Source apportionment of the particulate PAHs at Seoul, Korea: impact of long range transport to a megacity

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Source apportionment of the particulate PAHs at Seoul, Korea: impact of long range transport to a megacity

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Abstract

Northeast Asia including China, Korea, and Japan is one of the world's largest fossil fuel consumption regions. Seoul is a megacity in Northeast Asia and its emissions of air pollutants can affect the region and is also affected by the regional emissions. To understand the degree of this relationship, major sources of ambient particulate PAHs at Seoul, Korea were identified and quantified based on the measurement data between August 2002 and December 2003. The chemical mass balance (CMB) model was applied. Seven major emission sources were identified based on the emission data in Seoul and Northeast Asia: Gasoline and diesel vehicles, coal residential, coke oven, coal power plant, biomass burning, natural gas (NG) combustion. The major source of particulate PAHs at Seoul on the whole measurement period was gasoline and diesel vehicles, accounted for 31% of the measured particulate PAHs levels. However, the source contributions showed distinct seasonal variations. High contributions of biomass burning and coal (residential and coke oven) were shown in fall and winter accounted for 63% and 82% of the total PAHs concentration, respectively. Since these sources were not strong in and around Seoul, these might be related to transport from outside of Seoul, from China and/or North Korea. It implies that the air quality in the large urban city such as Seoul can be influenced by the long range transport of air pollutants such as PAHs.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic pollutants mainly formed during incomplete combustion processes of fossil fuels. Some of PAHs which mainly exist in the particle phase in the atmosphere are reported to be probable human carcinogens (ATSDR, 1995). Moreover, transformations of PAHs on particles such as nitro-PAHs are more toxic than parent PAHs (Marr et al., 2006; Sasaki et al., 1997). Thus, the studies for the PAHs in atmosphere have been progressed con-

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tinually since 1900 and PAHs are designated as one of the considered Persistent Toxic Substances (PTS) in central and northeast Asia (Region VII) under the Stockholm convention (UNEP, 2002). Recently, heterogeneous reactions of particulate PAHs might be as surrogates for heterogeneous chemistry of many type of organics and such reactions could change the particles hydrophilicity in cloud processing (Marr et al., 2006; Esteve et al., 2003, 2004, 2006).

The impact of air pollution in Northeast Asia to the region itself and all over the world has been recognized well. In addition, Northeast Asia is the world's largest coal consumption region (IEA, 2006). Thus, it has been speculated that emissions and the impact of PAHs would be large from this region.

Since Seoul, Korea is one of the mega-city in Northeast Asia with 10 million inhabitants and 2.5 million vehicles, the large emission of PAHs from Seoul itself might be expected. In addition, South Korea is surrounded by China and Japan as shown in Fig. 1, thus, Seoul might be influenced by transport of air pollutants from these areas in addition to local sources. Thus, understanding the contribution of the various emission sources to the ambient PAHs level in Seoul is essential in order to assess public exposure to PAHs and their associated health risks in Northeast Asia. Moreover, characterizing the emission sources of the ambient PAHs in Seoul will help to understand the effect of PAHs emission and transport from the mega-city in this region.

In Korea located in Northeast Asia, the criteria air pollutants such as SO_2, NO_x, CO, O_3, and PM10 (particulate matter with the aerodynamic diameter less than or equal to $10\,\mu$m) have been monitored extensively at 198 stations in 2004 (MOE, 2005). However, monitoring of PAHs in Korea has not been well established compared to the criteria air pollutants and their levels have been reported by only few studies (Bae et al., 2002; Park et al., 2002; Lee et al., 2005; Lee et al., 2006a). Bae et al. (2002) and Lee et al. (2006a) have measured the size distributions of particulate PAHs and their dry depositions in 1999 in several areas of Korea. They found that the ambient levels and dry deposition amounts of PAHs in rural areas were comparable to those in Seoul. Park et al. (2002) measured gaseous and particulate PAHs concentrations using a TSP

sampler at Seoul during four intensive sampling periods. However, in these studies, identifications of sources to the ambient PAHs concentrations have been not identified. Further, trend of the PAHs level was not identified in these studies.

Receptor models have been widely used as a tool in air pollution source apportionment studies. In the receptor model, the contributions from major sources are apportioned from the concentration profiles of pollutants found at a specific receptor site. Fundamentals of the receptor models have been described by Friedlander (1973) and Hopke (1991). The chemical mass balance (CMB) model is a class of receptor model. On the basis of the law of mass conservation, the CMB model calculation seeks to find the best-fit linear combination of the chemical compositions of the effluents from specific emission sources that is needed to reconstruct the chemical composition of chosen atmospheric samples (US EPA, 2004). The CMB model had been applied to the PAHs levels for some studies (Duval et al., 1982; Li et al., 2003). In addition, some CMB applications for ambient organic pollutants including PAHs as tracers for combustion sources were attempted in Beijing (Zheng et al., 2005) and southern California (Schauer et al., 1996). However, in Korea, no study has been carried out to apportion the major sources of PAHs.

The objective of this study is to understand the contribution of the major sources for PAH at Seoul by applying the CMB model and to quantify the impact of regional transport of PAHs to the air quality in Seoul.

2 Measurement data

Samples were collected on a 3 m high platform on the roof of Asan hall in Ewha Womans University, a five-story building of 15 m height. It is adjacent to a road in west, Mt. Ansan in north, and stands on a hill commanding the campus.

