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Impact of Energy Consumption in Northeast Asia to the Particulate PAHs Levels and Composition at Seoul

Da Bin Jung[1#], Ye Seul Cho[1#], In Sun Kim[2], Ji Yi Lee[3], Yong Pyo Kim[1*]

[1] *Departent of Environmental Science and Engineering, Ewha Womans University, 11-1 Daehyun-Dong, Seodaemun-Gu, Seoul, 120-750, Korea*
[2] *Inspection and Analysis Division, Metropolitan Air Quality Management Office, Ministry of Environment, Wongojan-ro 34, Danwon-gu, Ansan, Korea*
[3] *Department of Environmental Engineering, Chosun University, 375 Seosuk-Dong, Dong-Gu, Gwangju, 501-759, Korea*

ABSTRACT

The impact of the energy consumption and environmental policies in northeast Asia to the air quality in Seoul, a megacity in South Korea was studied by combining the results of receptor modeling, air parcel trajectory analysis, energy consumption trend, and policies in the region. A chemical mass balance (CMB) modeling study was carried out based on the measurement data of particulate PAHs during 2002–2003 and 2006–2007 along with backward trajectory analysis. The reliability of the modeling result was checked by performance test and sensitivity analysis by including loss term in the source profiles. For both periods transportation and coal consumption for coke oven were major sources for the PAHs level at Seoul. However, during 2006 to 2007, the contribution from coke oven became larger than transportation, while during 2002 to 2003 the contribution from transportation was higher. Furthermore, it was observed that when air parcels moved from north China or Shandong Province the relative contribution from coke oven was higher than when air parcels moved from northeast/north China and North Korea. This observation was in accordance with the trends of coal consumption and cokes production in north China, Shandong Province, and northeast China. On the other hand, the contribution from transportation decreased, mainly due to the emission reduction in Seoul through several policies regulating vehicular emissions. It was suggested that the impacts of China to the air quality of Seoul might continuously keep increasing for some years ahead since the consumptions of coal in general and in coke oven, in particular, are increasing. Thus, more strict policies with additional regulation and introduction of more stringent standards should be considered. Also, uncertainty and limitation of this study result was discussed and further research directions are suggested.

Keywords: Coal consumption; Coke oven; Source contribution; CMB.

INTRODUCTION

China, Japan, and South Korea consumed 19.9% (1st in the world), 4.1% (5th), and 2.2% (9th) of the world total primary energy, respectively in 2011. In addition, the increase rate of the primary energy consumption in China is very high, about 8% per year (EIA, 2014). One of the characteristics of energy consumption in China is that the fraction of the coal usage is high compared to other countries. Sixty eight percent of the primary energy consumption is from coal in China in 2012 and it consisted of a half of the total coal consumption in the world in 2012 (BP, 2013). The importance of coal as an energy source in China is more prominent by comparing with neighboring countries. The amount of coal consumption in China has changed from 1,680 to 2,788 million short tons between 2002 and 2007, while those of South Korea and North Korea were from 81 to 98 million short tons and from 32 to 30 million short tons, respectively (EIA, 2013).

Generally, usage of coal emits more air pollutants than cleaner fossil fuels such as natural gas or refined petroleum. In addition, the degree of sophistication of the control technology affects the emission of air pollutants. For example, the differences of the emissions factors between indigenous ovens and machinery coke ovens were about factor of 10–100 for total suspended particles (TSP) and factor of 10 for sulfur dioxide in China (Huo *et al.*, 2012). Consequently, resultant emissions of anthropogenic air pollutants, especially from coal consumption should be huge. For example, He *et al.* (2007) found a continuous increase of NO_2 concentration

[#] Both authors contributed equally to this work.

[*] Corresponding author.
Tel.: +822-3277-2832; Fax: +822-3277-3275
E-mail address: yong@ewha.ac.kr

during the past decade with a sharp linear increase rate of 14.1–20.5% per year during 2000 to 2005 from the satellite observation data. Also, a huge amount of organic aerosols are emitted into the atmosphere through incomplete combustion of biomass and fossil fuels.

Ambient aerosols affect various aspects of air quality and global environment. Recently, the effect of aerosols on the climate change is becoming prominent. Kim *et al.* (2011) estimated the radiative forcing due to aerosols at a background site in Korea and found that the aerosol composition change has caused the radiative forcing from negative to positive values between 1992 and 2008. Also, aerosols are detrimental to human health (see, for example, Maynard *et al.*, 2007).

Seoul is located in northwest of South Korea as shown in Fig. 1, quite close to north and northeast China, and Shandong peninsula. The distance between Seoul and Shandong peninsula is less than 500 km. In addition to the geographical proximity, air parcel movements arriving at Seoul are mostly from northwest and north except summer (Lee and Kim, 2007; Kim *et al.*, 2013). Thus, even though Seoul is a megacity with 10 million inhabitants and 3 million vehicles in 2012, impact of the emissions of air pollutants in China to the air quality over Seoul might be significant. In other words, the air quality over Seoul would be sensitive to both local emissions and transport from outside. For example, based on various measurement and modeling study results, Kim (2010) suggested that about 30% of the particulate matter with an aerodynamic diameter equal to 10 μm or less (PM_{10}) concentrations in Seoul be from outside, mostly from China in the early 2000s.

