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Atmospheric Deposition of Polycyclic Aromatic Hydrocarbons in an Urban and a Suburban Area of Korea from 2002 to 2004

H.-B. Moon,[1,2] K. Kannan,[2] S.-J. Lee,[1,3] G. Ok[3]

[1] Marine Environment Management Team, National Fisheries Research and Development Institute, 408-1, Sirang-ri, Gijang-eup, Gijang-gun, Busan 619-902, Korea
[2] Wadsworth Center, New York State Department of Health and Department of Environmental Health Sciences, School of Public Health, State University of New York at Albany, Empire State Plaza, PO Box 509, Albany, NY 12201-0509, USA
[3] Faculty of Earth Environmental Sciences, Pukyong National University, Nam-gu, Daeyeon3-dong, 599-1, Busan 608-737, Korea

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Abstract. Atmospheric bulk samples (wet and dry) were collected monthly during 2002 to 2004 from an urban and a suburban area in Korea for assessment of depositional flux and seasonal variations in the concentrations of polycyclic aromatic hydrocarbons (PAHs). PAH depositional flux ranged from 64.1 to 610 $\mu g/m^2/y$ for the urban area and from 65 to 460 $\mu g/m^2/y$ for the suburban area. The fluxes of PAHs measured in this study were comparable with those reported for urban and suburban areas in other countries. The fluxes of particulates and PAHs were higher in winter than in summer, consistent with the greater per capita consumption of fossil fuel in winter than in summer. Ambient temperature played a major role in the seasonal variability in PAH fluxes. Photochemical degradation of PAHs appears to occur during the summer months. The relationship of PAH depositional fluxes with major air pollutants, such as ozone, sulfur dioxide, carbon monoxide, nitrogen dioxide, and presence of particulate matter up to 10 μm in size (PM_{10}), was also investigated. Dominant PAH compounds in both the urban and the suburban locations were benzo[g,h,i]perylene, pyrene, and indeno[1,2,3-c,d]pyrene. Based on the PAH diagnostic ratios and a factor analysis, the major sources of PAHs in the urban and the suburban regions were found to be similar. Diesel exhaust, coal combustion, and gasoline emissions contributed predominantly to atmospheric PAH contamination.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants of public concern and are derived mainly from anthropogenic activities. PAHs are generated by fossil fuel combustion processes, including automobile exhaust, residential heating, coke and oil production, and incineration of organic matter (Baek *et al.* 1991; Hites *et al.* 1997). Because of their carcinogenic and mutagenic potential (International Agency for Research on Cancer [IARC] 1984), PAHs have been extensively studied in various environmental and biologic compartments (Yang *et al.* 1991; Baumard *et al.* 1998). A number of anthropogenic sources are responsible for PAH contamination of the atmosphere (Baek *et al.* 1991). PAHs are transported during long distances and become deposited in terrestrial and aquatic systems through wet and dry deposition (Hoff *et al.* 1996). Therefore, atmospheric transport and deposition constitute the primary pathway for distribution of PAHs from a variety of emission sources (Wild & Jones 1995). In the atmosphere, PAHs undergo photochemical decomposition by OH radical reaction (Valerio *et al.* 1984). Certain meteorologic conditions (*i.e.*, temperature, rainfall, wind speed, solar intensity, and humidity) can influence atmospheric deposition of PAHs (Gevao *et al.* 1998a; Motelay-Massei *et al.* 2003).

Until now, studies have focused on the levels and sources of PAHs in atmospheric particulates in Korea (Park *et al.* 2002a). No studies exist that describe depositional fluxes and seasonal variations of PAHs in Korea. Rapid industrialization and economic development in Korea may contribute to contamination by various pollutants, including PAHs. The objective of the present study was to determine atmospheric depositional fluxes and seasonal variations in concentrations of PAHs from an urban and a suburban location in Korea. The depositional fluxes of PAHs were examined in relation to meteorologic parameters and the concentrations of other air pollutants, such as ozone (O_3), carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and particulate matter up to 10 μm in size (PM_{10}). Finally, sources of PAHs were identified by means of diagnostic ratios and by a multifactorial statistical analysis.

Materials and Methods

Sampling Sites

Atmospheric deposition samples were collected in Daeyeon-dong (urban site) and Gijang-gun (suburban site) in Busan, Korea (Fig. 1).

