

TEMPORAL AND SPATIAL VARIETY OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) ATMOSPHERIC DEPOSITION IN CHENGDU ECONOMIC REGION, CHINA

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous; some of them have been paid more attention due to their carcinogenic and mutagenic properties. Atmospheric deposition is an important process for air-surface exchange of polycyclic aromatic hydrocarbons (PAHs). A year-round bulk (wet plus dry) deposition sampling campaign in mountain, plain, and basin sites was conducted in Chengdu Economic Region (CER), Sichuan Province, which is one of the largest agricultural provinces in China, and the total PAH emission ranked the first in China in 2003 with average emission of 5.35 kg km⁻². The spatial and temporal variations of particle deposition fluxes and the potential influences of climate and landform on the fate of PAHs were discussed. The atmospheric deposition of total PAHs deposition fluxes ranged from 176.8 g m⁻² yr⁻¹ to 1138.8 g m⁻² yr⁻¹, with highest flux (1138.8 g m⁻² yr⁻¹) at low mountain region with altitude less than 400 meters (Site S4), which maybe give an evidence of micro-cold-trapping effect in mountains. The deposition fluxes in cold seasons (spring and winter) were higher than in warm seasons (summer and autumn). The flux ratio of heavy molecular weight PAHs (HMW-PAHs, 5+6 rings PAHs) in autumn was more than in other seasons. The flux ratio of 4 rings PAHs increased in winter and spring.

Contaminant source seasonality and temperature were controlling factors for PAHs seasonal flux characteristics after the discussion on seasonal variations of PAHs and controlling factors.

Keywords: Polycyclic aromatic hydrocarbons, Atmospheric deposition, Chengdu Economic Region, Temporal and spatial variety

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous; some of them have been paid more attention due to their carcinogenic and mutagenic properties. They have been reported to contaminate the environment due to anthropogenic emissions or natural processes. PAHs can be transported from source regions to the Arctic (Wang *et al.* 2010), the Antarctic (Kukucka *et al.* 2010) and high mountains, such as Tibet Plateau (Wang *et al.* 2008). The atmosphere is a major pathway for the transport of PAHs on regional and global scales (Li *et al.* 2010). Deposition events are the most important processes that remove these chemicals from the atmosphere and become major PAHs contributors in remote pristine area (Ollivon *et al.* 2002, Terzi and Samara 2005).

China had the greatest PAH emission in the world. The total PAH emission was estimated at about 25,300 tons in 2003 (Theodore *et al.* 2008). The total PAH emission in Sichuan Province ranked the first in China in 2003 with average emission of 5.35 kg km⁻² (Zhang *et al.* 2007). Chengdu Economic Region (CER) located at the centre of Sichuan Province, which is an inescapable route for persistent organic compounds' transport from the eastern source region to high mountainous region near Tibet Plateau (Xing *et al.* 2010). Thus, influence of atmospheric

deposition in the area cannot be ignored. However, there were relatively few studies to describe the atmospheric deposition characteristics of PAHs in this area.

In this study, a year-round bulk deposition sampling campaign in mountain, plain, and basin sites was conducted in CER, from June 2007 to June 2008 seasonally. The spatial and temporal variations of particle deposition fluxes and the potential influences of climate and landform on the fate of PAHs were discussed.

2. Materials and methods

2.1. Sampling

A typical basin-mountain transect (BMT) was chosen in CER, including low hills in the east, plain in the intergrades and high mountains in the west, which is the eastern slope of Tibet Plateau (Fig. 1).

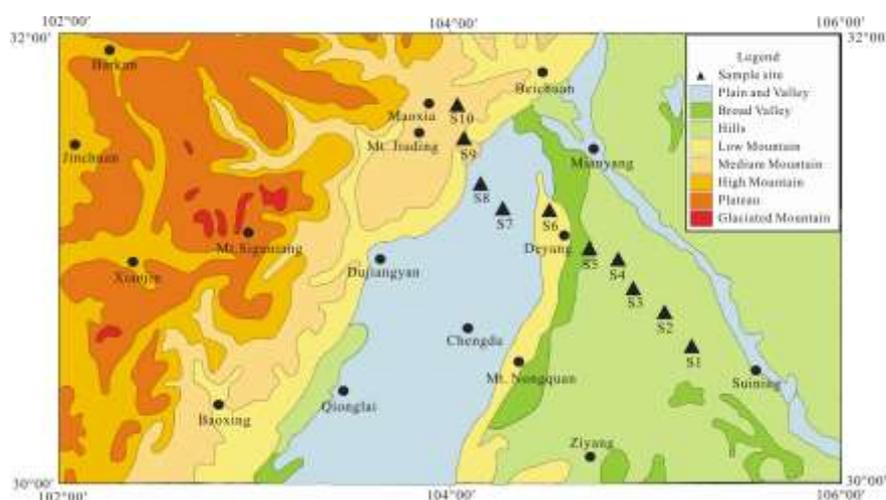


Figure 1: Sampling location for PAHs atmospheric deposition in the Chengdu Economic Region (CER), China

The atmospheric deposition samples were collected seasonally at ten locations along BMT from June 16, 2007 to June 27, 2008. Bulk atmospheric depositions collection was achieved using a holder as described by Ollivon (Ollivon *et al.* 2002). Totally, thirty-eight bulk deposition samples were collected. After collection, the samples were transported to laboratory as soon as possible and stored at 4 °C before analysis.

