

## Atmospheric Concentrations of PAHs in the Vapor and Particulate Phases in Chongju

Seung Shik Park\*, Young J. Kim<sup>1)</sup>, Chang H. Kang<sup>2)</sup>,  
Sung Yong Cho, Tae Young Kim and Seung Jai Kim

*Department of Environmental Engineering, Chonnam National University,  
Gwangju 500-757, Korea*

<sup>1)</sup>*Advanced Environmental Monitoring Research Center (ADEMRC), Gwangju Institute  
of Science and Technology, 1 Oryong-dong, Buk-ku, Gwangju 500-712, Korea*

<sup>2)</sup>*Department of Chemistry, Cheju National University, Aradong-1,  
Cheju 690-756, Korea*

(Received 7 April 2006, accepted 20 October 2006)

### Abstract

Four intensive seasonal sampling campaigns between October 1998 and October 1999 were undertaken at an urban site of Chongju, in which polyurethane foam (PUF) sampler was used to collect particulate- and vapor-phase polycyclic aromatic hydrocarbons (PAHs). The contribution to total (particulate+vapor) PAH concentration by the vapor phase component exceeded the particulate phase contribution by factor of ~2.6. Summed concentrations of phenanthrene (30.9%), pyrene (16.6%), naphthalene (11.3%) and fluoranthene (11.0%) account for significant amounts of the vapor-phase, while chrysene (12.5%), benzo[b]fluoranthene (11.6%), indeno[123-cd]pyrene (9.9%), benzo[ghi]perylene (9.5%), benzo[k]fluoranthene (9.4%), pyrene (8.9%), and benzo[a]pyrene (8.3%) are found to be the most common PAH compounds in the particulate phase. The results from application of principal component analysis to particulate-phase PAH data demonstrate that a combination of PAH and PM<sub>2.5</sub> inorganic data is a more powerful tracer of emission sources than PAH species data alone. Particulate-phase PAH species were found to be associated predominantly with emissions from diesel engine vehicles and incineration.

**Key words** : PAH, Contribution, Principal component analysis (PCA), Seasonal variation

### 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants, and of major health concern due to their highly carcinogenic and mutagenic properties (IARC, 1984). PAHs

are mostly produced from incomplete combustion of fossil fuels and organic materials, and PAHs emissions are almost entirely of anthropogenic origin (Seinfeld and Pandis, 1998; Harrison *et al.*, 1996). They are found in the atmosphere both in the gas and particle phases, depending on the vapor pressure of the PAH. Low molecular weight PAHs are found predominantly in the gas phase, while the ones with high molecular weight (four- to six-ring

\* Corresponding author.

Tel : +82-62-530-1863, E-mail : park8162@chonnam.ac.kr

PAHs) are often associated with the particle phase. In urban environment the vehicular traffic is considered to be the most significant contributor of atmospheric PAHs. The abundance and type of PAHs in urban areas exhibit seasonal fluctuations with generally higher concentrations in the wintertime (Ravindra *et al.*, 2006; Park *et al.*, 2002; Panther *et al.*, 1999; Harrison *et al.*, 1996). In many of the previous studies on PAHs, only the particulate phase was collected using filters due to their higher carcinogenic potential and the ease of sampling (Sanderson and Farant, 2005; Fang *et al.*, 2004; Schauer *et al.*, 2003; Kim Oanh *et al.*, 2000). The lighter PAH compounds, which are prevalent in the vapor phase, have weaker carcinogenic/mutagenic properties, but they are most abundant in the urban atmosphere and react with other pollutants to form more toxic derivatives. Thus, in order to estimate total PAH levels simultaneous measurements of both the vapor and particulate phases PAHs must be made.

Interest in the individual PAH species of aerosol has grown in part because of their potential for use as tracers in source apportionment models. PAHs as well as other organic compounds could be used to assist in distinguishing emissions from particular pollutant sources (De Raat and Meijere, 1991). These compounds might be also used to best advantage in combination with trace element data. Harrison *et al.* (1996) conducted multivariate source apportionment for the atmospheric PAHs by using the combined data of inorganic and PAH pollutants. In order to identify emission sources, principal component analysis (PCA) has extensively been applied to PAH compositional data (Ravindra *et al.*, 2006; Fang *et al.*, 2004; Park *et al.*, 2002).

Air quality monitoring stations are in operation to monitor criteria air pollutants such as SO<sub>2</sub>, NO<sub>2</sub>, CO, O<sub>3</sub>, and PM<sub>10</sub>. However, much less attention has been paid on monitoring PAH that requires more elaborate sampling and analytical protocols. Air monitoring of PAH in urban areas is required in order to establish air quality standards by assessing public exposure to PAH and their associated health risks. Some studies have examined PAHs associated with TSP and PM<sub>10</sub> aerosols in urban and remote

areas of Korea (Lee *et al.*, 2006; Panther *et al.*, 1999; Kim *et al.*, 1996). However, further investigation of PAHs in vapor and particulate phases is required to determine potential human health risks. In the present study, measurements of the concentration of 16 EPA priority PAH species in particulate and vapor phase samples collected with PUF sampler at an urban site of Chongju are reported. Seasonal variation is characterized and compared with the results from other urban areas. A further purpose of this study was to examine the possible emission sources of particulate PAH compounds collected at the urban site by applying PCA. We performed the PCA with both PAH data alone and combined data of particulate PAH and PM<sub>2.5</sub> inorganic pollutants.

## 2. EXPERIMENTAL METHODS

### 2.1 Ambient air sampling

Daily PAHs samples were taken at an urban atmosphere of Chongju. Chongju is a mid-size city with 0.6 million people in 153.5 km<sup>2</sup>. The number of vehicles in Chongju was about 130,000 in 2000. It is estimated that major emission sources in Chongju are industry, domestic heating, and vehicles. The sampling was conducted on a roof (*ca.* 30 m height) of a high school building about 300 m away from a road with heavy traffic. The sampling periods included four intensive periods; 18 Oct. ~ 27 Oct. 1998, 12 Mar. ~ 21 Mar. 1999, 20 June ~ 27 June 1999, and 5 Oct. ~ 17 Oct. 1999, respectively. For each 24-hr sample, measurements began at approximately 07:00.

