposition as BaP_{eq} . The PAH profile for deposition fluxes was characterized by 3–4 ring PAHs. PHE, FLA, PYR, BbF and CHR were the PAHs in highest deposition flux, accounting for 35.3%, 20.7%, 11.7%, 7.9% and 7.1% of PAH_{15} , respectively (Fig. S1), which is consistent with PAHs concentration in deposition samples.

The deposition fluxes of PAH_{15} in spring, summer, fall and winter are $0.37\text{--}4.04 \mu\text{g/m}^2/\text{day}$, $0.10\text{--}7.54 \mu\text{g/m}^2/\text{day}$, $0.72\text{--}7.46 \mu\text{g/m}^2/\text{day}$, and $0.96\text{--}55.75 \mu\text{g/m}^2/\text{day}$, with an average of $1.71 \pm 1.09 \mu\text{g/m}^2/\text{day}$, $1.82 \pm 1.64 \mu\text{g/m}^2/\text{day}$, $3.05 \pm 1.88 \mu\text{g/m}^2/\text{day}$, and $14.25 \pm 12.33 \mu\text{g/m}^2/\text{day}$, respectively. The highest PAHs deposition flux ($55.75 \mu\text{g/m}^2/\text{day}$) was measured in Baoding city, Hebei province, in winter, while the lowest one ($0.10 \mu\text{g/g}$) was measured in a national forest park in Yaoqiaoyu of Beijing city in summer. Deposition fluxes of PAHs in winter were significantly higher than those in other three seasons ($p < 0.01$), and they followed the order of winter $>$ fall $>$ summer $>$ spring, and PAH deposition in winter contributed nearly 75% of the annual flux.

The PAH deposition fluxes in the present study were comparable to those reported previously in northern China, where deposition flux of 15 PAHs was $4.88 \mu\text{g/m}^2/\text{day}$ in Tianjin (Wu et al., 2005), $5.14 \mu\text{g/m}^2/\text{day}$ in rural area of Beijing (Zhang et al., 2008). Our results were also similar to the PAH deposition fluxes in Taichung, Taiwan ($17.64 \mu\text{g/m}^2/\text{day}$, Fang et al., 2004), in Seoul, Korea ($5.5 \mu\text{g/m}^2/\text{day}$ and $12 \mu\text{g/m}^2/\text{day}$ in spring and winter, respectively, Bae et al., 2002), in Tampa Bay, USA ($6.8 \mu\text{g/m}^2/\text{day}$, Poor et al., 2004), in Izmit Bay, Turkey ($8.3 \mu\text{g/m}^2/\text{day}$, Pekey et al., 2007), in Bursa, Turkey ($2.7 \mu\text{g/m}^2/\text{day}$, Tasdemir and Esen, 2007), in Manchester and Cardiff, UK ($5.2 \mu\text{g/m}^2/\text{day}$ and $4.1 \mu\text{g/m}^2/\text{day}$, respectively, Halsall et al., 1997), and in Chicago ($18 \mu\text{g/m}^2/\text{day}$, Franz et al., 1998). However, our values were significantly higher than that in urban area of Paris (0.64

$\mu\text{g}/\text{m}^2/\text{day}$, Ollivon et al., 2002), in rural area of southern Germany ($0.55 \mu\text{g}/\text{m}^2/\text{day}$, Gocht et al., 2007), in Eastern Mediterranean ($0.46 \mu\text{g}/\text{m}^2/\text{day}$, Tsapakis et al., 2006), in rural area of France during heating time period ($0.13 \mu\text{g}/\text{m}^2/\text{day}$, Garban et al., 2002), in urban area of western Greece ($0.19 \mu\text{g}/\text{m}^2/\text{day}$, Terzi and Samara, 2005), in southern Ontario, Canada ($0.07 \mu\text{g}/\text{m}^2/\text{day}$, Su et al., 2007), in lake Michigan ($0.71 \mu\text{g}/\text{m}^2/\text{day}$, Franz et al., 1998), in New England coast ($0.22 \mu\text{g}/\text{m}^2/\text{day}$, Golomb et al., 2001), and in Galveston Bay, USA ($0.63 \mu\text{g}/\text{m}^2/\text{day}$, Park et al., 2001). Compared with these regions, there is middle or higher PAHs contamination for dry and wet deposition in Beijing–Tianjin region.