The chemical mass balance (CMB) model is a class of receptor model. In the receptor model, the contributions from major sources are apportioned from the concentration profiles of pollutants found at a specific receptor site (Watson *et al.*, 1984; US EPA, 2004). 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 has been widely applied because it (1) yields an approximately unbiased solution to the CMB equations, providing model assumptions are met; (2) uses all the available chemical measurements, not just "tracer" species; (3) estimates the uncertainty of the source contributions based on precisions of both the ambient concentrations and source profiles; and (4) gives chemical species with higher precisions in both the source and receptor measurements greater influence than species with lower precisions (Watson *et al.*, 1984).

Polycyclic Aromatic Hydrocarbons (PAHs) are potent organic pollutants that consist of several aromatic rings. PAHs are mainly produced by incomplete combustion processes and some of PAHs compounds which mainly exist in the particle phase in the atmosphere are reported to be probable human carcinogens (ATSDR, 1995). Since the proportions of the emitted compounds are different from sources, PAHs composition data can be a good indicator to identify their sources and relative contributions of those sources.

Lee *et al.* (2011) collected particulate PAHs from 2002 to 2003 in Seoul and applied the CMB model (Lee and Kim, 2007). Lee and Kim (2007) found that major sources of the PAHs in Seoul were transportation, coal combustion, and biomass burning. In addition, they suggested that a majority of the PAHs from coal combustion processes is from China while major sources of the PAHs from biomass burning are from China and North Korea based on the characteristics of energy consumption in the region and meteorological conditions. Kim *et al.* (2013) have applied

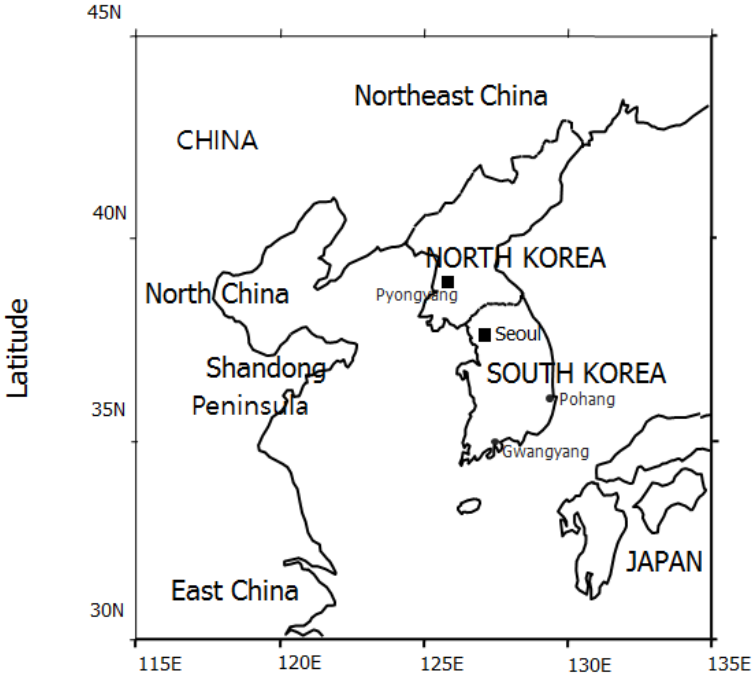

Fig. 1. Map of Northeast Asia.

backward trajectory analysis technique to the results of Lee and Kim (2007) and suggested that most of the PAHs from biomass burning observed in Seoul were from North Korea rather than China.

The objectives of this study are to identify the relative changes of the contribution of the major sources for PAH at Seoul during 2002–2003 and 2006–2007 by applying the CMB model and to analyze factors that affect changes of the major sources' contributions between the two periods. By doing so, it is expected to observe the change of both concentration and major contributors at a receptor site, Seoul due to the changes of the energy consumption amount and pattern and the environmental policies in Northeast Asia. In addition, limitations of this study are discussed and further research directions are suggested.

METHODOLOGY AND INPUT DATA

The CMB 8.2 model was used in this study (US EPA, 2004). The CMB model requires two types of data for estimating source contribution estimates; ambient measurement data and source profiles (US EPA, 2004). In this study, two sets of ambient measurement data were used. First data set was collected from August 2002 to December 2003 at Ewha Womans University, Seoul (37°33′N, 126°56′E), and second set was collected from August 2006 to August 2007 at Seoul National University, Seoul (37°27′N, 126°57′E). Sampling was carried out for 24 h at every sixth day with no rain for both periods. The detailed sampling procedure was explained in Lee *et al.* (2011) for 2002–2003 and Hong *et al.* (2009) for 2006–2007, respectively.

Seventeen 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 are excluded for further data analysis following Lee and Kim (2007). Therefore, the data of thirteen PAH compounds were analyzed (Phen, Anthr, Flt, Pyr, BaA, Chry, BbF, BeP, BaP, Ind, DahA, and Bghip). Sixty seven sample data for 2002–2003 and seventy three sample data for 2006–2007 were used in the CMB modeling.

The same source profiles were used for both periods since we are interested in the relative differences of the major contributors for two periods. The source profiles were selected based on the fuel consumption patterns in Seoul and the countries in Northeast Asia; coal for (1) power plant, (2) residential heating, and (3) coke oven, petroleum for (4) gasoline and (5) diesel vehicles, natural gas (NG) for (6) residential usage, and (7) biomass burning (Lee *et al.*, 2007; Kim *et al.*, 2013). The source profiles used in this study are summarized in Table 1. In this study, the sum of gasoline and diesel vehicles is reported as transportation. More information about PAHs data and source profile was available in Lee and Kim (2007) and Kim *et al.* (2013).