Total suspended particles (TSP) and vapor-phase PAH samples were obtained using a polyurethane foam (PUF) sampler (Graseby GPS1) containing quartz fiber filters (QFFs, Whatman, 102 mm diameter) and PUF, allowing a flow rate up to 280 L/min. These filter/sorbent systems are prone to sampling artifacts essentially due to "blow-off" of aerosol phase PAH to the PUF plug (Ligocki and Pankow, 1989). However, particulate phase PAH loss due to the blow-off artifact was not estimated in this work. The QFFs used for the TSP sampling were pre-

cleaned by baking at 550°C for 10 hr before use to minimize PAH blank in the QFFs. The QFFs were then extracted for 5 minutes in an ultrasonic bath with dichloromethane (DCM, HPLC grade) to minimize the contaminants. The pretreated QFFs were stored in solvent rinsed aluminum packages until used. The PUFs were pre-cleaned using supercritical fluid extraction method for 30 min with DCM, and dried under vacuum in a desiccator. They were then placed in a PUF cartridge and stored in freezer until use.

Additionally, a dichotomous PM<sub>10</sub> sampler (ASI/GMW series 241) and a PM<sub>2.5</sub> sampler equipped with a cyclone inlet (URG-2000-30EH, URG) were used to collect atmospheric aerosols. Filters used for the dichotomous PM<sub>10</sub> sampler were 37 mm Teflon disks (R2PJ037, Gelman Sciences) with a polyethylene support ring. The PM<sub>2.5</sub> samples taken from the sampler were used for the analysis of inorganic elemental components. The PM<sub>2.5</sub> sampler consisted of a cyclone inlet followed by a 47 mm Teflon (P5PJ047, Zefluor, Gelman Sciences) filter pack (URG-2000-30F, URG) and a vacuum pump. The PM<sub>2.5</sub> particles deposited on the filter were analyzed for eight ionic species. A single-channel Aethalometer (Magee Sci., AE-16U) equipped with a PM<sub>2.5</sub> inlet impactor was also operated with a 5-min time cycle to measure the aerosol black carbon (BC) concentrations at the same sampling site. Meteorological parameters such as wind speed, wind direction, and ambient temperature were measured continuously during the entire sampling periods at the measuring site. Sampling and analytical methods used in this study have been described in detail elsewhere (Park and Kim, 2005).

## 2.2 PAHs analysis

A QFF was transferred into a glass flask. The QFF was extracted with 30 mL of DCM for 30 min in an ultrasonic bath, and then mechanically shaken for 30 min. Then the QFFs were removed, and the extract was filtered through a membrane filter (Whatman PVDF syringe filter, 0.45 µm) and concentrated to 1 mL with an evaporator (Zymark, Turbovap 500). The extract was spiked with the internal standard

(d<sub>10</sub>-phenanthrene) prior to injection into gas chromatograph. Samples collected on the PUF foam were extracted with DCM for 30 min by the supercritical fluid extraction (SFE) apparatus (Autoclave Engineering, Model 08U-06-60-FS). The SFE typically uses supercritical CO<sub>2</sub> because of its low critical properties (T<sub>c</sub>=32°C, P<sub>c</sub>=72 atm), low toxicity and cost, and its ability to solvate a wide range of organics including high molecular weight and moderately polar organics. Before the extraction, 50 mL of organic modifier (CH<sub>2</sub>Cl<sub>2</sub>) was added to CO<sub>2</sub> to increase extraction efficiencies of some organic pollutants. The efficiency of SFE used in this study was about 83% under the conditions of 330 atm and 32°C. Extracts were concentrated using a Zymark evaporator to a volume of 1 mL. The internal standard d<sub>10</sub>-phenanthrene was added to the vials prior to injection into the gas chromatograph. The particulate and vapor-phase PAHs were quantified by GC-MS (HP 5890 Series II Plus/HP 5972 MSD) system. QFF and PUF field blanks were also analyzed with each set of field samples. The field blanks were prepared, stored, and handled by exactly the same procedures as used for the field samples. In this study, the 16 PAH species described in USEPA method 610 was determined; naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (B[b]F), benzo(k)fluoranthene (B[k]F), benzo(a)pyrene (BaP), indeno(1, 2, 3-cd)pyrene (IND), dibenzo(a, h)anthracene (DbahA), and benzo[ghi]perylene (BghiP). External PAH standards (16 PAH in a mixture) were used to quantify the individual analytes from the GC/MS analysis. Extraction recoveries were determined by spiking the standard solution onto the pre-extracted QFF and PUF samples. Extraction recovery for particulate-phase PAH was in the range 81 ~ 96% depending on PAH species with a mean value of 88%, while that for vapor-phase PAH was on average 83%, ranging from 69% (NAP) to 95% (PHEN). The accuracy of the analytical technique was tested through the use of a standard reference material (SRM 1649 urban dust sam-

**Table 1. Average PAH concentrations (ng/m<sup>3</sup>).**

(a) Average particulate+vapor PAHs

PAH	Particulate phase n=35	Vapor phase n=35	Total n=35	Seoul <sup>1</sup>	Kyungsan <sup>2</sup>	Birmingham <sup>3</sup>
NAP	0.11 (0.01~0.24)	3.70 (0.76~12.69)	3.81 (0.83~12.80)	11.23	382.00	7.54
ACY	0.07 (0.01~0.12)	3.29 (0.54~17.95)	3.36 (0.59~18.07)	7.39	57.56	9.06
ACE	0.14 (0.03~0.37)	1.30 (0.13~5.34)	1.43 (0.19~5.55)	3.35	—	8.87
FLU	0.16 (0.01~0.42)	2.91 (0.36~9.87)	3.07 (0.45~10.29)	6.46	21.35	10.35
PHEN	0.78 (0.06~4.28)	10.48 (1.26~35.05)	11.26 (1.83~35.88)	16.46	33.02	13.97
ANTH	0.09 (0.01~0.65)	1.28 (0.22~2.83)	1.37 (0.22~3.05)	2.70	3.25	2.55
FLT	1.03 (0.14~5.07)	3.57 (0.67~14.92)	4.60 (0.81~15.43)	8.10	6.26	7.26
PYR	1.13 (0.19~6.36)	5.93 (0.95~14.27)	7.06 (1.19~17.31)	12.56	4.85	20.67
BaA	0.91 (0.08~4.54)	0.64 (0.16~1.51)	1.55 (0.24~5.23)	2.62	2.12	2.97
CHR	1.69 (0.21~7.45)	0.83 (0.27~3.23)	2.52 (0.58~8.19)	3.62	4.58	3.55
B[b]F	1.71 (0.04~7.31)		1.71 (0.04~7.31)	2.69	1.36	1.27
B[k]F	1.20 (0.11~3.34)		1.20 (0.11~3.34)	2.21	0.51	0.68
BaP	1.12 (0.10~3.65)		1.12 (0.10~3.65)	2.55	0.82	0.53
IND	1.32 (0.13~4.29)		1.32 (0.13~4.29)	3.59	1.11	1.19
DBahA	0.21 (0.06~0.50)		0.21 (0.06~0.50)	0.55	0.24	0.45
BghiP	1.22 (0.15~4.14)		1.22 (0.15~4.14)	3.21	1.44	1.37
ΣPAHs	12.89 (2.38~52.50)	33.94 (5.47~82.44)	46.83 (8.05~134.46)	89.29	520.47	92.25