The sampling and analytical procedure used in this study was described in detail in Lee et al. (2006b). Sampling was carried out for 24 h at every sixth day with no rain from August 2002 to December 2003. Total of 68 samples were obtained. The

sampling procedures used in this study conformed to the methods of TO-13A (US EPA, 1999). In brief, a high volume TSP sampler (Ticsh, TE-1000) was operated at a calibrated flow rate of $0.225\,m^3\,min^{-1}$ to obtain a total sample volume of greater than $300\,m^3$ over the 24 h period. Particles were collected on the pre-baked (at 400°C for

5 5 h) quartz fiber filters (QFFs, Whatman, QM-A, 10.16 cm diameter).

Particulate PAHs samples collected on the QFFs were extracted by ultrasonication with dichloromethane (DCM) solvent. The extracts were filtrated through a $0.45\,\mu m$ pore size syringe filter. These extracts were concentrated at 20°C to a volume of 1 mL using an evaporator (Zymark, Turbovap 500). Then phenanthrene-D_{10} was added to

10 each concentrated sample solution as an internal standard for analysis.

Seventeen PAHs compounds were identified and quantified using a Hewlett Packard 5890 gas chromatograph (GC) equipped with a 5972 mass selective detector (MSD). The names of the analyzed PAH compounds and their abbreviations are given in Table 1. The QFFs field blanks were prepared and analyzed for each set of field samples

15 with the same procedure. The mean extraction recovery for particulate PAHs ranges from 80 to 94 % and these recoveries are accounted for in the concentration calculation. The accuracy of the analytical procedure was tested through the analysis of National Institute of Standards and Technology (NIST, USA) standard reference materials (SRM) 1649 urban dust sample. The extraction recoveries and analytical accuracy

20 results for the SRM 1649 samples are also presented in Table 1. The extraction and analysis methods adopted in this study gave reliable results.

In this study, 17 PAH compounds were identified and quantified. However, Nap, Ace, Acy, and Flu exist predominantly in the gas phase in the atmosphere. Because the major focus of this study is on the particulate PAHs concentration, these compounds

25 are excluded for further data analysis.

3   CMB modeling and identification of major sources

The CMB 8.2 program (US EPA, 2004) was used to estimate the source contribution of the ambient concentrations for the particulate PAHs. In running the CMB 8.2 model, default values were used for the option sets such as the iteration delta, the maximum source uncertainty and the minimum source projection. The option of source elimination was applied in all results. The diagnostics for the results explained by the CMB model (US EPA, 2004) are given in Table 2.

To select probable major sources of PAHs affecting at Seoul, major combustion and related activities at Seoul and Northeast Asia are investigated. In Fig. 2, the temporal trends of consumption for fossil fuels at Seoul between 1990 and 2003 are shown. The Ministry of Environment (MOE) in Korea has limited the use of solid fuel and heavy oils for heating and cooking in the Seoul metropolitan areas (SMA) since 1985 and strongly enforced the rule since 1995 (MOE, 2005). Thus, the amounts of coal consumption for residential, industrial, and commercial sectors at Seoul have been rapidly decreased since 1990 and the usage of coal has been negligible since 1995. The amount of natural gas (NG) consumption at Seoul has been rapidly increased since 1990. The amount of petroleum consumption at Seoul has not been changed much since 1990.

The major types for petroleum were butane (26%), gasoline (25%), diesel (24%), and propane (14%) at Seoul in 2003. These had been mainly used in transportation sector (94% of butane consumption, 99% of gasoline consumption, and 84% of diesel consumption were used for transportation (MOCIE, 2004)). Sixty percent of the total number of vehicles used gasoline vehicle at Seoul followed by diesel (27%) and liquefied petroleum gas (LPG) (12.5%). The major component of LPG is butane and LPG is used for taxi cabs. About 66% of NG was used in residential sector (heating, cooking, and others) and 22% in commercial sector at Seoul in 2003 (MOCIE, 2004). Thus, the main fossil fuels used at Seoul were petroleum for vehicles and NG for residential heating and cooking.

In Fig. 3a, the trends of the fossil fuel combustions in China, Japan, and Korea,

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three major air pollutant emission countries in Northeast Asia (Kim, 1999), are shown. The amounts of coal consumption in Japan and Korea have not been changed much since 1990. However, that in China has been rapidly increased since 2000. Moreover, the consumption of coal in China was the first in the world (about 34% of the world consumption in 2003) and about one order higher than those in Korea and Japan (BP, 2005). Thus, the influence of PAHs emission from coal combustions in China might influence the PAHs level in Korea significantly. Coal was mainly used for industry (49%), power plant (37%), and residential (14%) at China in 1995 (Streets et al., 2001). Streets et al. (2001) reported that BC emissions arose primarily from the production and use of coke in the steel industry and from uncontrolled coal-fired stokers in the industry sector. As mentioned before, because PAHs are associated with BC, coke oven in steel work might be an important source of PAHs in the industry sector.