3.3. Spatial variation

The geographic distribution of PAH_{15} deposition fluxes in four seasons was shown in Fig. 2. In general, the highest PAHs deposition flux areas were found in urban Beijing and Tianjin, east and southwest of Hebei province, and a number of large cities, e.g. Tangshan, Baoding, Cangzhou and Langfang. The areas with the lowest PAHs deposition flux are mountain area in northwest of Hebei province (Zhangjiakou) and north of Beijing (Huairou) with relatively low population density.

The spatial distribution of PAHs emission sources, atmospheric dispersion and deposition processes should control the geographical distribution pattern of PAHs concentration in bulk deposition and their deposition fluxes. Liu et al. (2008) described that PAHs in ambient air were significantly correlated with corresponding emission density in North China Plain, and Hafner et al. (2005) reported that a significant correlation existed between air PAHs concentration and population density. Furthermore, Garban et al. (2002) looked into the relationship between population density and bulk deposition level and found that the deposition fluxes were affected by local population density. Obviously, large population and more human activities often result in high energy consumption rate, and high emission rate of various kinds of combustion products including PAHs. In this study a positive linear correlation between log-transformed PAH_{15} deposition flux and log-transformed PAHs emission density was found ($n = 40$, $p < 0.01$, Fig. 3) by using seasonal high-resolution emission data (Zhang and Tao, 2008). There was better correlation in summer than other three seasons, and in fact, approximately 49% (r^2) of the total spatial variation of deposition fluxes can be explained by the emission source in summer, and 36%, 21% and 30% in spring, fall and winter, respectively. In fact, the deposition flux of PAHs was governed by two processes of local emission and long-range transport (Wang et al., 2010a). The influence of long-range transport was weaker in the summer than in the winter. As a result, the deposition flux of PAHs in the summer was at strong influence of local PAHs emission. In addition, the local population density can account for 34%, 53%, 32% and 38% of spatial distribution of deposition fluxes in spring, summer, fall and winter, respectively (Fig. S4). These results suggest that local anthropogenic activities greatly influence PAH deposition in Beijing–Tianjin region.

Furthermore, there is very good correlation between ambient air concentration of PAHs (unpublished data) and deposition fluxes of PAHs ($p < 0.01$) (Fig. S5). It is reported that PAHs in bulk deposition samples mainly come from particulate phase PAHs in the ambient air (Bidleman, 1988; Cousins et al., 1999), and the particulate phase PAHs deposition is about 20 times higher than gaseous PAHs deposition in Tianjin (Tao et al., 2003). In this study, the correlation between deposition fluxes and total PAHs concentrations was better than that for particulate and gaseous phase PAHs. In addition, only weak correlation was obtained between PAHs deposition fluxes and soil PAHs concentration (Wang et al., 2010b) (Fig. S6), indicating that different PAHs sources for deposition and soil in Beijing–Tianjin region was possible.

The annually averaged PAH₁₅ deposition flux in rural villages (25 sites, 3.91 µg/m²/day) and urban areas (13 sites, 8.28 µg/m²/day) was 3.8 and 9.1 times higher than that in background site (0.82 µg/m²/day), respectively, and there was significant difference ($p < 0.05$) for PAHs deposition fluxes between urban and rural village sites in all seasons. The PAHs deposition fluxes in background areas were significantly lower with those in all rural and urban areas ($p < 0.001$) (Fig. 4). The PAHs deposition flux of urban areas in winter (23.17 µg/m²/day) was significantly higher than that in spring (2.47 µg/m²/day), summer (3.07 µg/m²/day), and fall (4.42 µg/m²/day), and similar result was found in the rural village areas (10.46 µg/m²/day in winter; 1.41 µg/m²/day in spring; 1.34 µg/m²/day in summer; 2.41 µg/m²/day in fall). The emission sources and local population should be responsible for this spatial pattern.