There are two probable areas of uncertainties; (1) whether the used source profiles are valid for both periods since emission characteristics might be changed during the two periods and (2) whether the source profiles are altered during transport from sources to Seoul due to the loss processes such as photochemical reactions in the atmosphere. These will be discussed in 'CMB Modeling and Backward Trajectory Analysis Results' section.

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 result. And due to the lack of sufficient data for DahA and Ind in the used source profiles and strong photo-degradation of BaP

Table 1. Source composition of individual PAH compounds in the particle phase used for source profiles.

	Coal			Petroleum		NG combustion	Biomass burning
	Power plant	Residential	Coke oven	Gasoline vehicle	Diesel vehicle		
Phen	0.142	0.333	0.073	0.035	0.165	0.002	0.067
Anthr	0.016	0.070	0.020	0.004	0.022	0.000	0.010
Flt	0.160	0.216	0.045	0.078	0.176	0.167	0.127
Pyr	0.140	0.085	0.079	0.098	0.305	0.161	0.166
BaA	0.099	0.044	0.112	0.075	0.049	0.09	0.066
Chry	0.191	0.064	0.120	0.149	0.134	0.436	0.247
BbF	0.073	0.064	0.129	0.114	0.039	0.052	0.063
BkF	0.015	0.030	0.084	0.078	0.037	0.071	0.069
BeP	0.061	0.025	0.111	0.078	0.035	0.021	0.047
BaP	0.035	0.034	0.101	0.075	0.018	NA[a)]	0.068
Ind	0.025	0.018	0.038	0.018	ND[b)]	NA[a)]	0.013
DahA	0.005	NA[a)]	0.016	0.013	ND[b)]	NA[a)]	0.007
BghiP	0.039	0.016	0.071	0.184	0.022	NA[a)]	0.052

[a)] NA: Not analyzed, [b)] ND: Not detected.

1) The values of source composition for individual PAH compounds were normalized to the total PAHs concentration in each source.

2) References for the source profiles: Coal for power plant, residential, and coke oven- Li *et al.* (2003), gasoline and diesel vehicles- Rogge *et al.* (1993a), NG combustion – Rogge *et al.* (1993b), and biomass burning – Rogge *et al.* (1998).

and Anthr, these compounds were not selected as the fitting species (Lee and Kim, 2007). The target values for the diagnostics parameters (US EPA, 2004) are given in Table 3.

To understand the influence of transport of PAHs from outside of Korea to Seoul, backward trajectory analysis was performed for the sampling days using the HYSPLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (web address: http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Resources Laboratory, Silver Spring, MD, USA). Following the approach used in Kim *et al.* (2013), three day backward trajectory for each sampling day was calculated at the starting height of 1500 m.

Backward trajectories were classified into four cases based on the air parcel movement as shown in Table 4. Case 1 includes the air parcels passed through eastern or northern China and over the Yellow Sea before arriving at Seoul, so these air parcels did not pass over northeast China nor North Korea. The trajectories that passed through northeast/north China and North Korea are classified as case 2. The trajectories moved inside of South Korea and not passed over other countries were classified as case 3. The trajectories whose route could not be classified into case 1, 2, and 3 were classified as case 4. Classification of the areas of China is shown in Fig. 1. North China includes Beijing, Tianjin, Hebei, Shanxi, and Inner Mongolia Province and northeast China includes Liaoning, Jilin, and Heilongjiang Province, respectively.

RESULTS AND DISCUSSION

CMB Modeling and Backward Trajectory Analysis Results

In Table 2, the concentrations of the total particulate PAHs for both periods are shown. The concentrations of particulate PAHs decreased during these periods, from 26.93 ng m^{-3} in 2002–2003 to 17.24 ng m^{-3} in 2006–2007, representing a remarkable reduction of 37% within 5 years. The decreasing trend was observed for all season. Especially, in summer when the transport from Asian continent was thought to be minimum (Park *et al.*, 2004; Lee *et al.*, 2006), the concentration decrease was the highest, 57%. As will be discussed in this section, this reduction might be due to the emission reductions in South Korea, especially, in Seoul.

Estimated relative contribution of six sources for the particulate PAHs at Seoul for the two whole sampling periods and each season are shown in Fig. 2. During 2002 to 2003, the sources of particulate PAHs were transportation (26%), coke oven (19%), coal residential (16%), biomass burning (16%), NG combustion (5%), coal power plant (4%), and remaining 14% being unidentified. During 2006 to 2007, the major sources were coke oven (37%), transportation (22%), biomass burning (15%), coal residential (10%), and unidentified (16%). The major sources' ranking is changed from transportation followed by coke oven during 2002 to 2003 to coke oven followed by transportation during 2006 to 2007.

The absolute estimated amounts from the sources were decreased from 2002–2003 to 2006–2007 except for coke oven. The contribution from coke oven increased from 5.05 ng m^{-3} during 2002 to 2003 to 6.17 ng m^{-3} during 2006 to 2007, a 22% increase. The estimated contributions from biomass burning have decreased significantly, a reduction of 58% between the two periods. Also, the estimated contributions from coal power plant and NG combustion were negligible during 2006 to 2007. The estimated contributions from these two sources were also the least between 2002 and 2003. This is probably due to the high efficiency of combustion and particle control equipment in coal power plants and high efficiency combustion in NG combustion (Lee and Kim, 2007).