Correspondence to: H.-B. Moon; *email:* hbmoon@nfrdi.re.kr

Fig. 1. Sampling locations (●) of atmospheric bulk deposition samples, meteorologic parameters, and air pollutants from an urban area (Daeyeon-dong) of Busan City, Korea. Sampling locations of atmospheric bulk deposition samples (●, Gijang-gun) and meteorologic parameters (■, Ilkwang) from a suburban area of Busan City, Korea

Daeyeon-dong and Gijang-gun are located along the southeastern coast of Korea within 1 km of the ocean coastline. Daeyeon-dong is an urban area, with influences from vehicle emissions, and is moderately industrialized. Gijang-gun is located in a suburban area dominated by agricultural and fishery activities. The climate in the sampling locations is temperate, with temperatures ranging from −1.2°C to 32°C (annual average 15°C). The average annual rainfall during the sampling period was 1,870 mm, and there was no snowfall during that period. The average wind speed was 1.7 m/s.

Sample Collection

Bulk atmospheric deposition samples were collected monthly for 3 years from January 2002 to December 2004. The samplers were stainless steel pots with an inner diameter of 50 cm and a height of 50 cm and were covered by steel net with small mesh to avoid damages caused by birds and animals. The bulk samplers were set at 120 cm above the rooftops of a four-story building in the urban area (Daeyeon-dong) and on a three-story building in the suburban area (Gijang-gun). Three bulk samplers were employed to determine depositional fluxes of atmospheric particulates for each sampling site, and one of them was used to determine PAH depositional fluxes. Approximately 5 L of purified water was added to the sampler to cover the bottom surface with water. The water containing atmospheric particulates collected during every sampling period was transferred to polyethylene bottles, and the inner walls of the bulk sampler were wiped with precleaned glass wool. Sampling procedures have been reported elsewhere (Ogura *et al.* 2001; Moon *et al.* 2005).

Meteorologic data for the sampling locations were obtained from automatic weather system reports published by the Korea Meteorological Administration (2002, 2003, 2004). Data for air pollutants, such as O_3, SO_2, CO, NO_2, and PM_{10}, were taken from the air-quality monitoring reports of the Ministry of Environment (2002, 2003, 2004). For the urban area, PAH depositional fluxes, meteorologic parameters, and air pollutants were measured at the same site. For the suburban area, meteorologic data were from a nearby location (Ilkwang area) (Fig. 1).

Sample Preparation

Atmospheric deposition samples, collected by bulk sampler, were separated into particulate and liquid phases. Particle samples were isolated by filtration of water through glass fiber filters (Whatman GFF 47 mm, 0.7 µm, Middlesex, UK). Particle samples were dried in a desiccator and then weighed. The difference in weight before and after filtration was used to determine depositional flux of atmospheric particles. The liquid phase was extracted twice by liquid–liquid extraction using a mixture of methylene chloride and hexane (ultra residue analysis; J. T. Baker; Phillipsburg, NJ) (1:1, 100 mL). GFF and glass wool were extracted with 200 mL toluene (ultra residue analysis; J. T. Baker; Phillipsburg, NJ) for 5 hours under reflux after spiking with 7 species of internal standards (d_8-naphthalene, d_8-acenaphthylene, d_{12}-fluoranthene, d_{10}-phenanthrene, d_{10}-pyrene, d_{12}-benzo[a]pyrene, and d_{12}-benzo[g,h,i]perylene, ES-2044; Cambridge Isotope Laboratories, Andover, MA). The extracts were filtered through glass wool and concentrated to 1 to 2 mL in a rotary evaporator. The solvent was transferred to hexane and combined with liquid-phase extracts. Combined samples were adjusted to a volume of 10 mL.

The extracts were cleaned by passage through activated silica gel (neutral; 7734; 70 to 230 mesh; Merck, Darmstadt, Germany) column chromatography with successive eluants of hexane and 15% methylene chloride in hexane. The eluants were concentrated to approximately 1 mL and were evaporated at room temperature to 50 to 100 µL. The residues were dissolved with 50 µL *n*-nonane (pesticide analysis grade; Fluka) for instrumental analysis.

Instrumental Analysis

The aromatic fraction was analyzed by gas chromatograph (Agilent 6890) coupled with mass spectrometer (Agilent 5973N). The injector and interface temperatures were maintained at 250°C. The oven temperature program was from 80°C (1 minute) to 300°C (10 minutes) at 5°C /min. The carrier gas was helium at a constant flow rate of 1.2 mL/min. The capillary column used was a DB-5MS (30 m length, 0.25 mm i.d., 0.25-µm film thickness; J&W Scientific, Folsom, CA). The mass spectrometer was operated under the selected-ion monitoring mode using molecular ions of PAHs.

