SPATIAL DISTRIBUTION AND SEASONAL VARIATION OF ATMOSPHERIC POLYCYCLIC AROMATIC HYDROCARBONS IN THE MULTI INDUSTRIAL CITY OF ULSAN, SOUTH KOREA

Kwon HO, Park EJ, Jeong KS, Oh JY, Choi SD*

School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology (UNIST), UNIST-gil 50, Ulsan, 689-798, Republic of Korea

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are composed of two or more fused aromatic rings, and 16 PAHs were listed as priority pollutants by the US environmental protection agency (EPA). PAHs are an important environmental concern because some of them are carcinogens, and human can be directly exposed to atmospheric PAHs via inhalation. PAHs are emitted to the atmosphere mainly from anthropogenic sources and dispersed into surrounding areas. Therefore, atmospheric monitoring is a necessary step to know the human health risk of PAHs. Recently, polyurethane foam based passive air samplers (PUF-PAS) developed by the Environmental Canada have been widely used to investigate the source-receptor relationship of semi-volatile organic compounds. As PUF-PAS can be deployed at many sites, relatively high spatial resolution data can be acquired. In addition, seasonal variations of PAHs can be monitored because the optimum deployment time of PUF-PAS is about three months. Even though many previous PAS studies reported the seasonal variation and spatial distribution of PAHs, a relatively small number of studies focused on large-scale industrial cities.

The metropolitan city of Ulsan is a famous industrial city with petrochemical, automobile, non-ferrous, and ship building/heavy industries. According to the spatial distribution of PAHs reported in our previous study using PUF-PAS, major sources of PAHs in Ulsan were identified as industrial complexes[1]. However, the seasonal variation of PAHs was not investigated in the former study because the sampling was carried out only in the winter 2010. In this study, therefore, we seasonally collected passive air samples for one year and investigated the seasonal variation and spatial distribution of PAHs in Ulsan. To the best of our knowledge, this study is the first comprehensive monitoring study for the seasonal distribution of atmospheric PAHs with high spatial resolution data in Ulsan.

Materials and methods

Passive air sampling

We deployed 40 PUF-PAS in duplicate at 20 sites in Ulsan, Korea (Figure 1). The sampling sites can be classified into three groups: urban (U1−U10), rural (R1−R6), and industrial (I1−I4) sites. Among 20 sites, 14 sites were included in the local air monitoring network operated by the Ulsan Institute of Health and Environment (UIHE). On top of this network, we selected 7 new sampling sites to obtain more enhanced spatial resolution data; the 14 sites of UIHE network were mostly located in urban and industrial areas. We retrieved PUF disks in the spring (February 05−June 10, 2011), summer (June 10−August 25, 2011), fall (august 25−November 18, 2011), and winter (November 18, 2011−Febuary 23, 2012), respectively. Prior to the deployment of PUF-PAS, PUF disks were cleaned with acetone for 30 min and n-haxane for 30 min in a sonicator. The collected samples were stored in aluminium foil in polyethylene bags at -4℃ until instrumental analysis.

Meteorological condition

Meteorological data were obtained from the website of the Korea meteorological administration (KMA)[2]. The location of the Ulsan meteorological observatory is shown in Figure 1. The average meteorological conditions during the sampling periods were as follows: ambient air temperature = 13, 25, 18, and 3℃ (mean 14℃), wind speed = 2.5, 2.4, 2.0, and 2.5 m/s (mean 2.4 m/s), and total precipitation = 262, 648, 239, and 146 mm (mean 324 mm). Windrose diagrams for each season are depicted in Figure 2.

Instrumental analysis and QA/QC

The target compounds in this study were the 16 US-EPA priority PAHs: Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flt), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[k]fluoranthene (BkF), Benzo[b]fluoranthene (BbF), Benzo[a]pyrene (BaP), Indeno[123-cd]pyren (Ind), Dibenzo[ah]anthracene (DahA), and Bezo[ghi]perylene (BghiP).

The retrieved PUF disks were individually Soxhlet extracted for 20 h, and extracts were concentrated by a Turbo Vap. As surrogate standards, deuterated compounds (Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, and Perylene-d_{12}) were spiked into the PUF disks prior to extraction. The extract was cleaned up on a silica gel column. As an internal standard, *p*-terphenyl-d_{14} was added to the sample prior to GC injection. PAHs were analyzed by a gas chromatograph-mass spectrometer (GC/MS).

For quality assurance and quality control (QA/QC), every extraction batch of samples included a method blank to check contamination during experiment, and all data were corrected for average blank values. Method detection limits (MDL) were calculated by the multiplication of the standard deviations of seven replicates of the MDL standard and the Student's t value (3.14) for a 99% confidence level. The amount (ng) of each PAH collected in a PUF disk was converted to air concentration (ng/m^3) using an effective sampling rate (m^3/day)[1].