The contributions from the major sources for each season

Table 2. The measured concentrations of the total particulate PAHs for both periods and seasons (unit: ng m^{-3}).

Period	Spring	Summer	Fall	Winter	Total
2002–2003	21.77 ± 16.11	7.08 ± 3.67	21.35 ± 24.38	50.50 ± 32.34	26.93 ± 28.44
2006–2007	11.24 ± 5.13	3.00 ± 1.12	17.18 ± 13.22	35.79 ± 14.55	17.24 ± 15.82

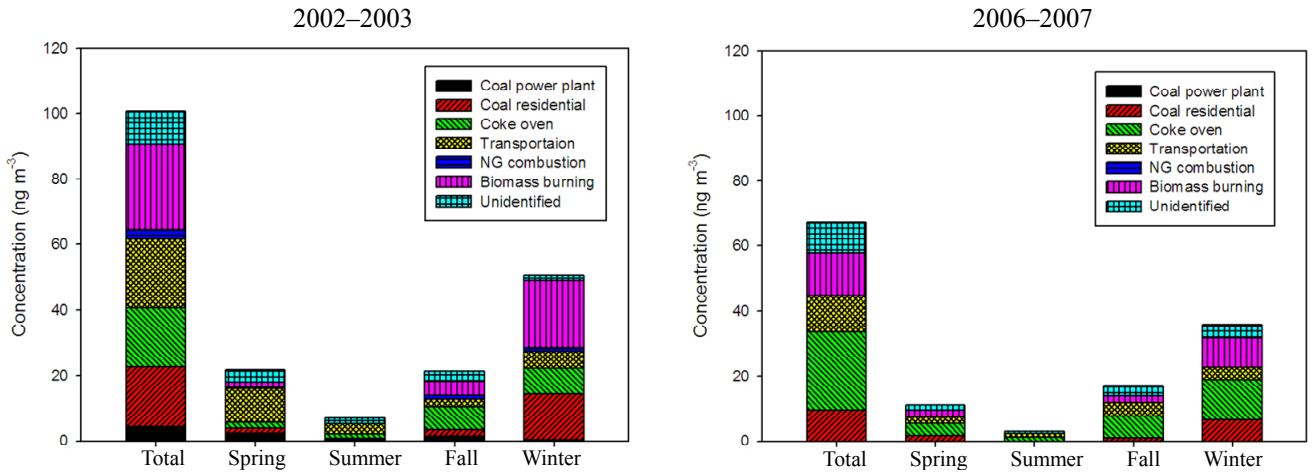

Fig. 2. Total and seasonal source contribution of particulate PAHs at Seoul for the two periods.

were also shown for both periods. In both periods, the estimated contributions from biomass burning in fall and winter were higher than other seasons. This was mainly due to the open burning after harvest in the fields (mainly in fall) and cooking and heating in rural areas (mainly in winter) (Kim *et al.*, 2013). The estimated contributions from coal residential were also higher in winter, mainly due to cooking and heating in the households (Lee and Kim, 2007).

It is necessary to check the validity of the modeling results since all the assumptions behind the CMB model might be not completely fulfilled. One example is that the actual source profiles might be changed while we used the same source profiles for the both periods. One way of checking the validity is to find whether the values of the diagnostic parameters are in the acceptable range. The chi-square is the weighted sum of squares of the differences between the calculated and measured fitting species concentrations. Chi-square values greater than 4 indicate that one or more species concentrations are not well explained by the source contribution estimates (US EPA, 2004). Percent mass is the ratio of the sum of the model-calculated source contribution estimates to the measured mass concentration. This ratio should equal 100%, although values ranging 80 to 120% are acceptable. If the measured mass is very low (< 5 to 10 μg m^{-3}), percent mass may be outside of this range because the uncertainty of the mass measurement is on the order of 1 to 2 μg m^{-3} (US EPA, 2004).

As shown in Table 3, the parameter values were generally in the acceptable ranges except two parameter values, percent mass and chi square in summer and/or fall. Also note that the values of chi squares during 2006 to 2007 were higher than that during 2002 to 2003. There might be two major reasons for this problem as suggested in previous chapter; (1) limitations of the used source profiles and (2) losses of PAHs during transport from the source(s) to the receptor site.

First, the source profiles except the coal usage (residential, coke oven, power plant) were based on the data from the US. In addition, source profiles of coal usage were based on coal consumption characteristics before 2003. Since coal consumption patterns of China between 2002 and 2007 should be different, there might be gaps between actual source profiles and the one used in this study. A literature survey on the more up-to-dated source profiles of particulate PAHs in China was carried out. However, the reported source profiles did not cover all the fuel types and, thus, it is hard to replace all the source profiles. One example is the data shown in Kong *et al.* (2013) in which the source profiles of PAHs in the stationary sources from coal combustion were reported but not domestic usage. Also, Zhang *et al.* (2007) studied the source profiles of organic species including PAHs from cereal straw burnings in China. Still this data set does not cover all the major biomass burning conditions in China. Thus, these source profiles were not used in this study.