In this study, 16 non-alkylated PAHs (48755-U; Supelco, Bellefonte, PA), recommended as priority pollutants by the United States Environmental Protection Agency, were analyzed. These include naphthalene (NaP), acenaphthylene (AcPy), acenaphthene (AcP), fluorene (Flu), Phenanthren (PhA), anthracene (AnT), fluoranthene (FluA), Pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indenol(1,2,3-c,d)pyrene (InI'), dibenzo(a,h)anthracene (DbA) and benzo(g,h,i)perylene (BghiP). To assess the quality of determinations by routine experimental procedure and instrumental conditions, we analyzed standard sediment reference material from the National Institute for Standards and Technology (Gaithersburg, MD) (SRM 1974a). The recovery results were in the range of 69% to 94% (mean 84%). All of the labeled internal standards were detected with no interferences. The average recovery for all bulk samples was 86% ± 12%. Procedural blanks were processed similarly to the

Table 1. Summary of depositional fluxes of air particulates and PAHs in an urban and a suburban area of Korea from 2002 to 2004

	Urban area (Daeyeon-dong)			Suburban area (Gijang-gun)		
Air particulates and PAHs	Min	Max	Mean	Min	Max	Mean
Air particulates ($g/m^2/y$)	18.8	98.5	40.5	8.63	76.9	27.7
PAHs ($\mu g/m^2/y$)						
NaP	0.36	18.9	8.53	0.13	28.4	9.12
AcPy	0.37	2.58	1.31	0.35	4.42	0.99
AcP	0.17	1.65	0.70	0.18	4.47	0.76
Flu	0.47	5.80	2.08	0.65	6.28	2.05
PhA	4.40	57.1	22.6	7.10	50.6	18.0
AnT	0.52	3.75	1.79	0.35	3.25	1.23
FluA	4.89	77.8	27.7	6.16	61.5	20.0
Pyr	5.74	241	37.6	5.38	157	25.8
BaA	1.02	13.9	6.73	1.07	12.2	3.87
Chr	6.06	66.2	29.1	4.94	53.7	19.0
BbF	3.65	72.0	29.9	4.06	60.8	19.6
BkF	2.55	35.7	11.0	2.09	40.4	7.71
BaP	3.41	66.4	23.1	1.74	43.2	10.7
InP	9.20	87.1	36.2	6.95	43.8	19.1
DbA	1.22	22.2	6.81	0.83	8.55	2.54
BghiP	13.0	157	50.5	7.50	127	24.5
ΣCPAH[a]	22.5	245	114	21.3	173	63.5
ΣPAH[b]	64.1	610	295	65.0	460	185

[a] The sum of the six carcinogenic PAHs of IARC recommendation.

[b] The sum of total PAHs.

Max = Maximum.

Min = Minimum.

samples, and the blanks did not contain quantifiable amounts of target compounds. Solvents were injected before and after the injection of standards as a check for any carryover. The calculated detection limit (S/N = 5) for individual PAH was 1 ng/g dry weight.

Results and Discussion

Depositional Fluxes of Air Particulates and PAHs

The atmospheric deposition fluxes of particles and PAHs at the two locations in Korea are listed in Table 1. The particle depositional flux in the urban area varied from 18.8 to 98.5 $g/m^2/y$ (mean 40.5), and in the suburban area it ranged from 8.63 to 76.9 $g/m^2/y$ (mean 27.7). The depositional flux of particles in the urban area was significantly higher than that in the suburban area (Student *t* test, $p < 0.05$).

Atmospheric depositional flux of total PAHs in bulk samples from the urban area varied from 64.1 to 610 $\mu g/m^2/y$ (mean 295) (Table 1). Total PAH depositional flux in the suburban area ranged from 65 to 460 $\mu g/m^2/y$ (mean 185). The atmospheric depositional flux of PAHs in the urban area was significantly higher than that in the suburban area (Student *t* test, $p < 0.05$). The sum of the six potential carcinogenic PAHs (BaA, BbF, BkF, benzo[a]pyrene [BaP], indeno[1,2,3-c,d]pyrene [InP], and dibenzo[a,h]anthracene [DbA]), as proposed by the IARC (1984), accounted for, on average, 39% and 35%, respectively, of the total PAH fluxes in the urban and in the suburban areas.