In case of petroleum (Fig. 3b), the amounts of petroleum consumption in Japan and Korea has not been changed much while that in China has been constantly increased since 1990. Total consumption of petroleum in Japan has been three of four times higher than in China and Korea in the early 1990s, but, petroleum consumption in China became larger than that in Japan in 2003. The fractions of the petroleum consumption in China and Japan in 2003 were 8.2 and 6.4% of the world consumption, respectively (BP, 2005). The major product groups for petroleum consumption in China and Japan were gasoline and middle distillates (about 57 and 68% of the total petroleum consumption, respectively) in 2003 (BP, 2005). Gasoline sector consisted of aviation and motor gasoline and light distillate feedstock. Middle distillates sector consisted of jet and heating kerosine, and gas and diesel oils. Although some heating fuels were included in the gasoline and middle distillates sectors, majority of petroleum be consumed for transport, especially, gasoline and diesel vehicles. In Korea, major products for petroleum consumption were naphtha (35% of the total consumption), diesel (20%), bunker-C (15%), and gasoline (8%) in 2003 (MOCIE, 2005). The NG consumption in Japan has been about three times higher than those in China and Korea since 1990 and the temporal trend were similar among China, Japan, and Korea (Fig. 3c).

Biomass burning activities have been wide spread in Asia; field burning after harvest, biofuel burning in rural areas for heating and cooking, and forest fire (Streets et al., 2003; Zheng et al., 2005; Lee et al., 2006a). The estimated annual amounts of biomass burned in whole Asia, China, Japan, and Korea were 727.3, 187, 3, and 1.9 Tg per year (Streets et al, 2003). Thus, China emitted 25.6% of the total biomass emissions in Asia. Thus, high contribution from biomass burning for PAHs in Northeast Asia including Seoul might be also expected.

Based on the fuel consumption patterns at Seoul and the countries in Northeast Asia, seven major PAHs sources were selected; petroleum for (1) gasoline and (2) diesel vehicles, coal for (3) residential heating, (4) coke oven emission, and (5) power plant, NG for (6) residential heating, and (7) biomass burning.

Fully developed local source profiles for Seoul and Northeast Asia are not available and the profiles in each country should be different. Thus, in this study, the best available estimates of the source profiles from previous studies in worldwide were adopted. Catalyst-equipped gasoline vehicle profile is used because leaded gasoline has been phased out since 1988 at Seoul (MOE, 2005). In China, Euro I emission standard for whole China and Euro II standard for metropolitan areas were adopted (He et al., 2001).

Butane was one of the major petroleum products used in Seoul for transportation. However, there is no available source profile for butane. Since the estimated PAHs emission amount from LPG consisting of butane was about one-tenth of that from gasoline in Korea (SNU, 2000) and the combustion efficiencies for butane and NG are very high, we does not include it in the analysis.

The source profiles of coal related emissions were obtained from Li et al. (2003) for power plant and residential and from Yang et al. (2002) for coke oven. The source profiles for gasoline and diesel vehicles were from Rogge et al. (1993a), biomass burning from Rogge et al. (1993b), and NG combustion from Rogge et al. (1998). These source profiles used in this study are summarized in Table 3. The source profiles are fractional compositions of individual PAH compounds and, thus, the sum of source profile value

for all PAH compounds is unity for each of the sources.

Due to the lack of sufficient data for DahA and Ind in the used source profiles and strong photodegradation of BaP and Anthr, these compounds were not selected as the fitting species in running the model. The source profiles used in this study contained only particulate phase PAHs. For uncertainties of the source profiles, 15% of the reported values were used since no information was reported on the accuracy of the values (Na, 2001; Zheng et al., 2005).

The ambient measurement data of particulate PAHs from August 2002 to December 2003 were used for the source apportionment study. In this study, to account for the loss of PAHs concentrations due to photodegradation and/or ozonolysis of the PAHs, the concentrations of individual PAHs compounds were normalized to that of BeP since photodegradation and ozonolysis of BeP would not be large compared to other compounds. For example, half-live of BeP under the simulated atmospheric condition was one order higher than that of BaP and Anthr (Katz et al., 1979). The uncertainties for the ambient data were used 15% (the variation of the measurement) of the concentration for individual PAH compounds since the uncertainity for the MDLs value of individual PAH compounds were very small.

4 Results and discussion

4.1 General characteristics

The CMB model was applied for the whole period and four seasons, respectively. Collinearity problem was not observed during the modeling due to the distinctively different marker species of the each source profiles. The statistical values for the model performance of this study were arranged in Table 2. Except summer, all of the statistical values in this study were in the acceptable ranges. In summer, due to the high photochemical reactions, these variations were out of range values. The degrees of freedom (DF = number of fitting species – number of fitting sources) were small (ranged from 3

to 8 in all results (n=68)) since the number of fitting species were limited. Due to the problem to accurately separate the contribution of gasoline and diesel vehicle emission at Seoul using the source profiles for USA, the sum of the contributions of gasoline and diesel vehicles was reported as transport in this study.

Six sources for particulate PAHs at Seoul on annual basis were identified by the CMB model as shown in Fig. 4. The major source of particulate PAHs was transport (31±22%), coke oven (16±7%), coal residential (15±9%), and biomass burning (14±15%). NG combustion (4±6%) and coal power plant (3±1%) were minor sources for the PAHs level at Seoul on the annual base.

Even on the seasonal base, the contributions from the coal power plant and NG were small. This is due to the high efficiency of combustion and particle control equipments in coal power plants and high efficiency combustion in NG combustion. The small contribution of NG combustion was also found by Zheng et al. (2002) and Schauer et al. (1996) in southeastern US. Thus, it is likely that the contribution from LPG be also small as stated in Sect. 3.

Zhang et al. (2005) carried out a source apportionment study for Beijing, China with more than 100 organic carbon (OC) species including some PAH compounds. The major sources for OC species in Beijing were gasoline and diesel vehicles (17.3±6.9 %), biomass burning (16.1±18.1%), dust (11.7±8.1%), and coal combustion (9.8±3.9%). The contribution of vehicles for OC species was also the highest on the annual base in Zhang et al. (2005).