The performance parameter values are within acceptable ranges in spring and winter. In spring, the transport from Asian continent to the Pacific is dominant (Park *et al.*, 2004). In winter, the energy consumption becomes higher and, thus, higher concentrations of combustion related aerosols such as PAHs should be observed (Lee *et al.*, 2006, 2011). In addition, our major interest is on whether the relative contribution of the major sources has been changed between two periods and, if so, what would be the main driving force for that change. Therefore, to our research purpose, the result shown in Table 3 would be enough, though there might be uncertainties.

Second, there were several factors that might affect the loss processes, examples are photochemical reactions and wet/dry depositions in the atmosphere. In the conventional CMB modeling these factors were not accounted for though there were a few studies to overcome these limitations (see, for example, Na and Kim, 2007). To check whether the loss process might change the relative contribution from the sources, a sensitivity analysis study was carried out (Cho *et al.*, 2014). Cho *et al.* (2014) have used both the modified CMB model employing a photochemical loss rate along with varying residence times and the standard CMB model that considers no loss for the PAHs data during 2006 to 2007 at Seoul, the same data set used in this study. It was found that by considering the first-order loss process, a better performance was obtained as compared to those obtained from the standard model in the CMB calculation. The modified model estimated higher contributions from coke oven, transportation, and biomass burning by 4 to 8%. However, the order of the relative importance of major sources was not changed, coke oven followed by transportation and biomass burning. Thus, they concluded that the standard CMB model results are reliable for identifying the relative importance of major sources. Therefore, for our purpose, the modeling result is sufficient, if not fully satisfactory.

Table 3. Target values and modeling result values for the model performance measures (target values were set by US EPA, 2004).

	Parameter	Target values	Whole period	Spring	Summer	Fall	Winter
2002–2003	R square (R^2)	0.8 to 1.0	0.94 ± 0.07	0.95 ± 0.04	0.90 ± 0.04	0.92 ± 0.09	0.99 ± 0.01
	Chi square (χ^2)	< 4.0	2.91 ± 2.76	2.31 ± 2.11	4.77 ± 2.27	4.01 ± 3.18	0.68 ± 0.69
	Percent mass (%)	100 ± 20	86 ± 12	82 ± 8	76 ± 7	85 ± 13	99 ± 3
	Degree of freedom (DF)	> 5	3–8				
2006–2007	R square (R^2)	0.8 to 1.0	0.92 ± 0.03	0.93 ± 0.02	0.89 ± 0.03	0.91 ± 0.03	0.94 ± 0.01
	Chi square (χ^2)	< 4.0	4.10 ± 1.17	3.75 ± 0.76	4.69 ± 1.42	4.49 ± 1.04	3.33 ± 0.85
	Percent mass (%)	100 ± 20	84 ± 6	86 ± 3	80 ± 6	81 ± 5	89 ± 4
	Degree of freedom (DF)	> 5	5–7				

As shown in Fig. 2, the measured PAHs concentrations decreased from 2002–2003 to 2006–2007. In addition, the estimated contribution from transportation was also decreased. According to Kim *et al.* (2013), the concentration of particulate PAHs produced by transportation was dominantly affected by generation in Seoul as local source rather than the transported impact from outside of Seoul. Since there is no emission inventory for PAHs in South Korea, we have studied the trend of the emission amount of PM_{10} from transportation as a proxy. The PM_{10} emissions from transportation kept increasing by 2002 and since 2004 the emissions started decreasing (MOE, 2003–2010). Despite the increase of the number of vehicle registration in Seoul from 2.77 million in 2003 to 2.91 million in 2007 (about 10% increase), the PM10 emissions from transportation have decreased from 35,000 ton in 2003 to 20,000 ton in 2007, representing a remarkable reduction of 45% within 4 years (MOE, 2003–2010). Decrease of PM_{10} emissions was attributed to (1) the strengthened environmental emission standard of PM_{10}, (2) reorganization of energy price system, and (3) reduction measures of air pollution from diesel vehicles such as strengthened the emission standards for new vehicles, strengthened management of operating vehicles (for example, installation of diesel particulate filters to certain diesel vehicles), and supply of low-emission vehicles car and others (MOE, 2010). Thus, through the reduction of PM_{10} emissions from 2002 to 2007, it is considered that source contribution of particulate PAHs for transportation was decreased during the same period.

The PAHs concentrations were categorized based on the estimated sources in Fig. 3 based on the classification applied to the trajectories in Table 4. Though the concentration of particulate PAHs produced by coal combustion varied depending on the trajectories, the contribution of coal combustion was relatively constant irrespective of the trajectories, about 36–44% during 2002 to 2003 and 48–50% during 2006 to 2007 of the total PAHs concentration. It is reported that all plants consuming coal with above certain sizes in South Korea should have effective control system since 1999. Therefore, the effect of coal combustion might be mainly caused by the PAHs transported from out of Seoul, especially from China.

Though the sum of the contributions from coal combustion related emissions was the same for both cases, the fraction of coke oven contribution varied widely, 43% in case 1 and 32% in case 2, respectively. As discussed before in this section, though there might be some degree of uncertainty, the relative importance of the estimated sources seems reasonable. Thus, the fact the coal combustion in coke oven was the most important estimated source of the PAHs observed in Seoul is an interesting one and will be discussed in subsequent sections.

