Atmospheric Polycyclic Aromatic Hydrocarbons (PAHs) in the Capital City of Seoul, South Korea: Spatial Distribution, Seasonal Variation, and Source Identification

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Introduction

Polycyclic aromatic hydrocarbons (PAHs), mostly emitted from incomplete combustion of fossil fuels, are known as hazardous air pollutants (HAPs) and persistent organic pollutants (POPs) due to their toxicity, persistency, long-range transport potential [1]. PAHs were listed in the 1998 Protocol on POPs under the Convention on Long-range Transboundary Air Pollution (LRTAP), adopted by the United Nations Economic Commission for Europe (UNECE). Moreover, the United States Environmental Protection Agency (US EPA) has listed 16 priority PAHs, including benzo[a]pyrene (BaP), which is classified as Group 1 by the International Agency for Research on Cancer (IARC). Large emissions of PAHs from human activities (e.g., vehicle emissions and domestic burning) are expected in Seoul, the capital city of South Korea with a population of 10.2 million and registered vehicles of 3.1 million. In previous studies, limited numbers of active air samplers were used for monitoring of PAHs [2], and thus high-resolution data on the spatial distribution of PAHs in Seoul have not been reported yet.

Recently, polyurethane foam-passive air samplers (PUF-PASs) have been widely used to identify the spatial distributions and temporal variations of semi-volatile organic compounds [3]. The PUF-PAS allows high-resolution data for PAHs than active air samplers due to their low cost and easy operation without electricity. Therefore, we deployed PUF-PASs in Seoul (1) to identify the levels and patterns of PAHs, (2) to investigate the spatial distributions and temporal variations of PAHs, and (3) to identify the major sources of PAHs.

Materials and Methods

Sampling and Analysis

Duplicated PUF-PASs were deployed at 36 sites in Seoul (Fig. 1), South Korea during the summer 2016 (August 09–September 06: 28 days) and winter 2017 (January 05–February 07: 33 days); the number of total samples is 144. The sampling sites are divided into 4 road (R1–R4), 6 background (B1–B6), and 26 urban (U1–U26) sites from criteria air pollutant, hazardous air pollutant, and background monitoring networks in Seoul. The retrieved PUF disks were stored in polyethylene zipper bags at -4 °C.

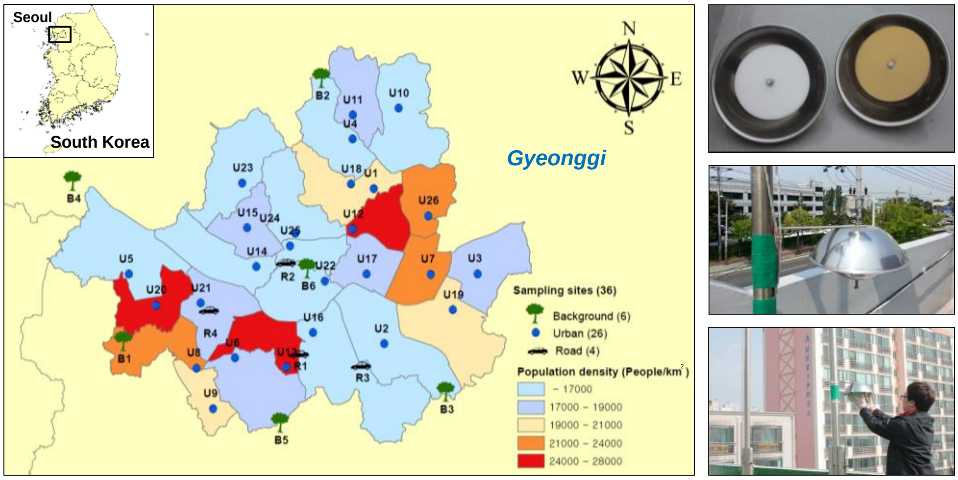

Figure 1. Location of 36 passive air sampling sites in Seoul. Photos of samplers are also shown.