The source contributions showed distinct seasonal variation (Fig. 5). The PAHs concentrations from transport emissions varied widely from 2.30 to 10.3 ng m^{-3} (10~49% of the total PAHs concentrations) at Seoul. The transport emissions were most district in spring (49%).

4.2 Effect of biomass burning

The contribution of biomass burning was distinct in fall and winter, accounting for 4.51 ng m^{-3} (21%) in fall and 20.3 ng m^{-3} (40%) in winter, respectively. No signifi-

cant biomass burning contributions for PAHs was found in spring and summer. The importance of the biomass burning to air quality in Northeast Asia was reported by several measurement and emission estimation studies related to the frequent biomass burning activities after harvesting during fall (He et al., 2001; Zheng et al., 2005; Lee
5 et al., 2006a). Also, forest fires, representing one of biomass burning were frequent in spring all over Northeast Asia (Lee et al., 2005). However, the highest biomass burning contribution was estimated in winter in this study. In order to verify the contribution of biomass burning in fall and winter, we tried to find the another particulate PAHs emission profile for biomass burning and only one suitable data set was obtained from
10 Schauer et al. (2001). Recently, some studies for biomass burning profile including PAH compounds were reported in Europe, but these showed the result of total (gas + particle) PAHs profile (e.g., Hedberg et al., 2002; Ross et al., 2002). When the source profile from Schauer et al. (2001) was used instead of the profile used in this study, the source contributions for particulate PAHs was also high in fall and winter.

15 Moreover, forest fires during sampling day in spring and summer were not distinctly observed in Northeast Asia (ATSR world fire atlas in Ionia web site, http://dup.esrin.esa.int/ionia/wfa/index.asp). Thus, it might be related to the heavy usage of biofuel during winter rather than forest fires in Northeast Asia, especially, in China. Biofuel dominated rural residential energy supply and BC emission from biofuel was estimated
20 to 45% of total in residential sector in China. Moreover, the BC emission from biomass burning in residential sector in China was about seven times higher than that in field combustion (Streets et al., 2001).

The remaining question is the degree of contribution from China from biomass burning. An indirect indicator is the PAHs level observed at Gosan, a background site in
25 Korea. Lee et al. (2006b) reported that the average level of particulate PAHs in cold period (from November to March between 2001 and 2004) was 6.43 ± 5.74 ng m^{-3} with the maximum value of 20.9 ng m^{-3} at Gosan. They claimed that most of the observed PAHs were from China based on the backward trajectory analysis and the ratio values of individual PAH compounds. This concentration level observed at Gosan is smaller

than the estimated average value of biomass contribution in winter (20.3 ng m^{-3}) at Seoul. Thus, it suggests that not all of the estimated biomass burning contribution in winter at Seoul were influenced by China and/or the transport pattern from China to Seoul was different from that to Gosan due to shorter distance between China and
5   Seoul.

    One possible PAHs source is North Korea. The information for the biomass burning in North Korea are not available, but, high emission of PAHs from biofuel in North Korea is also expected during winter. According to the report of IEA (2006), the amount of primary solid biomass used for fuel in 2003 was 42 795 GWh in North Korea, about
10 three times higher than that in South Korea, although the oil consumption in North Korea is far lower than that in South Korea, 1680 and 208 264×10^3 tonnes, respectively (IEA, 2006). In the report of IEA (2006), there is no consumption of NG in 2003 in North Korea.

4.3 Effect of coal combustion

15 The contribution of coal for residential usage increased drastically in winter (28%) compared to other seasons (8–10%). The amount of coal residential in winter (13.7 ng m^{-3}) was about one order higher than that in other season (0.62–2.14 ng m^{-3}) mainly due to the residential heating during winter. This finding is in agreement with the result by Zheng et al. (2005), in which the importance of coal combustion became obvious in
20 January accounting 13.9% of the measured OC species in January at Beijing. However, in the result of Zheng et al. (2005), the contribution of coal combustion was also high in October (12.7%). In this study, the contribution of coal residential was relatively low in fall (10%) compared to winter (28%). This is probably due to the impact of coal combustion in Beijing being local emissions while that Seoul being transport from
25 outside.

    The major fossil fuel for residential heating at Seoul and surrounding areas is NG. Thus, the influence of PAHs emission from coal residential might be transported from

the outside of Korea, especially from China due to the high consumption of coal for residential heating and cooking (He et al., 2001; Streets et al., 2001) and dominant wind direction being the westerly and northwesterly during winter as shown in Fig. 6 (Lee et al., 2006b). The backward trajectory of air parcels were calculated for 09:00 LT (sampling starting time) on the sampling days using the Hybrid Single-Particle Lagrangian Intergrated Trajectory (HYSPLIT4) model (http://www.arl.noaa.gov/ready/hysplit4.html) developed in National oceanic and atmospheric administration (NOAA).

Moreover, the contribution of PAHs from coal in North Korea might be significant. The coal consumption in South Korea was two times higher than that in North Korea, but, about 89% of total coal was consumed at power plants in South Korea (IEA, 2006). In North Korea, about 85% of total coal was consumed by industry sector and the coal consumption from industry sector in North Korea was three times higher compared to South Korea (IEA, 2006). As mentioned in Sect. 4.1, the emission of PAHs from the coal combustion power plant was small due to high combustion efficiency and particle control equipments. Thus, the contribution of coal combustion from South Korea might be small. While, there is a possibility that a significant fraction of the contribution from coal combustion be from North Korea in addition to the contribution from biomass burning.