For comparison, atmospheric depositional fluxes of PAHs reported for several other countries are listed in Table 2. PAH depositional flux determined in this study was comparable with those measured for several locations in the United States (Golombo *et al.* 1997; Park *et al.* 2001; 2002b); Paris, France (Ollivon *et al.* 2002); Cumbria, UK (Gevao *et al.* 1998a); Venice, Italy (Rossini *et al.* 2005a); Lake Gårdsjön, Sweden (Broström-Lundén & Löfgren 1998); Rörvik, Sweden (Broström-Lundén & Lövblad 1991); Lake Balaton, Hungary (Kiss *et al.* 2001); and Thessaloniki, Greece (Manoli *et al.* 2002). However, PAH depositional fluxes measured at industrial locations such as Tianjin in China (Wu *et al.* 2005), Tampa Bay, FL, United States (Poor *et al.* 2004), Manchester and Cardiff, UK (Halsall *et al.* 1997), and Porto Marghera, Italy (Rossini *et al.* 2005b) were approximately 10 times higher than those measured in our study. PAH depositional fluxes reported for Everux, France (Motelay-Massei *et al.* 2003) were lower than that found in our study. Overall, depositional fluxes of PAHs measured in this study were comparable with those from urban and suburban areas in other countries but lower than those from industrial areas in other countries.

Seasonal Variability of PAH Depositional Fluxes

The depositional flux of particles at both sampling sites were highest in winter and lowest in summer, consistent with the normal seasonal trend of atmospheric suspended particles (Halsall *et al.* 1997) (Fig. 2). The monthly depositional flux of PAHs varied considerably at both sampling sites. The PAH depositional flux measured in winter (<10°C median, November to March = 294 $\mu g/m^2/y$) was higher than that measured in summer (>20°C median, June to September = 172 $\mu g/m^2/y$). This seasonal trend is similar to that reported earlier (Halsall *et al.* 1997; Wu *et al.* 2005).

Table 2. Comparison of atmospheric depositional fluxes of PAHs measured in this study with those reported from other world locations

Location	*n*[a]	PAH flux (μg/m^2/y)	Sampling period	Reference	Remarks
Daeyeon-dong, Korea	16	64.1–610	2002–2004	This study	U
Gijang-gun, Korea	16	65.0–460	2002–2004	This study	SU
Tianjin, China	15	25.6–10,000	2002–2003	Wu *et al.* (2005)	I, U, SU
Tampa Bay, FL[b]	16	4,140	2002	Poor *et al.* (2004)	I
Manchester, UK	15	376–8833	1991–1992	Halsall *et al.* (1997)	I
Cardiff, UK	15	295–7154	1991–1992	Halsall *et al.* (1997)	I
Porto Marghera, Italy	16	26.3–3807	2003–2004	Rossini *et al.* (2005b)	I
Paris, France	14	61.2–731	1999–2000	Ollivon *et al.* (2002)	U
Venice, Italy	16	6.48–733	1998–1999	Rossini *et al.* (2005a)	U
Thessaloniki, Greece	15	73–401	1997	Manoli *et al.* (2002)	U
Nahant, MA	13	897	1992–1993	Golomb *et al.* (1997)	SU
Truno, MA	13	393	1992–1993	Golomb *et al.* (1997)	SU
Seabrook, TX	39	230	1995–1996	Park *et al.* (2001)	SU
Corpus Christi Bay, TX	39	250	1998–1999	Park *et al.* (2002b)	SU
Everux, France	14	0.85–51.8	2001–2002	Motelay-Massei *et al.* (2003)	SU
Cumbria, UK	12	120–915	1996	Gevao *et al.* (1998a)	R
Rörvik, Sweden	11	657	1990	Brorström-Lundén and Lövblad (1991)	R
Lake Balaton, Hungary	13	190-300	1996–1997	Kiss *et al.* (2001)	R
Lake Gårdsjön, Sweden	11	25.2–576	1991–1994	Brorström-Lundén and Löfgren (1998)	F

[a] *n* = Numbers of analyzed PAHs.
[b] Dry-deposition flux only.
U = Urban area.
SU = Suburban area.
I = Industrial area.
R = Rural area.
F = Forest.