PUF disks were extracted by Soxhlet extractors for 20 hours with 350 mL of hexane/acetone (9:1), then concentrated by using a Turbo-Vap (TurboVap® II, Uppsala, Sweden). Prior to the extraction, surrogate standards (Naphthalene-d_8, Acenaphthene-d_{10}, Phenantrene-d_{10}, Chrysene-d_{12}, and Perylene-d_{12}) were spiked into all the samples. The extracts were cleaned up on silica gel columns and evaporated again to 0.5 mL by a nitrogen evaporator. Lastly, it was transferred to a GC vial, and an internal standard (*p*-Terphenyl-d_{14}) was injected to the sample prior to instrumental analysis. The 16 US EPA priority PAHs were analyzed using a gas chromatograph/mass spectrometer (GC/MS, Agilent 7890N/5975C, SC, USA) with a DB-5MS column (30 m × 0.25 mm i.d., 0.25 µm film thickness).

Calculation of PAH Concentrations

The PUF-PAS can provide information on the amount of PAHs (ng/PAS) mostly in the gaseous phase, and the calculation of air concentration (ng/m^3) using the sampling rate (m^3/day) is required. In this study, an average sampling rate of 3.5 m^3/day from previous studies was used, and effective sampling volumes (m^3) of individual PAHs were calculated based on their physico-chemical properties. The concentrations of naphthalene, acenaphthylene, and acenaphthene were not considered due to low recoveries and potential sampling and analytical artifacts.

Diagnostic Ratios

Two diagnostic ratios were calculated to identify emission sources of PAHs: (1) the Flt/(Flt+Pyr) ratio evaluating petroleum combustion (<0.5) and coal/biomass burning (>0.5), and (2) the BaA/(BaA+Chr) ratio for vehicular emissions (>0.35), coal combustion (0.2–0.35), and petrogenic sources (<0.2).

Results and Discussion

Levels and Patterns of PAHs

Among the 13 PAHs, phenanthrene was the most dominant compound (Fig. 2), contributing 37–55% and 43–53% of the total concentrations in summer and winter, respectively. Fractions of low molecular weight (LMW) PAHs were dominant at all the sampling sites in two seasons (about 98%) in comparison with high molecular weight (HMW) PAHs (HMW). It demonstrates that PUF-PASs exclusively collected gaseous PAHs.

The concentrations of Σ_{13} PAHs were in a range of 2.2–41.6 ng/m^3 in summer and 11.4–59.4 ng/m^3 in winter. The results of statistical analysis (rank sum test) between summer and winter showed a statistical difference ($p<0.05$). Although there are no industrial complexes in Seoul, domestic burning and vehicular emissions could have contributed to the highest levels observed in winter. In addition, long-range transport of PAHs emitted from China and North Korea might play an important role in these elevated levels via prevailing northwestern winds.

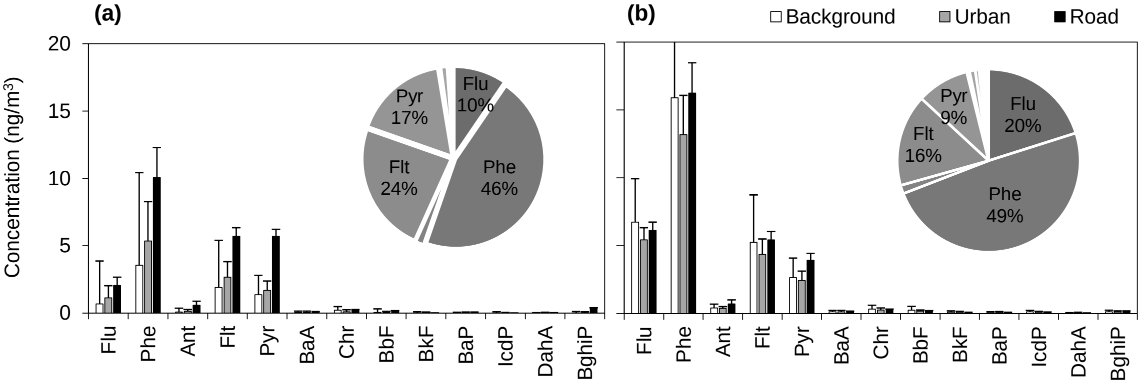

Figure 2. Concentrations of individual PAHs in (a) summer and (b) winter according to land use, and average fractions of major 4 PAHs.