The high contribution of PAHs concentrations from coke oven was observed in fall (6.64 ng m^{-3}, 31%) and winter (6.98 ng m^{-3}, 14%). In Korea, two steel works having coke oven were located at south-east (Pohang) and south-west (Gwangyang) of Korea shown in Fig. 1. The main directions of the wind at Pohang and Gwangyang were from southwest and northwest, respectively. In China, representative steel works are mainly located near to Beijing and Shanghai (Price et al., 2002). Moreover, the prevailing wind was the northwesterlies observed during the sampling period in fall and winter as shown in Fig. 6. The wind directions were variable in spring and summer. According to Streets et al. (2001), the BC emissions from coal in industry sector were 84% of total in China and this were mainly related to the production and use of coke in the steel works. Thus, it might be related to the transport from China not rather than the influence of

local emissions in Korea. Also, the influence of coke oven emission from North Korea is expected.

Because the coal residential profile used in this study was obtained for Europe, these might not be an accurate indicator to explain the influence from China. Thus, we tried to find PAHs emission profile from residential coal combustion measured in Northeast Asia, especially in China and only one suitable data set was obtained from Chen et al. (2004). When the source profile from Chen et al. (2004) was used instead of the profile used in this study, the seasonal trend of the source contributions for particulate PAHs was similar with this study result. But, there were some statistical problems such as the values of ^{2} being higher compared to the original result. It indicates that some PAH compounds concentrations were not well explained by the source contribution estimates of Chen et al. (2004). Thus, the source profile for coal residential shown in Table 3 by Li et al. (2003) was used in this study.

4.4 Implication

The high concentrations of particulate PAHs in winter at Seoul were mainly due to the increase of the emissions from biomass burning, the coal residential heating, and coke oven. These account for 82% of the total PAHs concentration and mainly transported from outside of Seoul, especially China. Moreover, the influence of PAHs emission from North Korea is expected even.

Seoul is the largest city in Korea, however, the long range transport of air pollutants such as PAHs was clearly observed. Therefore, in order to control the level of hazardous air pollutants such as PAHs at urban areas, the transport from outside of urban areas as well as the local emission source must be considered. Further, the international convention such as Stockholm convention should be needed for managing the level of PTS and health effect in global environment. Another implication is the potential impacts on climate change such as radiation balance because PAHs are associated with BC particles and the atmospheric behavior of PAHs is changed by the long-range transport from Northeast Asia.

It is important to note that application of local source profiles is the key for reliable CMB results. Uncertainty is inevitable when not using source profiles from local sources. Thus, further study is warranted to reduce the uncertainties related to the source profiles.

5 Summary

Seoul is a large city itself, besides, closely surrounded by China and Japan which have several mega-cities. Thus, Seoul might be influenced by transport of air pollutants from these areas in addition to local sources. The CMB model was used to apportion the major sources of particulate PAHs at Seoul based on the patterns of fossil fuel consumption in Seoul and Northeast Asia. The major source of particulate PAHs at Seoul on an annual basis was gasoline and diesel vehicles accounting for 31% of total particulate PAHs. The source contributions of PAHs showed distinct seasonal variation. Coal emission (residential and coke oven) and biomass burning became important in fall (63% of total PAHs) and winter (82% of total PAHs). Since these sources were strong in China and the prevailing wind was the northwesterlies observed during sampling period in fall and winter, it might be transported from the outside of Korea, especially from China. Moreover, the influence of PAHs emission from North Korea is expected.

Mega-cities in Asia are significant sources for air pollutants. Thus, the project named mega-cities: Asia managed from NOAA is going on to investigate the contribution of pollutant emissions from Asian mega-cities to local and regional air quality. Related to the project of mega-cities: Asia, this study implies that even the large urban city such as Seoul can be influenced by the long range transport of air pollutants such as PAHs emitted from the outside of Seoul, especially other mega cities. Thus, the transport from outside of urban areas must be considered even at urban areas in order to control the level of PTS such as PAHs at urban areas.

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Table 1. Particulate PAHs extraction recovery and analysis results of the NIST SRM-1649 urban dust samples.

PAH compounds	Abbrev.	Recovery (%)	Certified value (μg kg^{-1})	Measured value (μg kg^{-1})
Naphthalene	Naph	91	–	–
Acenaphthylene	Acy	84	–	–
Acenaphthene	Ace	84	–	–
Fluorene	Flu	91	–	–
Phenanthrene	Phen	80	4.14±0.37	4.67±0.49
Anthracene	Anthr	90	0.43±0.08	0.46±0.06
Fluoranthene	Flt	91	6.45±0.18	5.50±0.18
Pyrene	Pyr	94	5.29±0.25	4.37±0.22
Benz(a)anthracene	BaA	83	2.21±0.07	1.84±0.59
Chrysene	Chry	87	3.05±0.06	3.67±0.54
Benzo(b)fluoranthene	BbF	90	6.45±0.64	5.43±0.40
Benzo(k)fluoranthene	BkF	86	1.91±0.03	2.27±0.29
Benzo(e)pyrene	BeP	84	–	–
Benzo(a)pyrene	BaP	86	2.51±0.09	2.92±0.82
Indeno(1,2,3-c,d)pyrene	Ind	88	3.18±0.72	2.87±0.66
Dibenz(a,h)anthracene	DahA	92	0.29±0.02	0.35±0.04
Benzo(g,h,i)perylene	BghiP	88	4.01±0.91	3.68±0.69

Source apportionment of the ambient PAHs at Seoul, Korea

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Table 2. Target values and modeling result values for the model performance measures (target values were set by US EPA, 2004).