The estimated contribution from biomass burning was higher in case 2 than case 1 during 2006 to 2007, same as during 2002 to 2003 (Kim *et al.*, 2013), though the difference between two cases was diminished. It shows that the biomass burning was still a major emission source of PAHs for the air parcels moved over North Korea. This trend is in

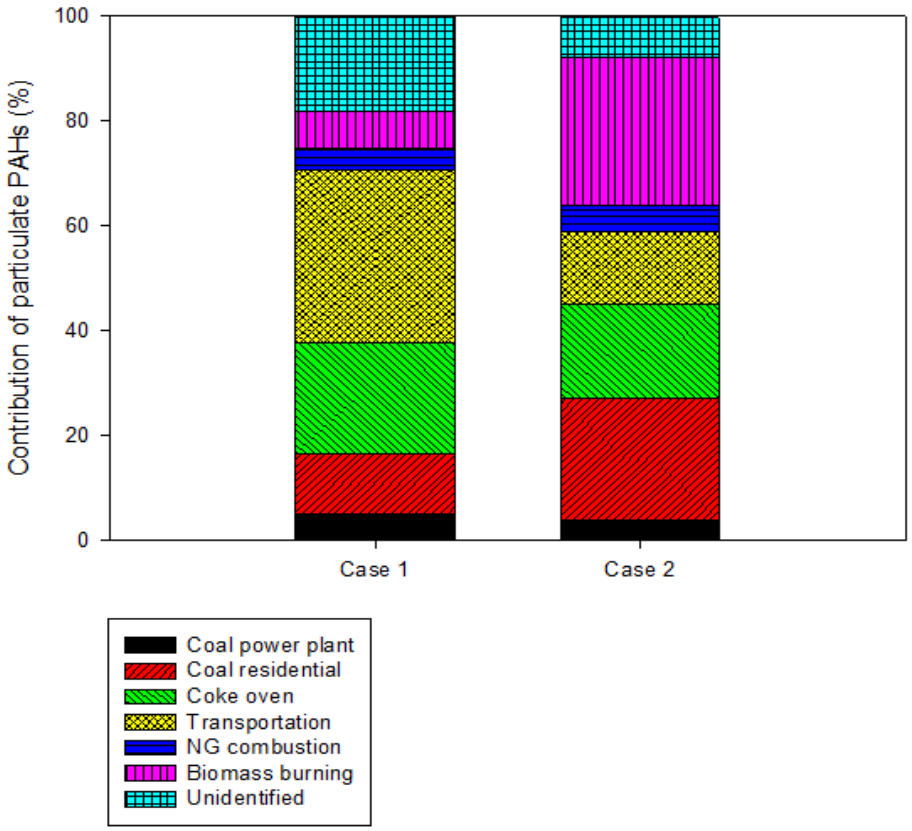

Fig. 3. The trajectory based variations of the contribution of particulate PAHs form major sources.

Table 4. The classification of backward trajectories and number of samples in each case.

Case	Classification	Number of samples	
		2002–2003	2006–2007
Case 1	South Korea + China (North)	39	18
Case 2	South Korea + China (Northeast, North) + North Korea	19	35
Case 3	South Korea	6	10
Case 4	Not be classified into other cases	3	10
	Total	67	73

accordance with a report that in North Korea biomass burning was a major fuel for household heating and cooking, especially, in rural areas (UNEP, 2012). UNEP (2012) reported with North Korean Government that the fractions of biofuels for heating and cooking the rural households in North Korea in 2009 were 77% and ~80%, respectively.

Energy Consumptions in Northeast Asia

There are three possible source regions for the estimated increase of high coal consumption for coke oven observed at Seoul; China, South Korea, and North Korea. The coal consumption has decreased between 2002 and 2007 in North Korea (EIA, 2013) and the consumption of coal for coke oven in 1998, in which a datum was available, was 88,000 tons, far smaller than either South Korea or China. Further, most steel works in which coke ovens were located were in east coast of North Korea. Therefore, influence from North Korea could not explain the estimated results.

The coal consumption amount has increased by about 20% from 2002 to 2007 in South Korea (EIA, 2013). Major energy sources of Seoul were petroleum and natural gas. In the Seoul Metropolitan Area, a couple of coal-fired power plant existed during 2002–2007 period with highly advanced control system. Therefore it is expected that there was little emission of particulate air pollutants by coal. In South Korea, between 2002 and 2007, there existed two steel works having coke oven which were located at south-east (Pohang) and south-west (Gwangyang) of Korea (Fig. 1). The main directions of the wind at Pohang and Gwangyang were from southwest and northwest, respectively (Lee and Kim, 2007). Thus, it is considered that their influence on PAHs in Seoul would be minimal. Also, there was no big difference of coke consumption in South Korea between 2002–2003 and 2006–2007 (IEA, 2011).

Coal consumption in China is increasing sharply compare to world coal consumption increase. China's coal consumption accounted for 31.7% of total world coal consumption in 2003, 39.3% in 2007, and 47.0% in 2011. Furthermore, China showed high dependence on coal, more than 70% of total domestic energy consumption (EIA, 2013).

Coke Oven in China

China applied most of domestic coke oven towards coke for her consumption (China energy statistical year book, 2007, 2008) so both coke production and consumption in China are increasing. The amount of coke oven has increased during the 2000s as shown in Fig. 4. From 2003 to 2007, the amount of coal consumption for coke oven increased from 142.3 million short tons to 260.8 million short tons, representing a 1.8 times increase as shown in Fig. 4. The ratio of the coke consumption to the total coal consumption (Coke Ratio) also increased from 7.8% to 10.6% from 2003 to 2007. Since winds to Seoul are mainly passing over north China, northeast China, and Shandong peninsula, this study especially focuses on the coke consumptions of these three regions.