Note: <sup>1</sup>Park *et al.* (2002), <sup>2</sup>Baek and Choi (1998), <sup>3</sup>Smith and Harrison (1996)

(b) Particulate phase PAHs

PAH	Oct. 1998 n=5	Mar. 1999 n=10	June 1999 n=8	Oct. 1999 n=12	Average n=35	Seoul <sup>1</sup>	Kyungsan <sup>2</sup>	Bangkok <sup>3</sup>	Hong Kong <sup>4</sup>	B'ham <sup>5</sup>
NAP	0.14	0.13	0.15	0.05	0.11±0.06	0.14	<0.01	1.15	0.92	0.42
ACY	0.10	0.08	0.07	0.04	0.07±0.03	0.12	0.02	1.57	1.83	0.37
ACE	0.34	0.20	0.08	0.04	0.14±0.11	0.21	—	1.50	1.37	0.95
FLU	0.31	0.25	0.13	0.04	0.16±0.13	0.26	0.06	0.32	1.09	0.64
PHEN	0.84	1.42	0.52	0.39	0.78±0.91	1.46	1.44	0.51	0.17	0.67
ANTH	0.11	0.16	0.05	0.04	0.09±0.11	0.18	0.41	0.55	0.47	0.28
FLT	1.29	2.09	0.21	0.59	1.03±1.09	2.27	1.50	0.95	0.45	0.76
PYR	1.27	2.32	0.31	0.64	1.13±1.21	2.25	1.60	0.54	0.14	1.46
BaA	1.25	1.64	0.17	0.65	0.91±0.94	1.82	1.36	0.38	0.33	0.81
CHR	2.39	2.97	0.40	1.19	1.69±1.60	2.78	3.23	0.54	0.35	1.21
B[b]F	2.01	3.38	0.30	1.14	1.71±1.87	2.74	1.31	1.12	0.30	1.11
B[k]F	1.99	1.84	0.21	1.00	1.20±0.89	2.15	0.49	0.49	0.13	0.63
BaP	2.10	1.68	0.17	0.89	1.12±0.95	2.55	0.80	0.98	0.15	0.48
IND	1.96	2.25	0.25	0.99	1.32±1.15	3.59	1.11	1.06	0.24	1.19
DBahA	0.46	0.25	0.09	0.15	0.21±0.15	0.55	0.24	1.14	0.08	0.43
BghiP	1.93	1.90	0.27	0.98	1.22±1.01	3.21	1.44	1.43	0.24	1.34
ΣPAHs	18.50	22.59	3.36	8.83	12.89±11.21	26.3	15.0	14.1	8.3	12.7

Note: <sup>1</sup>Park *et al.* (2002); Seoul, Korea, <sup>2</sup>Baek and Choi (1998); Kyungsan, Korea, <sup>3</sup>Kim Oanh *et al.* (2000), <sup>4</sup>Panther *et al.* (1999), <sup>5</sup>Smith and Harrison (1996); Birmingham, UK.

ple) supplied by the NIST. The ratios of certificated values to measured values for PAH species are in the range 0.83~1.20. The results have previously been described in detail elsewhere (Park *et al.*, 2002).

### 3. RESULTS AND DISCUSSION

#### 3.1 PAHs concentrations

Atmospheric concentrations of PAHs are listed in

Table 1. Average total (vapor+particulate) PAH concentrations were 46.8 ng/m<sup>3</sup>, ranging from 8.1 to 134.5 ng/m<sup>3</sup>. The average total PAH concentration in the particulate fractions was measured to be 12.9 ng/m<sup>3</sup> (2.4~52.5 ng/m<sup>3</sup>), while it was 33.9 ng/m<sup>3</sup> (5.5~82.4 ng/m<sup>3</sup>) in the vapor fractions. Average particulate phase PAHs concentrations in Chongju were about half of the concentrations in Seoul where concentrations ranged from 1.7 to 138.4 ng/m<sup>3</sup>, averaging 26.3 ng/m<sup>3</sup> (Park *et al.*, 2002). Also comparison of particulate phase PAHs measured in other cities worldwide shows that the PAH levels in Chongju (Table 1(b)) are comparable to those measured at cities such as Kyungsan, Bangkok, Hong Kong, and Birmingham (Kim Oanh *et al.*, 2000; Panther *et al.*, 1999; Baek and Choi, 1998; Smith and Harrison, 1996). Vapor-phase PAH fractions (78~98%) of the total PAH amount were much higher than particulate-phase PAH fractions for PAHs with molecular weight lower than molecular weight of pyrene. The contribution to total PAH concentration by the vapor phase component exceeded the particulate phase contribution by factor of ~2.6. CHR (12.5%), B[b]F (11.6%), IND (9.9%), BghiP (9.5%), B[k]F (9.4%), PYR (8.9%), and BaP (8.3%) were found to be the most common PAH compounds with relatively high concentrations in the particulate phase, whereas PHEN (30.9%), PYR (16.6%), NAP (11.3%), and FLT (11.0%) account for the major part of the vapor-phase PAHs. The PHEN was found to be almost exclusively in the vapor phase.