Parameter	Target	This study				
		Whole period	Spring	Summer	Fall	Winter
R square (r^2)	0.8 to 1.0	0.94±0.06	0.95±0.03	0.90±0.04	0.93±0.05	0.99±0.01
Chi square (χ^2)	< 4.0	2.66±2.35	1.79±1.36	4.72±2.24	3.52±2.38	0.68±0.67
Percent mass (%)	100±20	83±10	82±4	72±9	83±9	94±2
Degrees of freedom (DF)	> 5	5±1 (n=68)				
C/M ratio (Calculated/Measured)	0.5 to 2.0	0.96±0.26 (n=680)				
R/U ratio (Residuals/Uncertainties)	−2.0 to 2.0	−0.39±1.39 (n=680)				

Table 3. Source composition of individual PAH compounds in the particle phase used for source profiles.

	Coal			Petroleum			
	Power plant	Coke oven	Residential	Gasoline vehicle	Diesel vehicle	NG combustion	Biomass burning
Phen	0.142	0.124	0.333	0.035	0.165	0.002	0.067
Anthr	0.016	0.024	0.070	0.004	0.022	0.000	0.010
Flt	0.160	0.084	0.216	0.078	0.176	0.167	0.127
Pyr	0.140	0.110	0.085	0.098	0.305	0.161	0.166
BaA	0.099	0.245	0.044	0.075	0.049	0.090	0.066
Chry	0.191	0.069	0.064	0.149	0.134	0.436	0.247
BbF	0.073	0.130	0.064	0.114	0.039	0.052	0.063
BkF	0.015	0.020	0.030	0.078	0.036	0.071	0.069
BeP	0.061	0.063	0.025	0.078	0.035	0.021	0.047
BaP	0.035	0.010	0.034	0.075	0.018	NA[a)]	0.068
Ind	0.025	0.023	0.018	0.018	ND[b)]	NA[a)]	0.013
DahA	0.005	0.008	NA[a)]	0.013	ND[b)]	NA[a)]	0.007
BghiP	0.039	0.089	0.016	0.184	0.022	NA[a)]	0.052