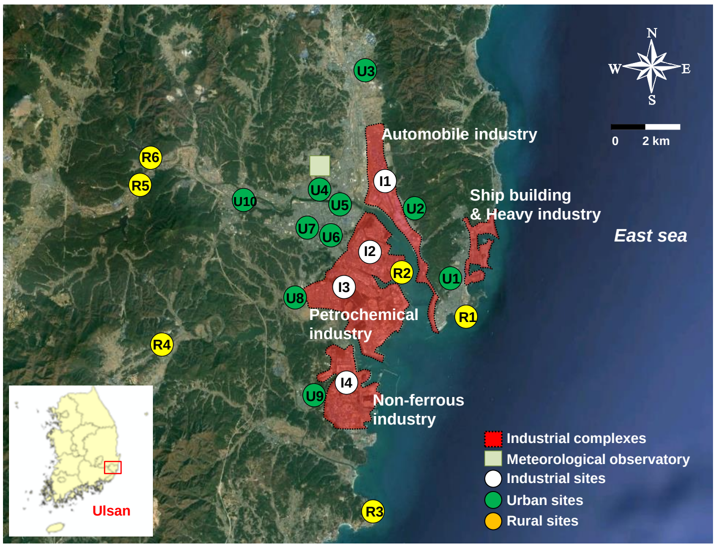

Figure 1. Location of passive air sampling sites and the meteorological observatory in Ulsan, South Korea.

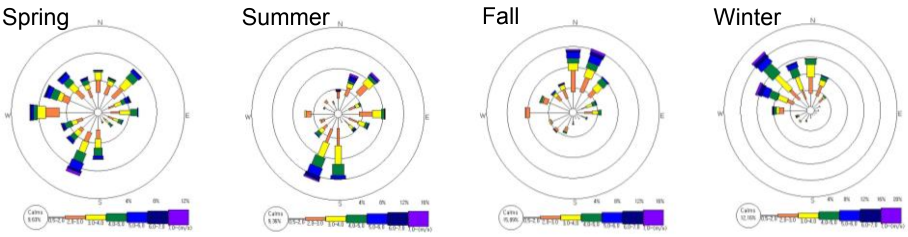

Figure 2. Seasonal wind patterns in Ulsan: spring (February 05−June 10, 2011), summer (June 10−August 25, 2011), fall (august 25−November 18, 2011), and winter (November 18, 2011−Febuary 23, 2012).

Results and discussion

Levels and profiles of PAHs

The mean and median concentrations of total 13 PAHs ($\sum_{13}$PAHs except Nap, Acy, and Ace) measured at the 20 sampling sites were listed in Table 1. The average concentration of $\sum_{13}$PAHs during four seasons was 20 ng/m^3 (median 16 ng/m^3), and those in spring, summer, fall, and winter were 14 (12) ng/m^3, 20 (14) ng/m^3, 18 (16) ng/m^3, and 28 (25) ng/m^3, respectively. The highest concentration of $\sum_{13}$PAHs was observed in winter due to residential heating.

Regarding each compound, the average concentrations of low molecular weight (LMW) PAHs (3−4 rings: Flu−Chr) were 19 times higher than those of high molecular weight (HMW) PAHs (5−6 rings: BbF−BghiP). Among the 13 PAHs, Phe was the most dominant compound contributing 41% of $\sum_{13}$PAHs. Flt, Pyr, and Flu were next major compounds, and most HMW PAHs were detected below 1 ng/m^3 (Figure 3). The composition of PAHs in this study area was similar to those in previous studies, and the dominance of LMW PAHs indicates that PUF-PAS can exclusively collected volatile PAHs in the gaseous phase.[1]

Table 1. Mean and median concentrations of 13 PAHs at 20 sites during four seasons in Ulsan, South Korea. BDL represents 'below detection limit'.

	Spring		Summer		Fall		Winter		Average	
ng/m^3	Mean	Median	Mean	Median	Mean	Median	Mean	Median	Mean	Median
Flu	1.7	1.6	1.85	1.76	3.1	2.9	4.6	4.3	2.8	2.4
Phe	5.2	4.7	7.26	5.71	7.5	6.5	13	12	8.3	6.8
Ant	0.92	0.48	0.62	0.57	0.44	0.40	0.42	0.38	0.60	0.48
Flt	2.6	2.1	4.81	2.02	3.0	2.5	4.9	4.3	3.8	3.0
Pyr	2.0	1.5	4.45	2.27	2.4	1.9	3.5	2.9	3.1	2.2
BaA	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Chr	0.25	0.22	0.35	0.21	0.14	0.11	0.27	0.24	0.25	0.19
BbF	0.31	0.27	0.36	0.35	0.35	0.31	0.43	0.38	0.36	0.34
BkF	0.29	0.28	0.29	0.30	0.19	0.18	0.18	0.17	0.24	0.24
BaP	0.21	0.19	0.25	0.23	0.13	0.14	0.19	0.13	0.20	0.19
Ind	0.20	0.18	0.15	0.16	0.19	0.20	0.20	0.13	0.18	0.17
DahA	0.19	0.18	0.34	0.35	0.20	0.17	0.09	0.02	0.20	0.18
BghiP	0.28	0.15	0.24	0.17	0.24	0.19	0.34	0.21	0.27	0.18
13 PAHs	14	12	20	14	18	16	28	25	20	16

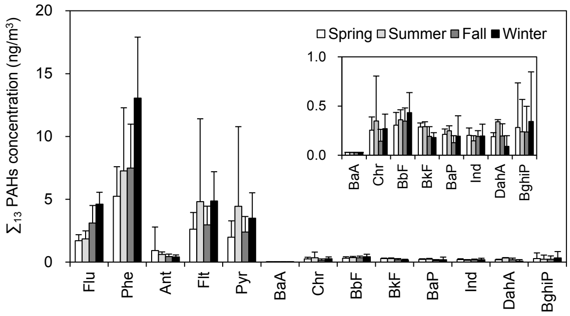

Figure 3. Seasonal profiles of average concentrations of 13 PAHs at 20 sites in Ulsan, South Korea.