### 3.2 Seasonal characteristics of PAHs

#### 3.2.1 Characteristics of vapor- and particulate phase PAHs

Figure 1 is box-and-whisker plot showing seasonal variation of total PAH concentration. As shown in the Figure 1, seasonal variation in total PAHs was evident, i.e., higher in cold season (March) and lower in warm season (June). Data relative to the warm and the cold seasons campaigns are compared (Table 2). The average ratio of cold to warm total PAH is 4.8, which is similar to the val-

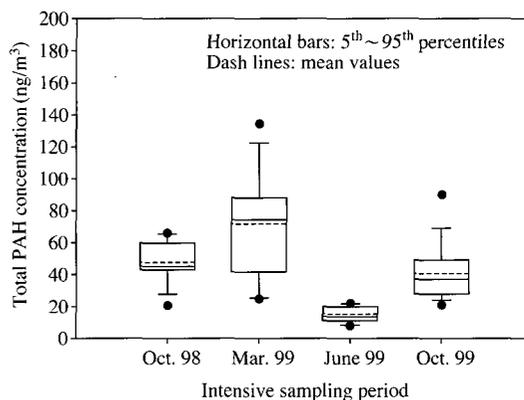


Fig. 1. Seasonal variation of total PAH (vapor+particulate phase) concentrations. Dashed lines are the means. The horizontal solid lines are the 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles; the dots are the 5<sup>th</sup> and 95<sup>th</sup> percentiles.

Table 2. Ratios of cold (March) to warm (June) seasons PAHs concentrations.

	Unit	June	March	Ratio
Ambient temp.	°C	18.3~24.9	0.2~13.5	
Total PAHs	ng/m <sup>3</sup>	14.9	71.1	4.8
Vapor PAHs	ng/m <sup>3</sup>	11.5	48.5	4.2
Particulate PAHs	ng/m <sup>3</sup>	3.4	22.6	6.7
Volatile PAHs <sup>a</sup>	ng/m <sup>3</sup>	1.0	2.2	2.2
Semivolatile PAHs <sup>a</sup>	ng/m <sup>3</sup>	1.1	9.0	8.4
Nonvolatile PAHs <sup>a</sup>	ng/m <sup>3</sup>	1.3	11.3	8.8

<sup>a</sup>Volatile PAHs indicate 2- and 3-ring PAH species; Semi-volatile PAHs: 4-ring PAH species; Nonvolatile PAHs: 5- and 6-ring PAHs

ues reported in Seoul (Park *et al.*, 2002) and Birmingham, UK (Smith and Harrison, 1996). Figure 2 shows the relative contributions of individual compounds to the total vapor- and particulate-phase PAH concentrations for warm and cold periods. Daily average ambient temperatures in warm and cold seasons were in the range of 18.3~24.9 and 0.2~13.5°C, respectively. The vapor-phase distributions for warm and cold seasons were dominated by low molecular weight species with the largest relative contributions to total vapor phase PAHs from PHEN followed by PYR and NAP.

Particulate phase PAHs were measured to be present in greater concentrations in cold season than

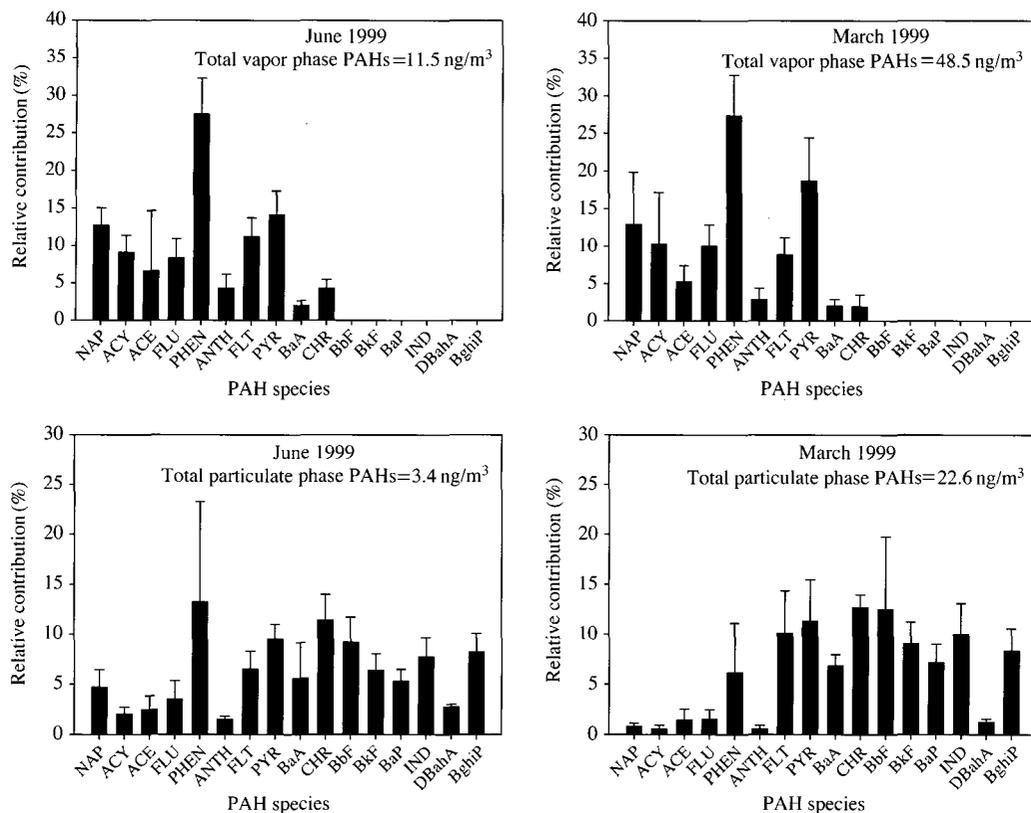


Fig. 2. Distribution patterns of the vapor and particulate phase PAHs as the relative contributions of total PAHs.

in the warm season by factor of 6.7. This result was consistent with the findings reported in the literature: higher concentrations of PAHs in cold season than in warm season by factors of 2~10 (Park *et al.*, 2002; Caricchia *et al.*, 1999; Smith and Harrison, 1996). In warm season, the highest contribution came from PHEN followed by semi- and nonvolatile PAHs. While the PAH distribution in particulate phase for the cold period was dominated by high molecular weight compounds, with contributions ranging from 8.3% (BghiP) to 12.6% (CHR), which are typically associated with atmospheric soot particles of combustion origin (Seinfeld and Pandis, 1998). Higher wintertime concentrations could be due to lower atmospheric mixing heights and lower temperatures (Park *et al.*, 2002), which are favorable conditions for poor dispersion. Previous studies

have also suggested that increased fossil fuel usage for space heating causes the enhanced particulate PAH concentrations in the cold season (Park *et al.*, 2002; Panther *et al.*, 1999; Harrison *et al.*, 1996; Aceves and Grimalt, 1993). Pearson correlation analysis indicates that ambient temperature and particulate phase PAH show a moderate level of negative correlation ( $r = -0.56$ ,  $p < 0.0001$ ), indicating that higher temperatures are associated with lower particle-associated PAH concentrations.