[a)] NA: Not analyzed, [b)] ND: Not detected.
The values of source composition for individual PAH compounds were normalized to total PAHs concentration in each source.
References for the source profiles: Coal for power plant and residential – Li et al. (2005), coke oven – Yang et al. (2002), gasoline and diesel vehicles. – Rogge et al. (1993a), NG combustion – Rogge et al. (1998), and biomass burning – Rogge et al. (1993b).
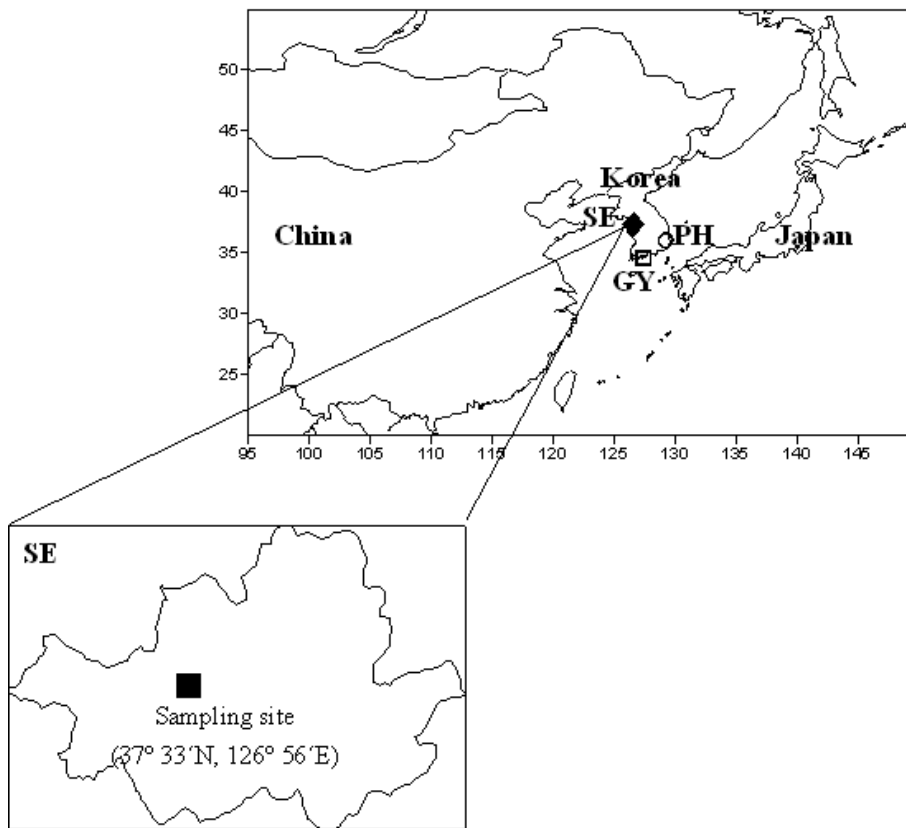
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Fig. 1. Map of the sampling site (SE) and coke oven locations (PH and GY) in Korea. (SE: Seoul, PH: Pohang, GY: Gwangyang).
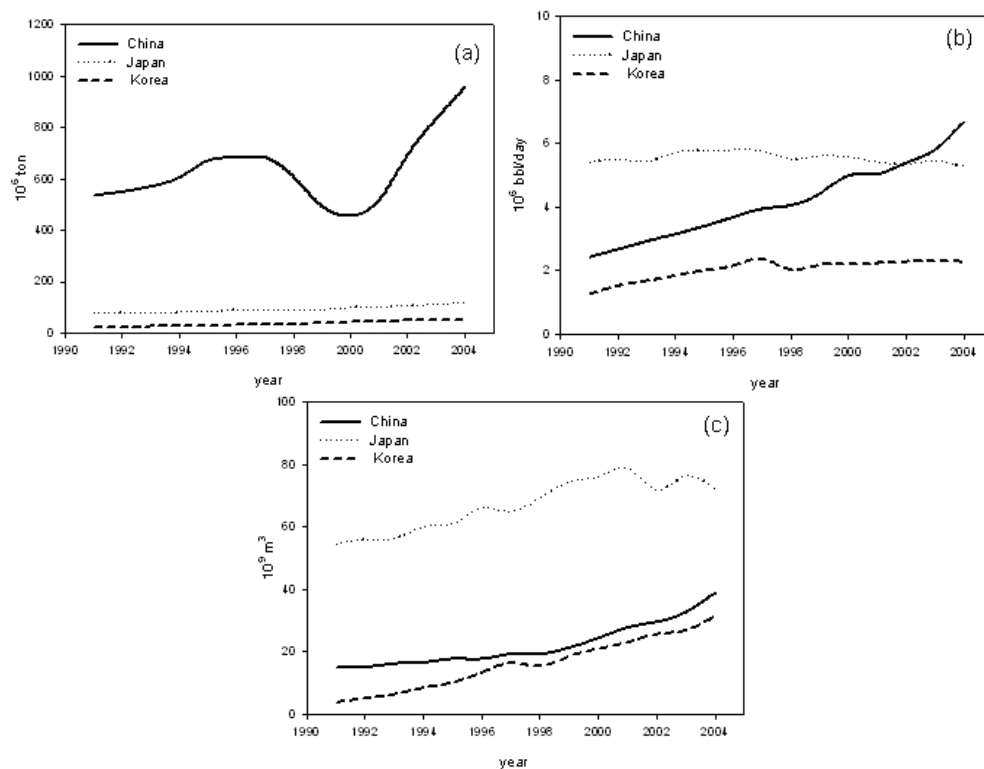
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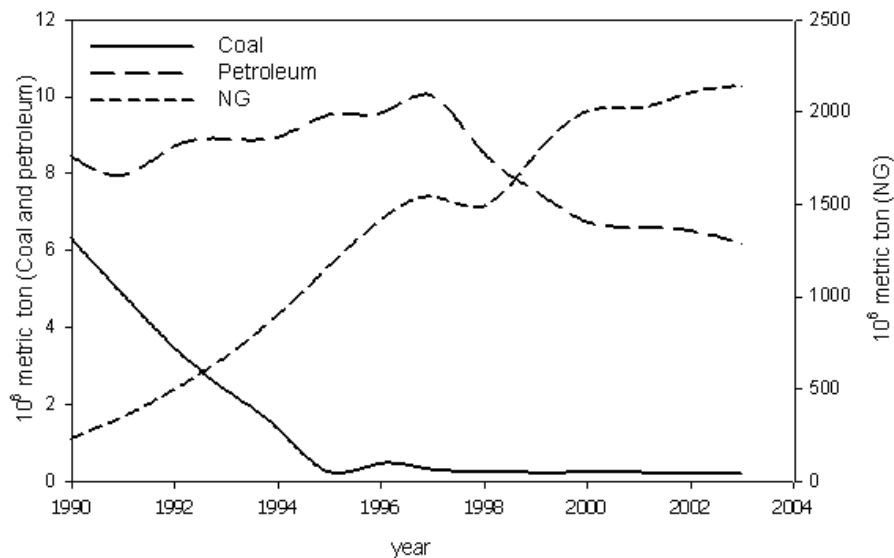
Fig. 2. Temporal trend of the consumption for fossil fuels at Seoul (MOCIE, 2004). Petroleum includes gasoline, diesel, kerosene, bunker-C, propane, and butane. NG stands for natural gas.