Seasonal variation of PAH levels

Concentrations of $\sum_{13}$PAHs during four seasons are shown in Figure 4, which also presents a reverse seasonal trend between residential energy consumption[3] and air temperature. The highest concentrations were observed in winter because fossil fuels such as coal, oil, and natural gas for residential/commercial heating are mainly used in winter. The residential energy consumption in winter was four times larger than that in summer.

In addition, the level of $\sum_{13}$PAHs in summer could be significantly influenced by wet deposition during heavy-rainfall events. The rainfall of summer was four times higher than that of winter. Thus, the main factor for the seasonal variation of atmospheric PAHs might be the variations of fossil fuel consumption and meteorological conditions. However, the level of $\sum_{13}$PAHs in summer was not lower than those in spring and fall, despite the lowest fuel consumption and the highest precipitation. This unexpected observation was due to seasonal wind patterns and the location of industrial complexes emitting large amounts of air pollutants throughout the year. As the industrial complexes are located along the east coast, large amounts of PAHs might be transported from the industrial complexes to surrounding areas in summer (See Figure 2).

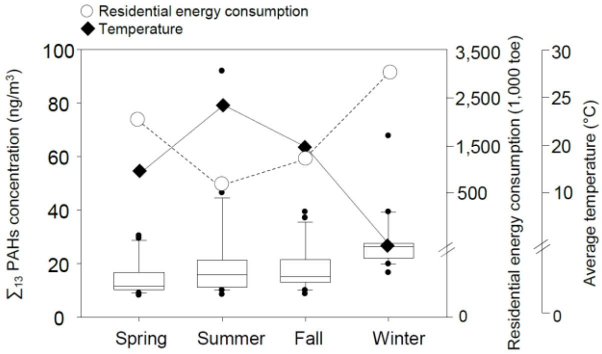

Figure 4. Box plot of concentrations of $\sum_{13}$PAHs in four seasons at 20 sites in Ulsan. The residential energy consumption and ambient air temperature data are also shown.

Spatial distribution of PAHs

The spatial distribution of $\sum_{13}$PAHs was plotted on the population density map of Ulsan (Figure 5). A mean population density of Ulsan in 2010 was 8,000 people/km^2, and the bars indicated the average concentration of $\sum_{13}$PAHs at each site. There was a gradient of average levels of $\sum_{13}$PAHs in four seasons: industrial (30 ng/m^3) > rural (21 ng/m^3) > urban (16 ng/m^3) sites. Each season also showed the same gradient of $\sum_{13}$PAHs (industrial > rural > urban). However, the levels of $\sum_{13}$PAHs at the rural and urban sites were not statistically different (rank sum test: p value > 0.05) because of major wind directions and the source-receptor relationship. These results indicate that the industrial area was more polluted by PAHs than other areas, and the rural area was moderately polluted like the urban area.

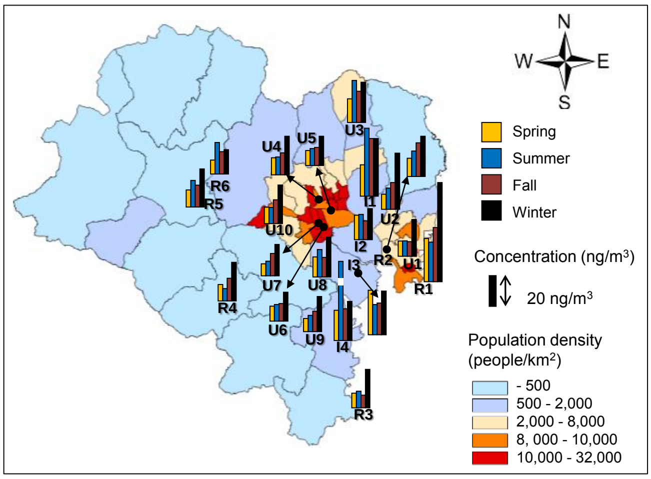

Figure 5. Spatial distribution of $\sum_{13}$PAHs on the population density map of Ulsan, South Korea.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2010-0003424).

References

1. Choi SD, Kwon HO, Lee YS, Park EJ, Oh JY. (2012); *J Hazard Mater*.241–242: 252–258.
2. Korea Meteorological Administration (KMA) (http://www.kma.go.kr/)
3. Korea Statistical Information Service (KSIS) (http://kosis.kr/)