### 3.2.2 Characteristics of particulate phase PAHs with its volatility

Based on molecular weight and volatility, particulate phase PAHs are split into three subgroups: volatile (2- and 3-ring PAHs; NAP, ACY, ACE, FLU, PHEN, and ANTH); semi-volatile (4-ring PAHs;

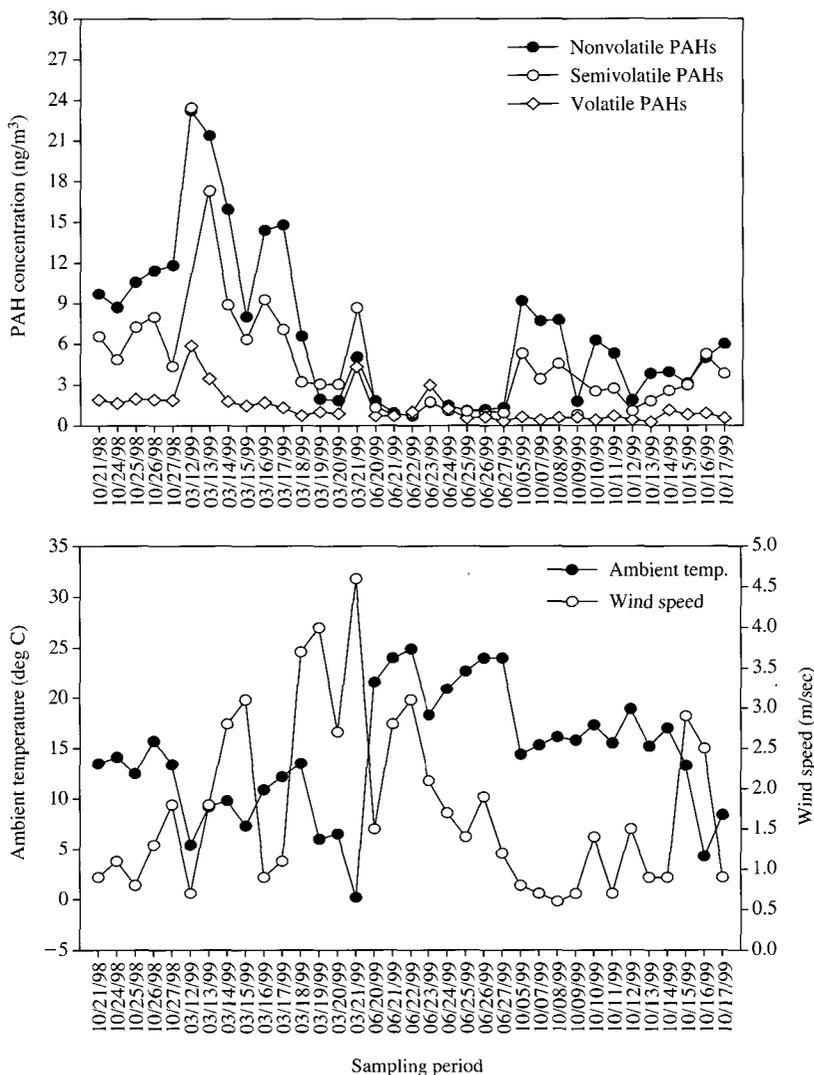


Fig. 3. Time-series plots of particulate PAHs concentrations, ambient temperature, and wind speed.

FLT, PYR, BaA, and CHR); and nonvolatile (5- and 6-ring PAHs; B[b]F, b[k]F, BaP, IND, DBaHA, and BghiP). Figure 3 illustrates time series variations of volatile, semi-volatile, and nonvolatile PAHs, ambient temperature, and wind speed, respectively. The concentrations of semi-volatile and nonvolatile PAHs exhibited clear seasonal variations. For the volatile PAHs, however, a clear variation was not observed. Particulate phase PAH concentrations during the cold sampling period of March showed a

severe variation of concentration levels, ranging from 5.8 to 52.5 ng/m<sup>3</sup>. The enhanced concentrations of PAHs in March could be attributed to low ambient temperature and low wind speed as shown in Figure 3. Pearson correlation analyses yielded that nonvolatile total PAHs showed strong correlation coefficients ( $r > 0.96$ ,  $p < 0.001$ ) with individual non-volatile PAH species, and semi-volatile PAHs also were closely correlated with individual semi-volatile PAH species ( $r > 0.96$ ,  $p < 0.001$ ). However,

correlation coefficient for the volatile PAHs was considerably varied with individual volatile PAH species, with an  $r$  of 0.53~0.98 ( $p < 0.01$ ). This analysis implies that the semi- and non-volatile PAHs obtained at our sampling location are emitted from similar sources of PAH, while this may not be true for the volatile PAHs. Therefore, these results suggest that common source, i.e., traffic, was not the only source of the volatile PAHs measured at our sampling site. Despite high correlation coefficients, the actual mass concentration ratios of BaP, IND and BghiP to nonvolatile total PAHs varied to a factor of  $\sim 2$ . Also the concentration ratios of FLT, PYR, BaA and CHR to semi-volatile total PAHs varied by up to a factor of 2~3. Thus, none of the investigated PAH was found to be suitable for a single tracer that would allow an accurate quantitative estimation of semi-volatile, nonvolatile, or total PAHs group concentrations in the ambient air.

Average concentrations of volatile, semi-volatile, and nonvolatile PAHs were 1.3, 4.8, and 6.8  $\text{ng}/\text{m}^3$ , respectively, with their respective fractions of 13.7%, 35.6%, and 50.7%. Their concentrations were 1.0, 1.1, and 1.3  $\text{ng}/\text{m}^3$  in warm season, while they were 2.2, 9.0, 11.3  $\text{ng}/\text{m}^3$  in cold season, respectively. The mass concentration ratios of volatile, semi-volatile and nonvolatile PAHs were higher in the cold season than in warm season by factors of 2.2, 8.4, and 8.8, respectively, which show some difference compared with cold-to-warm mass ratios for the total particulate phase PAHs. This suggests that the ratios can be varied depending on the emission sources, molecular size and volatility (Schauer *et al.*, 2003). Another possible cause could be attributed to gas-particle partitioning due to ambient temperature (Yamasaki *et al.*, 1982). The partitioning of semi-volatile 4-ring PAHs between gas and particles phase of atmospheric aerosols can be significantly influenced by temperature and aerosol mass concentration (Finlayson-Pitts and Pitts, 2000). Moderate correlations were observed for semi-volatile PAHs and  $\text{PM}_{2.5}$  ( $r=0.58$ ,  $p < 0.05$ ), or  $\text{PM}_{10}$  mass concentration ( $r=0.70$ ,  $p < 0.05$ ), and daily average ambient temperature were negatively correlated with semi-volatile PAHs ( $r=0.60$ ,  $p < 0.05$ ). Therefore, it