2.2. Sample extraction and analysis

The atmospheric deposition samples were thawed and homogenized by shaking. Then the mixture was separated into the dissolved and particle depositions by ultrasonic percolator and passed through a 0.45 μm glass fiber filter membrane. For particle deposition samples, the same extraction procedure was used as soil extraction described in our previous work (Theodore *et al.* 2008, Wang *et al.* 2009) and water samples were extracted using liquid–liquid extraction (LLE) method described by Arias (2009) and Lohmann (2009) (Arias *et al.* 2009, Lohmann *et al.* 2009).

PAHs were analyzed using Agilent 6890N/5975MSD GC-MS, DB-5 capillary column coupled with a HP-5972 mass selective detector operated in the electron impact mode (70 eV). The procedure is same as used in previous published paper (Theodore *et al.* 2008, Wang *et al.* 2009). The quantification of 15 PAHs (acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b] fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (Ind), dibenz[a,h]anthracene (DbahA), and benzo[g,h,i]perylene (BghiP)) is accomplished by comparison with reference compounds from a standard calibration solution.

2.3. Quality control and quality assurance

Laboratory and field blanks were extracted and analyzed in the same way as the samples. There was no significant difference (t test significance <95%) between in the laboratory and field blanks for analytes' concentrations. The average recoveries of surrogates naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂ were 48-55%, 70-74%, 72-88%, 67-83% and 84-91%, respectively. The values of PAHs were corrected by surrogate recoveries.

3. Results and discussion

3.1. Spatial distribution characteristic of deposition fluxes

The results showed that the atmospheric deposition of total PAH deposition fluxes ranged from 176.8 $\mu\text{g m}^{-2} \text{yr}^{-1}$ to 1138.8 $\mu\text{g m}^{-2} \text{yr}^{-1}$ with a geometric mean of 409.7 $\mu\text{g m}^{-2} \text{yr}^{-1}$. Due to the different physicochemical properties and predominant source areas, varied spatial trends were observed (Fig. 2). Generally, the fluxes were showing a waving mode. Highest fluxes were observed in low mountain region with altitude less than 400 meters (Site S4), following by high fluxes at Site S7. At Site S4, the altitude was higher than the nearby sites (S3 and S5); probably a micro-cold-trapping effect associated with local source of PAHs caused the higher deposition.

Seasonally, the deposition fluxes in cold seasons including spring and winter were higher than in warm seasons which are summer and autumn. The flux ratio of heavy molecular weight PAHs (HMW-PAHs, 5+6 rings PAHs) in autumn was more than in other seasons. The flux ratio of 4 rings PAHs increased in winter and spring. Seasonality of contaminant sources, temperature and precipitation are responsible for seasonal variation of atmospheric PAHs deposition fluxes.