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Fig. 3. Temporal trend of **(a)** coal, **(b)** petroleum, and **(c)** NG consumption in China, Japan, and Korea since 1990 (BP, 2005; MOCIE, 2005).
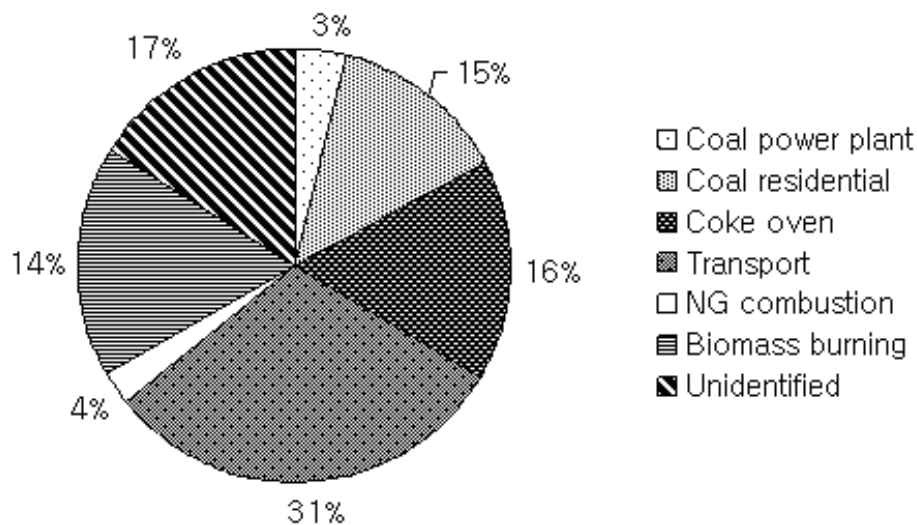
Fig. 4. The fraction of annual source contributions for particulate PAHs at Seoul.
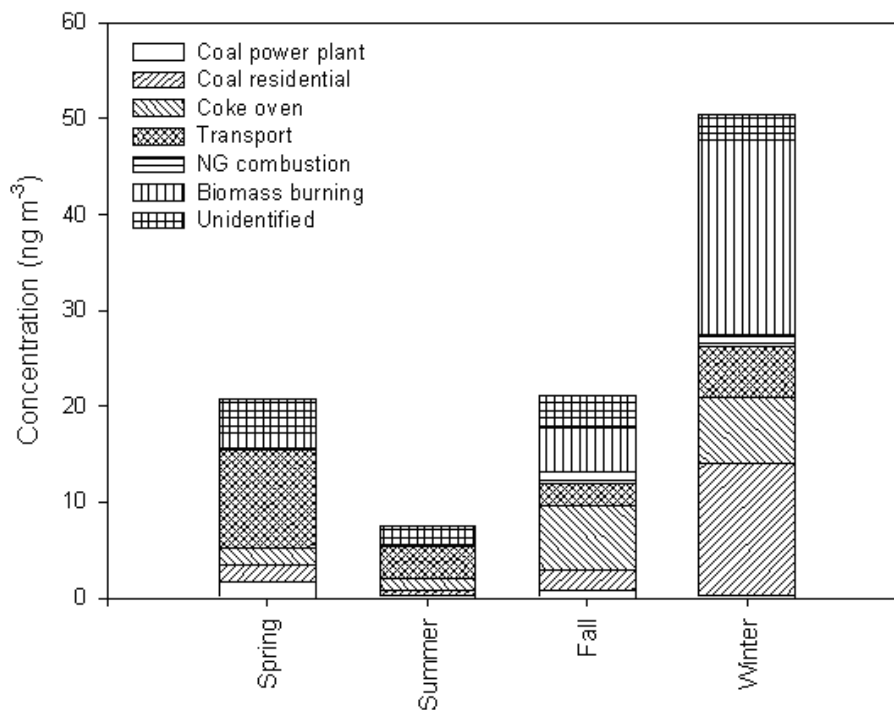
Fig. 5. Seasonal source contributions to particulate PAHs at Seoul.

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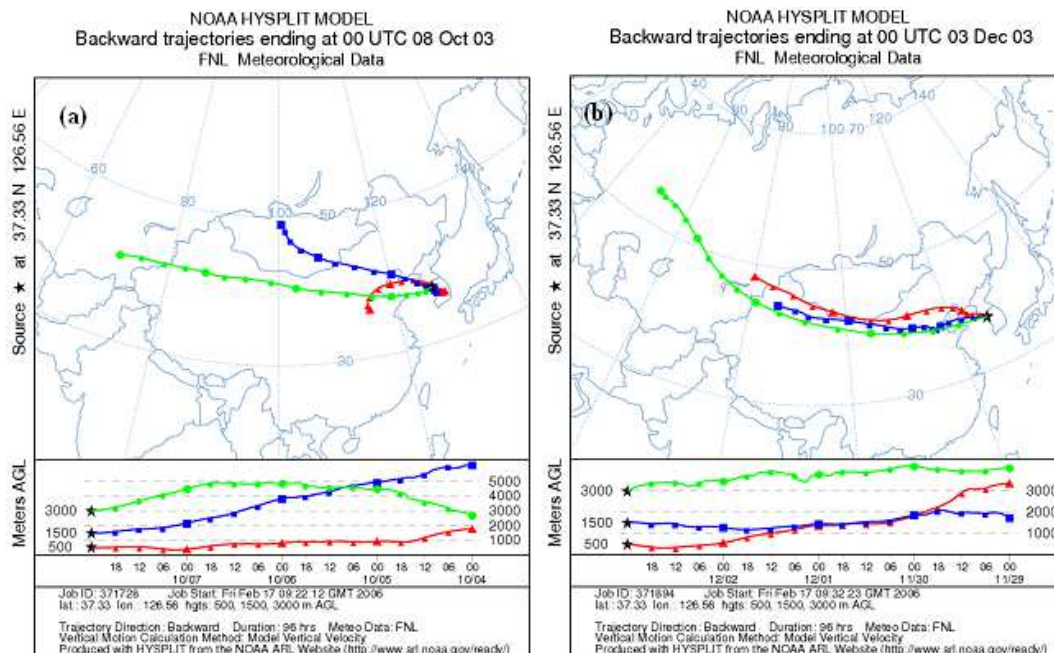
Fig. 6. Typical air parcels movement arriving at Seoul during the sampling period in **(a)** fall and **(b)** winter.

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