implies that both the particle mass concentration and ambient temperature can affect the gas-particle partitioning of semi-volatile PAHs in the atmosphere. Previous studies have reported that nonvolatile PAHs are enhanced by emissions from domestic heating using fossil fuels (Marr *et al.*, 1999; Khalili *et al.*, 1995). The diesel engine vehicles are dominant source of semi-volatile (FLT and PYR) and nonvolatile (B[b]F, B[k]F, IND, and BghiP) PAHs (Miguel and Pereira, 1989; Duval and Friedlander, 1981). The increased concentration of nonvolatile PAHs in cold season may reflect increased fossil fuel combustion for domestic heating, along with low boundary layer and low ambient temperature.

### 3.3 Principal component analysis

#### 3.3.1 Identification of emission sources of PAHs with individual PAH data

In order to identify the source types of particulate PAH emissions, principal component analysis (PCA) was performed using a SAS statistical package (SAS ver. 6.2). In this study, each factor from PCA is associated with a source characterization by its most representative PAH species. Source groupings were

**Table 3. Varimax Rotated Factor Loading for Particulate PAHs.**

	Factor 1	Factor 2	Factor 3	Communality
NAP	-0.024	0.230	<b>0.744</b>	0.606
ACY	0.265	0.260	<b>0.868</b>	0.891
ACE	0.441	-0.017	<b>0.827</b>	0.879
FLU	0.271	0.390	<b>0.820</b>	0.899
PHEN	0.177	<b>0.880</b>	0.360	0.935
ANTH	0.467	<b>0.795</b>	0.243	0.910
FLT	0.533	<b>0.768</b>	0.243	0.933
PYR	0.559	<b>0.780</b>	0.213	0.967
BaA	<b>0.765</b>	0.604	0.143	0.970
CHR	<b>0.759</b>	0.606	0.197	0.983
B(b+k)F	<b>0.863</b>	0.443	0.147	0.962
BaP	<b>0.903</b>	0.308	0.237	0.966
IND	<b>0.878</b>	0.314	0.213	0.915
DBahA	<b>0.796</b>	0.104	0.538	0.935
BghiP	<b>0.884</b>	0.330	0.225	0.941
Eigenvalue	6.09	4.12	3.48	13.7
% variance explained	40.6	27.5	23.2	

Loadings greater than 0.7 are in bold.

determined by using PCA with VARIMAX rotation for 15 PAH species data. Only those factors corresponding to eigenvalues  $> 1.0$  were retained (Table 3). There are three factors with eigenvalue over 1 and the sum of variance is 91.3%. From the analysis, it is investigated that the PAH species are distinguished largely by both molecular weight and number of rings in the molecule.

Factor 1 consists mainly of multi-ringed heavier PAHs, which are prevalent in the particulate phase. Variance accounted for by this factor is 40.6%. This factor is likely related to characteristics of motor vehicles exhaust and coal combustion, especially indicating the prevalence of traffic emissions. Some studies suggest that B[b]F, B[k]F, IND, BghiP, FLT and PYR indicate towards diesel-powered vehicles (Khalili *et al.*, 1995; Miguel and Pereira, 1989; Duval and Friedlander, 1981). Other studies, however, reported that diesel emission has high factor loading for FLT, PHEN, ANTH and PYR (Fang *et al.*, 2004; Caricchia *et al.*, 1999). FLT, PYR and especially BghiP have also been suggested as indicators of gasoline powered vehicles (Khalili *et al.*, 1995; Duval and Friedlander 1981), whereas Guo *et al.* (2004) reported that BaA, BaP, B[b]F, BghiP and IND indicate source markers of gasoline engine emissions. Emission from the coal combustion is reported to have a relatively high fraction of ANTH, PHEN, PYR, BaA, and CHR (Harrison *et al.*, 1996). Based on these observations, the factor 1 positively indicates towards motor vehicular emission, along with emission of coal combustion.

Factor 2 associated with PHEN, ANTH, FLT, and PYR, represents clearly the emissions from oil combustion and incineration. FLT and PYR are emitted from oil combustion, and PHEN, FLT and PYR from incinerators (Harrison *et al.*, 1996; Khalili *et al.*, 1995; Duval and Friedlander, 1981). Factor 3 includes the lighter PAHs (NAP, ACY, ACE, and FLU), which are prevalent in the vapor phase. Naphthalene (NAP) is produced through burning of fuels such as petroleum and coal, tobacco or wood. It has been used in mothballs and moth flakes. The major commercial use of naphthalene is in the manufacture of polyvinyl chloride plastics (ATSDR,

Agency for Toxic Substances and Disease Registry (<http://www.atsdr.cdc.gov/tfacts67.html>). Acenaphthene is used to make dyes, plastics and pesticides, and has also been found in cigarette smoke, in the exhaust from automobiles and in wood preservatives (<http://www.epa.gov/epaoswer/hazwaste/minimize/factshts>). Fluorene is used to make dyes, plastics and pesticides. It has been also found in vehicle exhaust, coal combustion, wildfires, and agricultural burning (<http://www.epa.gov/epaoswer/hazwaste/minimize/factshts>). Therefore, components related to this factor are likely associated with a mixture of several sources, especially plastics and vehicle exhausts.