As shown in Table 5, the coal consumption in north China increased and the consumption amount was larger than either northeast China or Shandong Province, occupying about 30% of total Chinese coal consumption. Also, the Coke Ratio was 12.4% in 2002 and 12.5% in 2007, respectively, showing no variation (China energy statistical year book, 2007, 2008). Still, it was a large coke consumption region, accounting for more than three times than northeast China or Shandong Province and the coke consumption amount actually increase by factor of two from 2002 to 2007. In northeast China, the Coke Ratio increased from 6.7% and 6.6% in 2002 and 2003, respectively, to 8.2 % and 8.9 % in 2006 and 2007, respectively and the amount of coke consumption increased more than twice from 2003 to 2007 (China energy statistical year book, 2007, 2008). Finally, the coal consumption of Shandong Province increased more than six times from 2002 to 2007 and the Coke Ratio also increased from 8.9% to 12.6%. The coke consumption in Shandong Province increased drastically from 2002 and 2006. The ratio of the coke consumption in Shandong Province to that in whole China increased from 3.3% to 8.7% between 2002 and 2006 (China energy statistical year book, 2007, 2008). To sum it up, the coke consumption amount in these areas increased drastically from 2002 to 2007 and the coke consumption amounts in both north China and Shandong Province were more than five times that northeast China.

As shown in Fig. 3, when air parcels moved from north China or Shandong Province (case1), the estimated relative contribution from coke oven was higher than when air parcels moved from northeast China and North Korea (case 2). The contribution from coke oven also increased from 2002–2003 to 2006–2007. That large increase might be caused by the increases of coke oven in both north China and Shandong Province, especially, from Shandong Province. Shandong Province is geographically closest region to Seoul in China and the increasing rate between 2002 and 2007 was the highest

Therefore, considering geological conditions and the trends of coal and coke consumption in eastern and northern China, the particulate PAHs from coke oven observed at Seoul seemed to be affected by the three regions in China, especially, from north China and Shandong Province.

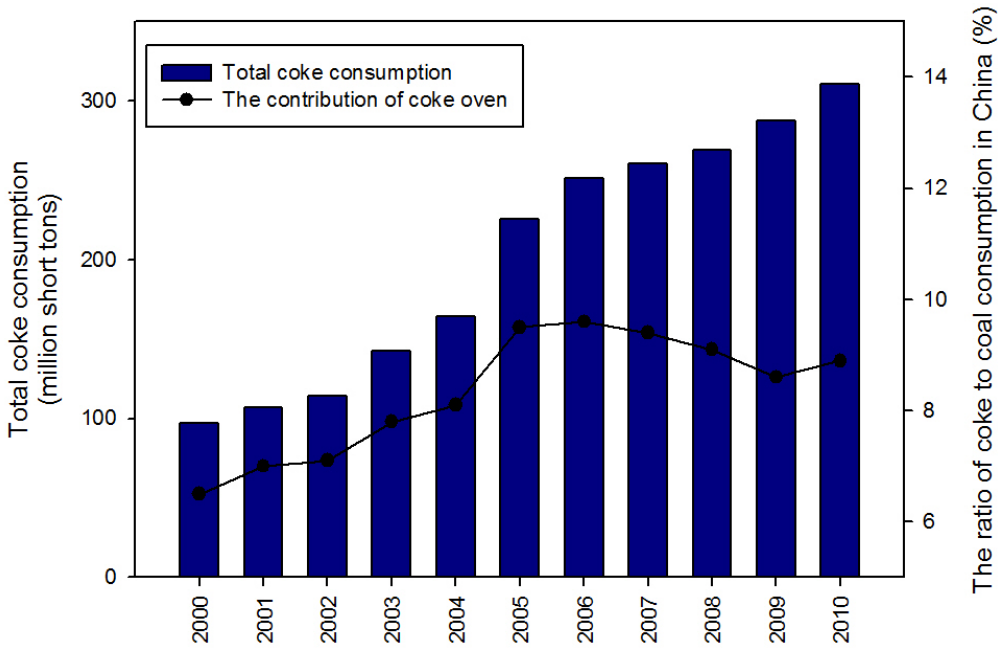

Fig. 4. Total coke consumption in China and the contribution of coke oven for total coal consumption in China (IEA, 2011).

Table 5. Trend of the total coal and coke consumption in north China, northeast China and Shandong (China energy statistical year book, 2008) (unit: 10,000 short ton).

		2000	2001	**2002**	**2003**	2004	2005	**2006**	**2007**
North	Coal	37,478	39,072	**44,118**	**49,562**	57,346	67,016	**72,751**	**79,195**
	Coke	3,391	3,371	**5,491**	**6,735**	7,330	8,179	**9,776**	**9,893**
	(fraction)	(9.0%)	(8.6%)	**(12.4%)**	**(13.6%)**	(12.8%)	(12.2%)	**(13.4%)**	**(12.5%)**
Northeast	Coal	19,610	19,105	**19,562**	**22,146**	25,007	28,432	**30,785**	**32,924**
	Coke	1,122	1,122	**1,318**	**1,468**	1,168	2,182	**2,538**	**2,934**
	(fraction)	(5.7%)	(5.9%)	**(6.7%)**	**(6.6%)**	(4.7%)	(7.7%)	**(8.2%)**	**(8.9%)**
Shandong	Coal	8,698	11,098	**12,938**	**15,166**	18,270	26,056	**29,838**	**32,719**
	Coke	425	461	**416**	**660**	1,236	1,993	**2,414**	**2,593**
	(fraction)	(4.9%)	(4.2%)	**(3.2%)**	**(4.4%)**	(6.8%)	(7.6%)	**(8.1%)**	**(7.9%)**