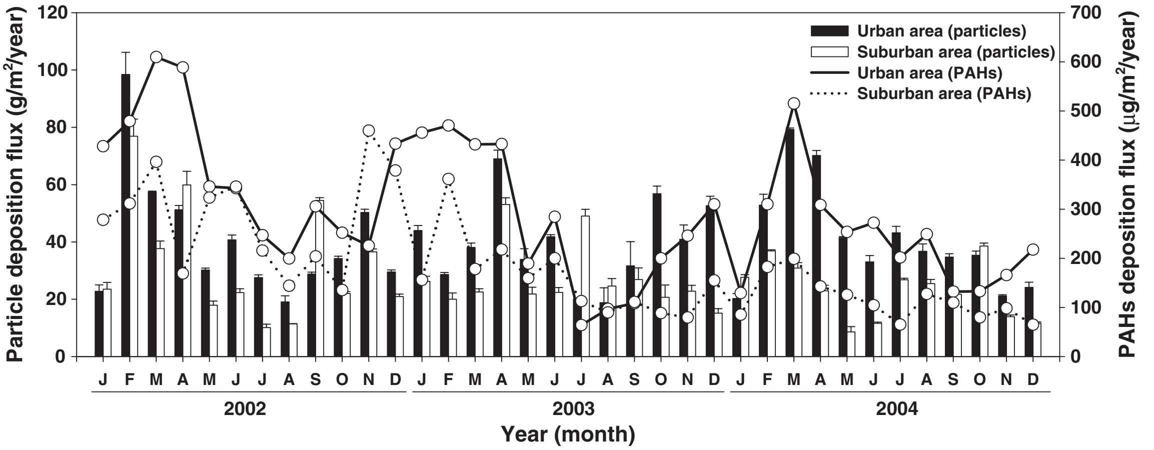

Fig. 2. Monthly variation of depositional fluxes of atmospheric particles and PAHs in an urban and a suburban area of Korea from 2002 to 2004. Vertical lines represent SDs of atmospheric depositional fluxes of air particulates (n = 3/each month)

Seasonal variations in PAH depositional fluxes are generally attributed to high emission rates of fossil fuel during winter. Total consumption of fossil fuel (coal and petroleum) in Busan City is approximately 1.4 times higher in winter (November to March 2003) than in summer (June to September 2003) (KEMCO 2004). Domestic heating is a source of PAHs in the atmosphere worldwide (Baek *et al.* 1991; Manoli *et al.* 2002; Wu *et al.* 2005).

Regression analysis was performed to investigate the relationship between PAH and particulate depositional fluxes. No apparent relationship was found between the fluxes of total PAHs and atmospheric particles in either the urban ($r = 0.50$, $p < 0.01$) or the suburban ($r = 0.23$) location. However, the PAH depositional fluxes and total suspended particles <10 μm (*i.e.*, PM_{10}) showed a positive correlation ($r = 0.72$, $p < 0.001$), suggesting that PAHs are associated with fine rather than coarse particles. Kaupp and McLachlan (1999) reported that PAHs in the atmospheric particulates were primarily associated with fine particles <1.35 μm aerodynamic diameter.

Relationships Between PAH Depositional Fluxes and Meteorologic Parameters

Correlation coefficients for the relationship between PAH depositional fluxes and meteorologic parameters at the urban location are listed in Table 3. Meteorologic parameters, such

Table 3. Pearson product-moment correlation coefficients between PAH depositional fluxes and some parameters in bulk deposition samples from an urban area of Korea

Parameters	ΣPAHS	LMW	HMW	Temperature	Rainfall	Wind speed	O_3	CO	SO_2	NO_2
LMW	0.888***									
HMW	0.889***	0.581***								
Temperature	−0.507**	−0.372*	−0.538**							
Rainfall	−0.220	−0.185	−0.228	0.550**						
Wind speed	0.065	0.042	0.069	0.207	0.384*					
O_3	0.163	0.087	0.167	0.358*	0.359*	0.344*				
CO	0.198	0.229	0.137	−0.343*	−0.060	−0.051	−0.426**			
SO_2	0.467**	0.357*	0.470**	−0.099	−0.125	−0.385*	0.148	0.026		
NO_2	0.668***	0.616***	0.574***	−0.666***	−0.410*	−0.383*	−0.043	0.404*	0.540**	
PM_{10}	0.685***	0.792***	0.428**	−0.222	−0.043	−0.104	0.204	0.216	0.622***	0.678***

* $0.01 < p < 0.05$.
** $0.001 < p < 0.01$.
*** $p < 0.001$.