4. Conclusions

The concentrations of PAHs in bulk deposition samples (dry and wet deposition) were measured to examine the seasonal variation, spatial distribution, emission sources and deposition fluxes in remote, rural and urban areas of Beijing–Tianjin region, North China during spring, summer, fall and winter in 2007–2008. The annually averaged PAHs concentrations and deposition flux were 11.81 ± 4.61 µg/g and 5.22 ± 3.89 µg/m²/day respectively, and PHE, FLA, PYR, BbF and CHR had the highest deposition flux, accounting for 35.3%, 20.7%, 11.7%, 7.9% and 7.1% of total PAHs deposition, respectively. More exposure risk for PAHs from deposition existed in the fall for the local inhabitants. The deposition fluxes in the spring, summer, fall and winter were 1.71 ± 1.09 µg/m²/day, 1.82 ± 1.64 µg/m²/day, 3.05 ± 1.88 µg/m²/day, and 14.25 ± 12.33 µg/m²/day, respectively. The source diagnostics indicated that coal and biomass burning were the predominant sources of PAHs in this region, and there are greater PAHs deposition fluxes in winter than in other seasons due to more emission sources. In addition, the annually averaged PAHs deposition flux in rural villages (3.91 µg/m²/day) and urban areas (8.28 µg/m²/day) were 3.8 and 9.1 times higher than that in background area (0.82 µg/m²/day). This spatial variation of deposition fluxes of PAHs was related with the PAHs emission sources, local population and ambient air concentration of PAHs, and the PAHs emission sources alone can explain 36%, 49%, 21% and 30% of spatial variation of PAHs deposition in spring, summer, fall and winter, respectively.

Supplementary Material

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Acknowledgments

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

Fig. 2. Spatial distribution of PAHs deposition fluxes in spring, summer, fall and winter, respectively.

Fig. 3.
The correlation between bulk deposition fluxes and emission density of PAHs in spring, summer, fall and winter, respectively.

Fig. 4. Deposition fluxes of PAHs in background, rural village and urban sites in spring, summer, fall and winter, respectively.

Table 1

Concentrations of 15 PAHs in deposition samples in the spring, summer, fall and winter, respectively ($\mu\text{g/g}$).

	Spring ($n = 37$)	Summer ($n = 39$)	Fall ($n = 38$)	Winter ($n = 39$)	Annually Average ($n = 40$)
ACE	0.01 $\pm$ 0.01	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01
ACY	0.01 $\pm$ 0.01	0.05 $\pm$ 0.05	0.05 $\pm$ 0.03	0.08 $\pm$ 0.01	0.05 $\pm$ 0.04
FLO	0.06 $\pm$ 0.04	0.16 $\pm$ 0.10	0.18 $\pm$ 0.12	0.46 $\pm$ 0.47	0.22 $\pm$ 0.15
PHE	0.55 $\pm$ 0.39	1.18 $\pm$ 0.72	2.12 $\pm$ 1.26	9.43 $\pm$ 6.93	3.33 $\pm$ 2.00
ANT	0.05 $\pm$ 0.03	0.15 $\pm$ 0.10	0.19 $\pm$ 0.09	0.56 $\pm$ 0.39	0.24 $\pm$ 0.13
FLA	0.40 $\pm$ 0.27	1.38 $\pm$ 0.93	2.89 $\pm$ 1.49	4.81 $\pm$ 4.19	2.38 $\pm$ 1.35
PYR	0.24 $\pm$ 0.14	0.76 $\pm$ 0.48	1.73 $\pm$ 0.76	2.65 $\pm$ 2.16	1.35 $\pm$ 0.72
BaA	0.14 $\pm$ 0.11	0.38 $\pm$ 0.26	0.57 $\pm$ 0.43	0.51 $\pm$ 0.30	0.40 $\pm$ 0.17
CHR	0.40 $\pm$ 0.18	0.88 $\pm$ 0.44	1.49 $\pm$ 0.89	1.28 $\pm$ 0.59	1.02 $\pm$ 0.33
BbF	0.37 $\pm$ 0.17	1.17 $\pm$ 0.59	1.97 $\pm$ 1.35	1.37 $\pm$ 0.61	1.22 $\pm$ 0.42
BkF	0.12 $\pm$ 0.05	0.40 $\pm$ 0.19	0.46 $\pm$ 0.30	0.31 $\pm$ 0.16	0.32 $\pm$ 0.10
BaP	0.13 $\pm$ 0.08	0.27 $\pm$ 0.16	0.68 $\pm$ 0.67	0.38 $\pm$ 0.22	0.37 $\pm$ 0.20
DahA	0.06 $\pm$ 0.06	0.10 $\pm$ 0.05	0.10 $\pm$ 0.09	0.08 $\pm$ 0.04	0.08 $\pm$ 0.04
IcdP	0.10 $\pm$ 0.08	0.69 $\pm$ 0.35	0.79 $\pm$ 0.65	0.43 $\pm$ 0.31	0.50 $\pm$ 0.21
BghiP	0.10 $\pm$ 0.05	0.42 $\pm$ 0.22	0.51 $\pm$ 0.39	0.27 $\pm$ 0.17	0.32 $\pm$ 0.13
PAH ₁₅	2.73 $\pm$ 1.37	8.00 $\pm$ 4.35	13.74 $\pm$ 6.75	22.63 $\pm$ 13.66	11.81 $\pm$ 4.61