Energy efficiencies and emission levels vary significantly across different coking technologies. Generally, coke production technologies in China can be classified into five categories; indigenous ovens, modified indigenous ovens, machinery ovens, vertical coke ovens, and heat recovery ovens (Huo *et al.*, 2012). Indigenous and modified ovens are poor in energy efficiencies and emissions. Thus, in 1999, China Government forbade new projects from using indigenous/modified ovens (State Economic and Trade Commission of China, 1999). After that, the production capacity of indigenous/modified ovens decreased gradually, but there were still a small amount of indigenous/modified ovens in operation (Huo *et al.*, 2012). In 2006, the National Development and Reform Commission of China (NDRC) issued an announcement requiring local authorities to phase out all indigenous/modified coke capacities completely (NDRC, 2006).

Thanks to the technology and economic policies that favored the advanced coke production technologies and large-scale coking units, the energy efficiency of coking has improved significantly in China as indigenous ovens and small machinery ovens were phased out from the coke industry (Huo *et al.*, 2012). The energy consumption rate of coking processes decreased from 150 kg of coal equivalent per ton of coke product (kgce t^{-1}) (kgce t^{-1} of product is a common unit used in national energy efficiency standards in China) in 2002 to about 130 kgce t^{-1} in 2007, representing a remarkable reduction. Despite the improvement in energy efficiency between 2002 and 2007, the coal consumption of coke making was doubled because the coke production increased significantly (Huo *et al.*, 2012).

According to Huo *et al.* (2012), in spite of the prompt technology shift taken place in the coke industry which was characterized by the elimination of old, inefficient, and polluting indigenous ovens and small machinery ones, the amount of PM_{10}, $PM_{2.5}$, and black carbon (BC, PAHs are considered as a part of BC) emissions shows a rapid rise since 2000. And the trend of each pollutant emission was similar to the trend of coke production. Thus, since the coke production will continue to increase, they suggested

more measures focusing on energy-saving technologies (e.g., the coke dry quenching technology, making extensive use of waste heat, etc.) need to be taken.

CONCLUSIONS

Air quality in Seoul is influenced by not only local sources but outside sources due to the geographical and the meteorological conditions in the region. And the degree of the outside effects would be increasing since the emissions and, thus, ambient concentrations of the criterial air pollutants from Seoul proper and surrounding metropolitan area were decreasing (Kim and Yeo, 2013). Therefore, it is important to identify and quantify the source contributions of air pollutants observed at Seoul to develop effective control strategies against them.

A long term measurement of one class of the hazardous air pollutants, particulate PAHs, was carried out during 2002–2003 and 2006–2007 and the CMB model was applied to the results along with backward air parcel trajectory analysis to estimate the major contributors for the PAHs concentration at Seoul. Since the main objective of the study was to find out the variation of the major contributors between the two periods, the same source profiles were used for the CMB modeling.

During 2002 to 2003, transportation and coal consumption in coke oven for coke production were major sources for the PAHs level at Seoul. During 2006 to 2007, the major sources were not changed, however, the order of contributions was reversed; coke oven and transportation. The increase of contributions from coke oven was remarkable. Considering geographical conditions and air parcel trajectories, the trends of coal consumption and coke production in north China, Shandong Province, and northeast China were studied. It was found that the coke oven in north China was dominant among various regions in China and the increase rate of coke oven in Shandong Province were very high. These statistical results were in accordance with the observation that when air parcels moved from north China or Shandong Province the relative contribution from coke oven was higher than when air parcels moved from northeast/north China and North Korea.

On the other hand, the contribution from transportation decreased. It was mainly due to the emission reduction in Seoul through several regulations regarding to vehicular emissions such as more strict emission standards for new vehicles and installation of control equipment for operating diesel vehicles. This suggestion is further supported by the fact that the particulate PAHs concentration decreased between the two periods.

It was surmised that the relative contribution for the particulate PAHs concentrations at Seoul from outside, especially, from China has increased from 2002 to 2007. Moreover, effects of China to the air quality of Seoul might continuously keep increasing for some years ahead since the consumptions of coal in general and that in coke oven, in particular, is increasing. Thus, additional regulation and introduction of more stringent standards should be considered.

Evidently, the study result might contain uncertainties mainly due to the uncertainty of the used source profiles for the different periods and the change of the source profiles due to loss process. The used source profiles were mainly from the results in the USA and obtained in the 1990s. Still, it was found that the reported source profiles in China would not cover whole fuel types or combustion types. Thus, it was decided not to change source profiles. We have carried out performance test based on performance parameters and it was found that the performance parameter values for the modeling result were generally within the acceptable ranges. Also, since loss processes such as photochemical reactions and depositions would alter the source profiles during transport, the CMB result for the measurement data in Seoul might contain uncertainties. Still, it was shown that the loss process does not alter the major findings.

To reduce these uncertainties, it is desirable to use a receptor model that does not use source profiles and compare that result with the CMB modeling result. Also, comparing with the comprehensive 3-dimensional chemical transport modeling result be desirable.

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