as temperature, rainfall, and wind speed, were collected along with atmospheric deposition samples. Wind direction varied considerably during the 3-year study period and therefore was not included in the analysis. Among the meteorologic parameters, ambient temperature was highly correlated with PAH depositional flux. In particular, the negative correlation of ambient temperature with higher molecular-weight (HMW; 5 to 6 rings) PAHs ($r = -0.54$) was greater than that for lower molecular-weight (LMW; 3 to 4 rings) PAHs ($r = -0.37$), indicating temperature-dependent gas and particle partitioning of PAHs (Terzi & Samara 2004). Ambient temperature has been shown to be an important factor in PAH depositional flux (Motelay-Massei *et al.* 2003). Depositional fluxes are expected to be positively influenced by the amount of rainfall. However, in the present study, the correlation between PAH depositional flux and rainfall was negative and small. This is because most particles containing toxic chemicals are scavenged from the atmosphere at the beginning of the rain event (Koester & Hites 1992). No significant correlation was observed between PAH depositional fluxes and wind speed.

An important removal process for PAHs from the atmosphere is photochemical degradation (Valerio *et al.* 1984). The relative ratios of BeP and BaP can give some indication of the degree of photochemical degradation of PAHs in the atmosphere (Duan *et al.* 2005). Under simulated sunlight conditions, BeP, with a half-life of 21.1 hours, is more stable to photolysis than BaP, which has a half-life of 5.3 hours (Panther *et al.* 1999). The monthly variation in BeP:BaP ratios in atmospheric bulk deposition samples from the urban and the suburban area during the sampling period is presented in Figure 3. The relative ratio of BeP to BaP was 2.5 ± 0.7 in deposition samples from the urban area and 2.8 ± 1.6 in samples from the suburban area, indicating some extent of photochemical degradation. In particular, the atmospheric deposition samples collected during July to August from both sampling sites were characterized by higher ratios of BeP to BaP than were those from other months. This suggests higher rates of photolysis of PAHs during summer months, when there is a longer period of daylight, and stronger solar intensity. Photochemical degradation of PAHs is an important factor that governs seasonal variability in PAH depositional flux.

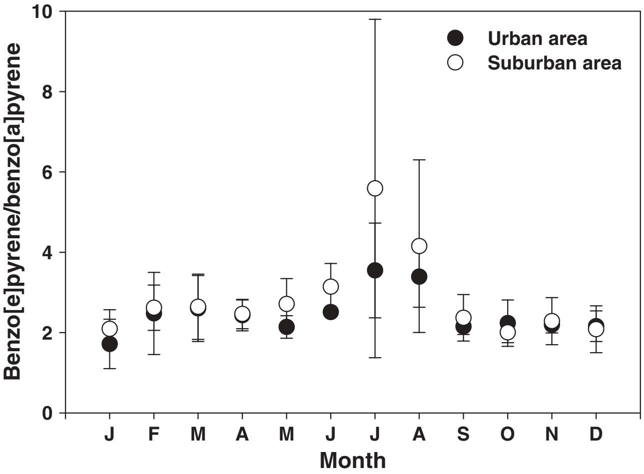

Fig. 3. Averaged monthly variation of benzo[e]pyrene/benzo[a]pyrene ratios in bulk atmospheric deposition samples in an urban (●) and a suburban (○) area during the sampling period (January 2002 to Dec 2004). Closed and open circles represent the average ratio of benzo[e]pyrene/benzo[a]pyrene, and vertical bars represent SDs of the ratios (n = 3/each month)

Relationships of PAH Depositional Fluxes with Air Pollutants

Correlation between PAH depositional fluxes and concentrations of five air pollutants—O_3, CO, SO_2, NO_2, PM_{10}—measured at the urban sampling area are listed in Table 3. No significant correlation of PAH deposition flux with O_3 or CO was found, whereas significant positive correlation was found with SO_2, NO_2, and PM_{10}. The positive relationship between PAH fluxes and SO_2 ($r = 0.47$) and NO_2 ($r = 0.67$) in the atmosphere suggests that PAHs, SO_2, and NO_2 originated from the same sources, such as combustion-related activities (Park *et al.* 2002a). Interestingly, the positive correlation between SO_2 and the HMW PAHs ($r = 0.47$) was stronger than that for the LMW PAHs ($r = 0.36$). In contrast, the correlation between NO_2 and the LMW PAHs (r= 0.62) was stronger than that for the HMW PAHs ($r = 0.79$). This suggests that NO_2 and the LMW PAHs originate from low-temperature