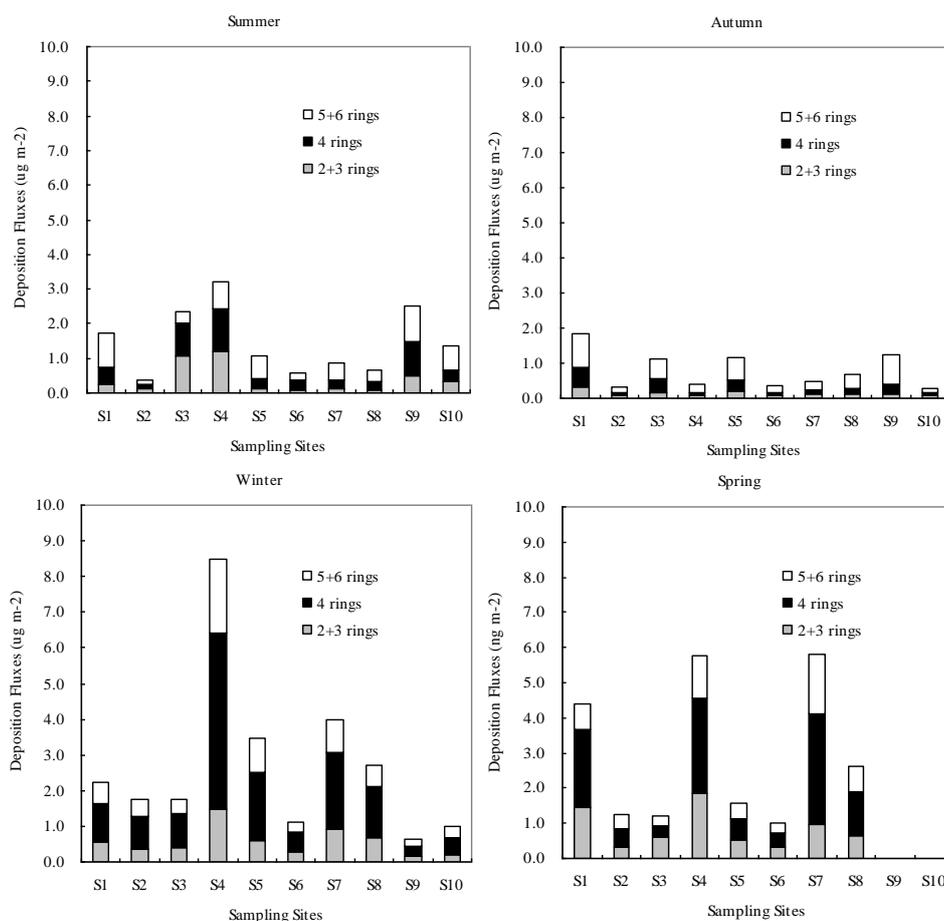


Figure 2: Comparison of PAHs deposition fluxes in different seasons at all sampling sites

In Sichuan Province, a lot of straw was burned off in open air to be wiped off during seeding season, like spring, which increased the concentration of PAHs, especially LMW-PAHs in the air, resulted in more deposition fluxes in spring sampling. Another reason for the seasonality of contaminant source was long range atmospheric transport from different wind directions. From the backward trajectories of air flow (Fig. 3) in this region, there was a new source during autumn from the east of China (the red line), which is more developed than Sichuan Province. Probably higher ratio of heavy molecular weight PAHs (HMW-PAHs, 5+6 rings PAHs) was in the air flow from the east province of China.

Temperature is generally thought to be a crucial factor in controlling behaviours of POPs, such as the partition between gas/particles. Increasing warming heating was used in winter. Impact of the ambient temperature on the deposition fluxes was shown by higher concentrations in winter and lower values in summer. In addition, there was significant increase in the contribution of the LMW-PAHs to total PAHs in the cold seasons.

The intensity and rate of precipitation could affect the atmospheric washout ratio of pollutants, which can influence the deposition fluxes of POPs (Li *et al.* 2010). The frequent rainfalls facilitate the transport of contaminants from air to ground (Lei and Wania 2004). In the study, the average rainfall of summer, autumn, winter and spring were 542 mm, 164 mm, 54 mm, and 215 mm, respectively. However, the deposition fluxes in summer were generally less than in spring and winter indicated high concentration of PAHs in air during spring and winter.

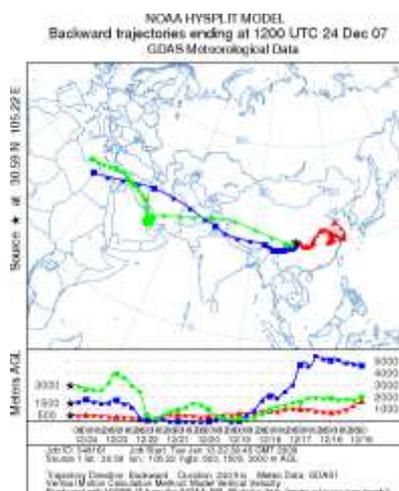


Figure 3: Backward trajectories of air flow in autumn

4. Conclusions

Atmospheric depositions of PAHs were collected at a basin-mountain transect in Chengdu Economic Region over a whole year. The atmospheric deposition of total PAH deposition fluxes ranged from $176.8 \mu\text{g m}^{-2} \text{yr}^{-1}$ to $1138.8 \mu\text{g m}^{-2} \text{yr}^{-1}$ with a geometric mean of $409.7 \mu\text{g m}^{-2} \text{yr}^{-1}$. Spatially, highest fluxes were observed in low mountain region with altitude less than 400 meters, which maybe give an evidence of micro-cold-trapping effect in mountains. High value at Site S7 could be attributed to the high consumption of diesel and coal in Jiangyang District. The seasonal variations of deposition fluxes showed higher fluxes in cold seasons (winter and spring), and lower ones in the warm seasons (summer and autumn). The flux ratio of 4 rings PAHs increased in winter and spring. Pollutant source seasonality and temperature were controlling factors for PAHs seasonal flux characteristic.

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