### 3.3.2 Identification of emission sources of PAHs with a combination of PAH and PM<sub>2.5</sub> inorganic data

As explained in the section 3.3.1, it was difficult to find out the exact source types with individual PAH species information only because the source markers suggested in the literature show some degree of similarity and overlap between the profiles from different emission source types. Thus, we repeated PCA using some PAH species with high factor loading and PM<sub>2.5</sub> chemical compositional data to identify more reliable PAH source types (Table 4). Factor 1, with high factor loadings on Mg, Al, Ca, Fe, and EC (elemental carbon) indicates the presence of road dust source. Previous studies indicate that Fe component in particulate matter is associated with traffic emissions in urban environment, especially diesel engines (Park and Kim, 2004; Sweet *et al.*, 1993; Hopke *et al.*, 1980). High factor loadings of components BaA, CHR, B[b+k]F, BaP, IND, and BghiP appeared in the factor 1 of the Table 3 is clearly responsible for motor vehicle emissions, especially predominance of diesel vehicles emission. This result was compared with diagnostic ratios of individual PAH species generally used to characterize emission sources. Earlier studies have reported that ratio of BaP/BghiP  $> 0.6$  is expected to indicate traffic-related emissions, while lower ratio indicates contributions from other PAH sources (Park *et al.*, 2002). The average BaP/BghiP ratio in this study

**Table 4. Varimax rotated factor loading for combined data of PM<sub>2.5</sub> aerosol and particulate PAH species (24-hr average data).**

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communality
Mg	<b>0.749</b>	0.292	0.262	0.064	0.148	-0.384	0.887
Al	<b>0.836</b>	0.272	0.270	0.010	0.013	0.083	0.853
S	0.001	<b>0.889</b>	0.088	-0.051	0.204	0.252	0.906
K	0.223	<b>0.883</b>	0.168	0.240	-0.061	-0.029	0.919
Ca	<b>0.794</b>	<u>0.454</u>	0.258	0.011	0.071	-0.031	0.910
V	0.199	0.225	-0.043	-0.214	<b>0.787</b>	-0.239	0.815
Mn	0.225	0.266	0.079	<b>0.857</b>	-0.163	0.118	0.904
Fe	<b>0.758</b>	0.340	0.341	0.351	0.056	-0.024	0.933
Ni	<u>0.410</u>	0.135	-0.178	0.373	<b>0.653</b>	0.333	0.894
Cu	0.122	0.319	0.372	0.097	-0.289	<b>0.729</b>	0.878
Zn	0.146	0.241	<b>0.896</b>	0.121	-0.051	0.083	0.907
Pb	0.258	<b>0.607</b>	<u>0.579</u>	0.340	0.023	0.116	0.900
EC	<b>0.649</b>	0.142	0.234	<b>0.624</b>	0.002	-0.094	0.893
NO <sub>3</sub> <sup>-</sup>	0.205	<b>0.622</b>	0.158	0.368	<u>0.558</u>	0.079	0.907
SO <sub>4</sub> <sup>2-</sup>	0.041	<b>0.960</b>	-0.020	0.157	0.137	-0.004	0.967
NH <sub>4</sub> <sup>+</sup>	0.030	<b>0.840</b>	0.024	0.329	0.370	0.032	0.953
PHEN	0.363	-0.034	<b>0.888</b>	-0.019	-0.072	-0.030	0.927
ANTH	<u>0.563</u>	0.108	<b>0.749</b>	0.086	0.000	0.092	0.905
FLT	<b>0.627</b>	0.035	<b>0.730</b>	0.121	0.027	-0.021	0.943
PYR	<b>0.641</b>	0.054	<b>0.725</b>	0.134	0.067	0.007	0.962
B (b+k)F	<b>0.861</b>	0.033	0.336	0.284	0.154	0.067	0.965
IND	<b>0.872</b>	0.016	0.235	0.282	0.142	0.158	0.939
BghiP	<b>0.842</b>	0.010	0.276	0.332	0.070	0.203	0.942
Sum							21.01
Eigenvalue	6.80	4.77	4.41	2.22	1.76	1.05	21.01
% variance explained	29.6	20.7	19.2	9.6	7.7	4.6	91.4%

Loadings >0.6 are in bold, and >0.4 are underlined.

was 0.89, implying that the observed PAHs were governed by vehicles emissions. When PAHs are influenced by vehicle emissions, the IND/BghiP ratio can be used to characterize the different engine types: ~0.4 for gasoline engines and ~1.0 for diesel engines (Caricchia *et al.*, 1999). In this study, the average IND/BghiP ratio was 1.05, implying a greater influence of diesel vehicle emissions. Results from the diagnostic ratios are well in accordance with the ones of the PCA. Factor 2 correlates with constituents NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup>, representing the secondary aerosol formation process. Factor 3 is related to Zn, Pb, PHEN, ANTH, FLT, and PYR species, clearly suggesting the source markers of incineration. Based on previous studies (Kidwell *et al.*, 1996; Dzubay *et al.*, 1988), the metals of Zn, Pb, Cu, Fe, and Cd, especially Zn, Pb, and Cd, have been found to be major constituents of the emis-

sions from municipal and waste incinerators. It is also known that PHEN, FLT, and especially PYR are emitted from the incineration (Duval and Friedlander, 1981). Thus high factor loadings of PHEN, ANTH, FLT, and PYR appeared in the factor 2 of the Table 3 are clearly associated with the characteristics of incineration.

#### 4. CONCLUSION

Daily ambient air PAH samples were collected at an urban site of Chongju, and analyzed for 16 PAH species by GC/MSD/SIM technique. Average concentrations of volatile (two- and three-ring), semi-volatile (four-ring) and nonvolatile (five- and six-ring) particulate-phase PAHs accounted for 13.7%, 35.6%, and 50.7% of total particulate-phase PAH

levels, respectively. Their concentration ratio was greater in March than in June by factors of 2.2, 8.4, and 8.8, respectively; implying that seasonal variation of individual PAH species can be varied depending on molecular size, volatility, and emission sources. Principle component analysis (PCA) was performed to extract possible emission source types of PAHs with both PAH data alone and combined data of PAH and PM<sub>2.5</sub> inorganic data. Because of the similarity of PAH profiles from different source types, the results of the PCA demonstrate that a combination of PAH and PM<sub>2.5</sub> inorganic data provides a more reliable result to better understanding PAH emission sources than PAH species data alone. It was found in the PCA that diesel vehicles and incineration were the possible major PAH emission sources in this sampling site.

## ACKNOWLEDGEMENT

This work was financially supported by Chonnam National University in 2005. The authors wish to acknowledge a grant-in-aid for research from the Second stage of BK 21.