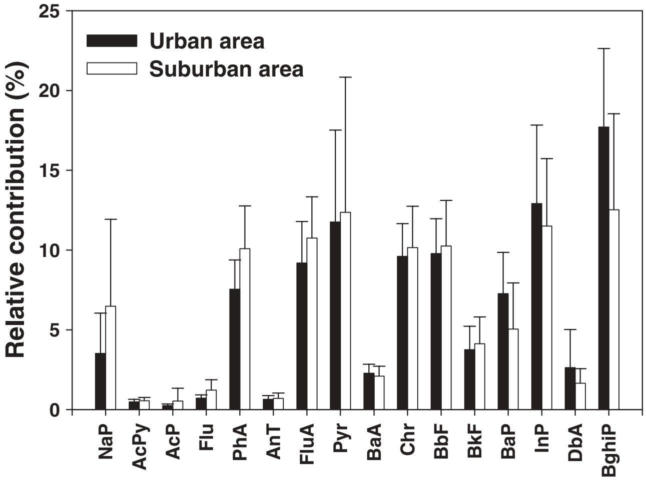

Fig. 4. Comparison of averaged profiles of PAHs in bulk atmospheric depositional samples from an urban and a suburban area of Korea. Vertical bars indicate SDs ($n = 36$ for each location)

combustion processes, whereas SO_2 and the HMW PAHs likely originate from high-temperature combustion activities (*e.g.*, industries). The correlation between PAH fluxes and PM_{10} was significantly positive ($r = 0.68$). In particular, the relationship between PM_{10} and the LMW PAHs ($r= 0.79$) was stronger than that for the HMW PAHs ($r = 0.43$). This is because the fine particles in the atmosphere are primarily associated with three- and four-ring PAHs such as phenanthrene (PhA), fluoranthene (FluA), pyrene (Pyr), and chrysene (Chr) (Kulkarni & Venkataraman 2000; Guo *et al.* 2003).

Profiles and Diagnostic Ratios of PAHs

The profiles of PAHs in bulk deposition from the urban and the suburban area of Korea are shown in Figure 4. Although PAH profiles for the two sampling sites did not differ significantly (Student *t* test, $p > 0.05$), the dominant PAH compounds did differ slightly between the two sampling sites. In the urban area, the predominant compounds were benzo[g,h,i]perylene (BghiP), InP, Pyr, BbF, Chr, and FluA, collectively accounting for, on average, 71% of the total PAHs. In the suburban area, Pyr, BghiP, InP, FluA, BbF, and Chr collectively accounted for, on average, 68% of the total PAHs. These PAH profiles are comparable with those reported for atmospheric suspended particles from other countries (Bourotte *et al.* 2005; Rehwagen *et al.* 2005).

Although several constraints exist, molecular ratios of some marker PAHs have been used to identify sources of PAHs in the environment (Panther *et al.* 1999; Guo *et al.* 2003). The results of common diagnostic ratios used in this study (FluA:FluA + Pyr, InP:BghiP, and InP:InP + BghiP) are listed in Table 4. With the exception of the InP:BghiP ratio, the diagnostic ratios were similar between the urban and suburban areas, suggesting the presence of similar sources at these two locations. The FluA:FluA + Pyr ratio <0.4 implies the predominance of unburned petroleum, and the ratio from 0.4 to 0.5 indicates the combustion of liquid fossil fuels; the ratio >0.5 suggests grass, wood, and coal combustion (Yunker *et al.* 2002). In this study, the FluA:FluA + Pyr ratio was 0.45 ± 0.07 for the urban area and 0.51 ± 0.08 for the suburban area. This suggests that combustion of liquid fossil fuels (gasoline and diesel) is the major source of PAHs in the urban area, and grass, wood, and coal combustion may contribute PAH contamination in the suburban area. The InP:BghiP ratio in gasoline exhaust is 0.4, whereas this ratio for diesel exhaust is approximately 1.0 (Caricchia *et al.* 1999). In this study, the InP:BghiP ratio in atmospheric depositional samples was 0.76 ± 0.31 for urban samples and 1.06 ± 0.38 for suburban samples. This suggests both diesel and gasoline emissions as sources in the urban area and the predominance of diesel emissions in the suburban area. The InP:InP + BghiP ratio determined in this study indicate a significant contribution from diesel exhaust (Rogge *et al.* 1993; Simcik *et al.* 1999). On the basis of the diagnostic ratios of PAHs, emissions from gasoline and diesel engines are identified as major sources of PAHs at our study locations.