Spatial Distribution of PAHs

Seasonal contour plots clearly depict the spatial distribution of Σ_{13} PAHs (Fig. 3). In summer, the concentrations at all the road sites were higher than those at the urban and background sites (Road > urban > background), indicating that vehicular exhaust is one of the major sources of PAHs in urban areas. Unlike other urban sites, one urban site (U8) showed a similar level of PAHs with those at the road sites probably due to the emission from a national industrial complex, which is located 1.5 km southwest from U8.

On the other hand, the spatial distribution of Σ_{13} PAHs in winter was different from that in summer. For example, there were no statistical differences among the road, urban, and background sites. Even though the concentrations at roadside sites (R2 and R3) were relatively high, those at urban and background sites (U3, U3, U7, B4, and B5) were much higher than those at other sites. As these sites are located in outskirt districts of Seoul, they could be more influenced by domestic burning in their districts or outside of Seoul. Note that the spatial distributions of Σ_{13} PAHs in downtown Seoul were similar in both seasons.

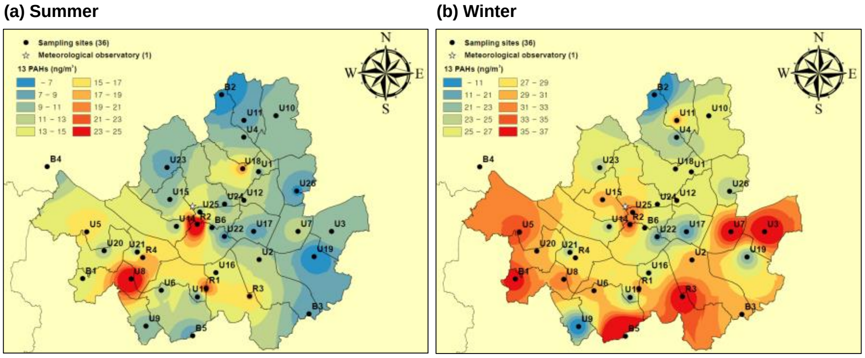

Figure 3. Spatial distribution of total PAH concentrations in (a) summer and (b) winter. ArcGIS 10.4 was used for this contour map.

Source Identification

Two diagnostic ratios were plotted in Fig. 4. According to the Flt/(Flt+Pyr) ratio, coal and biomass burning were dominant in both seasons. However, coal and biomass are not major fuels in Seoul, thus this diagnostic ratio is not proper for this dataset. Meanwhile, three road samples clearly indicated vehicular emissions. The BaA/(BaA+Chr) ratio suggested that a major source of PAHs is fossil fuel (coal and oils) combustion. The winter samples were more clustered, implying that the influence of domestic sources of PAHs is stronger in winter. Furthermore, long-range transport of PAHs emitted from wood and coal combustions in China and North Korea in winter might enhance the strength of source effects. On the other hand, in summer, as the domestic combustion and long-range transport decreased, the influence of other sources increased.

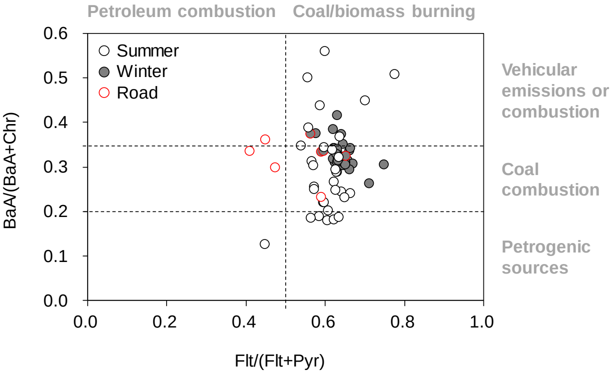

Figure 4. Scatter plot of Flt/(Flt+Pyr) and BaA/(BaA+Chr)

Acknowledgements

This work was funded by the Korea Ministry of Environment (MOE) as "Advanced Technology Program for Environmental Industry" (2016000160002).

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