## REFERENCES

- Aceves, M. and J.O. Grimalt (1993) Seasonally dependent size distributions of Aliphatic and polycyclic aromatic hydrocarbons in urban aerosols from densely populated areas, *Environmental Science and Technology*, 27, 2896-2908.
- Baek, S.O. and J.S. Choi (1998) Effect of ambient temperatures on the distribution of atmospheric concentrations of polycyclic aromatic hydrocarbons in the vapor and particulate phases, *Journal of Korea Air Pollution Research Association*, 14, 117-131.
- Caricchia, A.M., S. Chiavarini, and M. Pessa (1999) Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy), *Atmospheric Environment*, 33, 3731-3738.
- De Raat, W.K. and F.A. Meijere (1991) Polycyclic aromatic hydrocarbon concentrations in ambient airborne particles from local traffic and distant sources; variation of the PAH profile, *The Science of the Total Environment*, 103, 1-17.
- Duval, M.M. and S.K. Friedlander (1981) Source resolution of polycyclic aromatic hydrocarbons in the Los Angeles atmosphere, EPA-600/2-81-161, U.S. EPA, Washington, DC.
- Dzubay, T.G., R.K. Stevens, G.E. Gordon, I. Olmez, A.E. Sheffield, and W.J. Courtney (1988) A composite receptor method applied to Philadelphia aerosol, *Environmental Science and Technology*, 22, 46-52.
- Fang, G.-C., Y.-S. Wu, M.-H. Chen, T.T. Ho, S.H. Huang, and J.Y. Rau (2004) Polycyclic aromatic hydrocarbons study in Taichung, Taiwan, during 2002 ~ 2003, *Atmospheric Environment*, 38, 3385-3391.
- Finlayson-Pitts, B.J. and J.N. Pitts (2000) *Chemistry of the upper and lower atmosphere*; Academic Press: San Diego.
- Guo, H., S.C. Lee, K.F. Ho, X.M. Wang, and S.C. Zou (2004) Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong, *Atmospheric Environment*, 38, 5307-5317.
- Harrison, R.M., D.J.T. Smith, and L. Luhana (1996) Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K., *Environmental Science and Technology*, 30, 825-832.
- Hopke, P.K., R.E. Lamb, and D.F.S. Natusch (1980) Multi-element characterization of urban roadway dust, *Environmental Science and Technology* 14, 164-172.
- IARC (1984) Polynuclear aromatic compounds, Part 3, chemical environmental and experimental data, IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans, vol. 34, IARC, Lyon, France.
- Khalili, N.R., P.A. Scheff, and T.M. Holsen (1995) PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions, *Atmospheric Environment*, 29, 533-542.
- Kidwell, C.B., F. Divita, and J.M. Ondov (1996) Identification of an incinerator plume from ground-level submicrometer aerosol sampling with a micro-orifice impactor, *Journal of Aerosol Science*, 27, Suppl 1, S29-S30.

- Kim Oanh, N.T., L.B. Reutergardh, N.Tr. Dung, M.-H. Yu, W.-X. Yao, and H.X. Co (2000) Polycyclic aromatic hydrocarbons in the airborne particulate matter at a location 40 km north of Bangkok, Thailand, *Atmospheric Environment*, 34, 4557-4563.
- Kim, S.C., T.J. Lee, and D.S. Kim (1996) Trends in concentrations of polycyclic aromatic hydrocarbons of PM-10 in Suwon area, *Journal of Korea Air Pollution Research Association*, 12, 341-350.
- Lee, J.Y., Y.P. Kim, C.-H. Kang, Y.S. Ghim, and N. Kaneyasu (2006) Temporal trend and long-range transport of particulate polycyclic aromatic hydrocarbons at Gosan in northeast Asia between 2001 and 2004, *Journal of Geophysical Research*, 111, D11303.
- Ligoeki, M.P. and J.F. Pankow (1989) Measurements of the gas/particle distributions of atmospheric organic compounds, *Environmental Science and Technology*, 23, 75-83.
- Marr, L.C., T.W. Kirchstetter, R.A. Harley, A.H. Miguel, S.V. Hering, and S.K. Hammond (1999) Characterization of polycyclic aromatic hydrocarbons in motor vehicles fuels and exhaust emissions, *Environmental Science and Technology*, 33, 3091-3099.
- Miguel, A.H. and P.A.P. Pereira (1989) Benzo(k)fluoranthene, Benzo(ghi)perylene, and Indeno(1, 2-cd)pyrene : New tracers of automotive emissions in receptor modeling, *Aerosol Science and Technology*, 10, 292-295.
- Panther, B.C., M.A. Hooper, and N.J. Tapper (1999) A comparison of air particulate matter and associated polycyclic aromatic hydrocarbons in some tropical and temperate urban environments, *Atmospheric Environment*, 33, 4087-4099.
- Park, S.S., Y.J. Kim, and C.H. Kang (2002) Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea, *Atmospheric Environment*, 36, 2917-2924.
- Park, S.S. and Y.J. Kim (2004) PM<sub>2.5</sub> particles and size-segregated ionic species measured during fall season in three urban sites in Korea, *Atmospheric Environment*, 38, 1459-1471.
- Park, S.S. and Y.J. Kim (2005) Source contributions to fine particulate matter in an urban atmosphere, *Chemosphere*, 59, 217-226.
- Ravindra, K., L. Bencs, E. Wauters, J. Hoog, F. Deutsch, E. Roekens, N. Bleux, P. Berghmans, and R.V. Grieben (2006) Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities, *Atmospheric Environment* (in press).
- Sanderson, E.G. and J.-P. Farant (2005) Atmospheric size distribution of PAHs: Evidence of a high-volume sampling artifact, *Environmental Science and Technology*, 39, 7631-7637.
- Schauer, C., R. Niessner, and U. Poschl (2003) Polycyclic aromatic hydrocarbons in urban air particulate matter: Decadal and seasonal trends, chemical degradation, and sampling artifacts, *Environmental Science and Technology*, 37, 2861-2868.
- Seinfeld, J. and S.N. Pandis (1998) *Atmospheric Chemistry and Physics; From air pollution to climate change*. John Wiley & Sons, New York.
- Smith, D.J.T. and R.M. Harrison (1996) Concentrations, trends and vehicle source profile of polynuclear aromatic hydrocarbons in the U.K. atmosphere, *Atmospheric Environment*, 30, 2513-2525.
- Statistical Analysis System (SAS) (1997) SAS base programming for SAS@6.2, SAS Institute Inc.
- Sweet, C.W., S.J. Vermette, and S. Landsberger (1993) Sources of toxic trace elements in urban air in Illinois, *Environmental Science and Technology*, 27, 2502-2510.
- Yamasaki, H., K. Kuwata, and H. Miyamoto (1982) Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons, *Environmental Science and Technology*, 16, 189-194.