Table 4. Diagnostic PAH ratios (average ± SD) in atmospheric deposition from an urban and a suburban area of Korea

Ratios	Urban area	Suburban area
FluA:FluA + Pyr	0.45 ± 0.07	0.51 ± 0.08
InP:BghiP	0.76 ± 0.31	1.06 ± 0.38
InP:InP + BghiP	0.42 ± 0.10	0.50 ± 0.10

Factor Analysis

To further characterize the emission sources of PAHs to the atmosphere, we performed factor analysis. The 16 PAH compounds measured at both sites were subjected to factor analysis with Varimax rotation. The factors, with correlation-matrix eigenvalues >1 for the urban and the suburban areas, are listed in Table 5.

For the urban area, three factors accounted for 84% of the total variance in the data. Factor 1, which explained 58% of the variance, showed high loadings for FluA, PhA, fluoreine (Flu), and anthracene (AnT). The presence of these compounds can be attributed to both coal combustion (Harrison *et al.* 1996; Mastral *et al.* 1996) and diesel exhaust emissions (Miguel *et al.* 1998; Ho *et al.* 2002). In addition, factor 1 had relatively high loadings for acenapthylene (AcPy), acenapthene (AcP), benzo[a]anthracene (BaA), and chrysene (Chr). Simcik *et al.* (1999) suggested that AcPy is indicative of vehicle emissions. BaA and Chr were the major components of emissions from coal combustion (Duval & Friedlander 1981). Thus, factor 1 may be related to sources from both coal combustion and diesel exhaust. Factor 2, which explained 16% of the variance, had high loadings for BghiP and BaP and a moderate loading for InP, all of which are indicators of gasoline emissions. Miguel *et al.* (1998) reported that particle samples collected from a tunnel were enriched with BghiP; such enrichment is characteristic of vehicular emissions from gasoline engines. Guo *et al.* (2003) also noted that BaP, BghiP, and InP are indicators of gasoline emissions. Factor 3, which explained 11% of the variance, showed high loadings for DbA and InP and moderate loadings for naphthalene (NaP) and

Table 5. Factor analysis of PAHs in atmospheric bulk deposition from an urban and a suburban area of Korea (Factor loading >0.5 listed)

	Urban area			Suburban area			
Variable	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 4
NaP			0.70				0.72
AcPy	0.85			0.82			
AcP	0.86						0.80
Flu	0.92			0.65			
PhA	0.93			0.79			
AnT	0.87			0.89			
FluA	0.93			0.81			
Pyr	0.64					0.74	
BaA	0.83			0.86			
Chr	0.83			0.77	0.52		
BbF	0.78			0.78	0.55		
BkF	0.53		0.68	0.81			
BaP		0.90			0.80		
InP			0.78		0.86		
DbA			0.85		0.73		
BghiP		0.94			0.85		
% of the explained variance	57.5	15.5	11.1	53.3	12.5	9.32	6.98

benzo[k]fluoranthene (BkF). It is not possible to associate this factor with one or more sources because each compound with a high loading in factor 3 has a different source. Indeed, there exist numerous poorly defined sources of PAH in urban environments. Therefore, factor 3 suggests influence from multiple sources.

For the suburban area, four factors were obtained, collectively accounting for 82% of the total variance in the data. Factor 1, which accounted for 53% of the variance, had high loadings for AnT, AcPy, and BaA and moderate loadings for FluA, BkF, and PhA. These compounds are associated with both coal combustion and diesel exhaust, as mentioned previously. Factor 2, which accounted for 13% of the variance, had high loadings for the HMW PAHs, such as InP, BghiP, BaP, and DbA, the main components of gasoline vehicles. Thus, factor 2 is evidently related to gasoline vehicles. Factor 3, which accounted for 9.3% of the variance, had a high loading only for Pyr, indicating that Pyr was derived from other sources. Duval and Friedlander (1981) showed municipal solid waste incineration to be a source of Pyr, suggesting that our factor 3 can be assigned to incineration-related sources. Factor 4, which accounted for 7.0% of the variance, had high loadings for AcP and NaP. Because these compounds are present mainly in the gas phase and are removed by wet deposition, it is probable that their sources are located in the vicinity of the collection site. Therefore, this factor may be associated with a stationary local combustion source.

The results obtained through factor analysis for our atmospheric depositional samples provided better insight into PAH sources than did the data from the diagnostic ratios. However, there exists considerable similarity among the profiles of PAHs from different source categories.

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