Table 2

15 PAHs compounds deposition fluxes ($\mu\text{g}/\text{m}^2/\text{day}$) and dustfall flux ($\text{g}/\text{m}^2/\text{day}$) for spring, summer, fall and winter, respectively.

	Spring ($n = 37$)	Summer ($n = 39$)	Fall ($n = 38$)	Winter ($n = 39$)	Annually Average ($n = 40$)
ACE	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.02	0.01 ± 0.01
ACY	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.06 ± 0.12	0.02 ± 0.03
FLO	0.04 ± 0.03	0.04 ± 0.04	0.05 ± 0.04	0.32 ± 0.46	0.11 ± 0.13
PHE	0.35 ± 0.29	0.28 ± 0.28	0.53 ± 0.47	6.19 ± 6.61	1.84 ± 1.83
ANT	0.03 ± 0.02	0.04 ± 0.04	0.05 ± 0.04	0.34 ± 0.30	0.11 ± 0.09
FLA	0.26 ± 0.22	0.32 ± 0.33	0.68 ± 0.50	3.04 ± 3.26	1.08 ± 0.99
PYR	0.15 ± 0.11	0.18 ± 0.17	0.41 ± 0.30	1.68 ± 1.70	0.61 ± 0.53
BaA	0.09 ± 0.08	0.09 ± 0.09	0.12 ± 0.09	0.30 ± 0.22	0.15 ± 0.09
CHR	0.25 ± 0.15	0.20 ± 0.19	0.31 ± 0.19	0.71 ± 0.38	0.37 ± 0.19
BbF	0.22 ± 0.13	0.25 ± 0.20	0.39 ± 0.22	0.79 ± 0.49	0.41 ± 0.21
BkF	0.07 ± 0.04	0.09 ± 0.07	0.09 ± 0.05	0.17 ± 0.09	0.11 ± 0.05
BaP	0.08 ± 0.06	0.06 ± 0.06	0.13 ± 0.09	0.22 ± 0.18	0.12 ± 0.07
DahA	0.04 ± 0.05	0.02 ± 0.02	0.02 ± 0.02	0.04 ± 0.03	0.03 ± 0.02
IcdP	0.06 ± 0.05	0.15 ± 0.11	0.16 ± 0.10	0.23 ± 0.17	0.15 ± 0.07
BghiP	0.06 ± 0.04	0.09 ± 0.07	0.10 ± 0.06	0.16 ± 0.13	0.10 ± 0.06
PAH ₁₅	1.71 ± 1.09	1.82 ± 1.64	3.05 ± 1.88	14.25 ± 12.33	5.22 ± 3.89
Flux of dustfall	0.63 ± 0.24	0.21 ± 0.13	0.24 ± 0.14	0.62 ± 0.29	0.42 ± 0.29