

## Characterization of Regional Influence of Fine Carbonaceous Particles at Gosan, Korea

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. Author JSH designed the study. Author KJM performed the statistical analysis, wrote the protocol and first draft of the manuscript. Authors BJK and YSG managed the analyses of the study. All authors read and approved the final manuscript.*

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### **ABSTRACT**

**Aims:** This study aimed to study the long-range transport of anthropogenic carbonaceous aerosol at Gosan, Korea

**Study Design:** Chemical composition of fine particles (aerodynamic diameter < 2.5  $\mu\text{m}$ ) and PAHs of TSP measured at Gosan during six intensive measurement periods covering four seasons. And the chemical characteristics of particulate matter were classified and compared each other according to the major source areas identified by using backward trajectory analysis in order to study the impact of distant source regions on the carbonaceous aerosol at Gosan, Korea.

**Place and Duration of Study:** Sample: Gosan, Jeju Island in Republic of Korea, from 13 to 25 Nov. 2001, from 29 Mar. to 11 Apr. 2002, from 27 Aug. to 11 Sep. 2002, from 14 to 26 Feb 2003, from 6 to 22 Jun. 2003, and from 18 Aug. to 1 Sep. 2003.

**Methodology:** In order to investigate the chemical composition of fine particles, 7 major ion components, 21 trace elements, organic and elemental carbon of  $\text{PM}_{2.5}$  were measured. In addition, particulate hazardous pollutants including 17 polycyclic aromatic hydrocarbons (PAHs) were analyzed. The measured data were classified according to the dominant source area identified with the three-day backward trajectory analysis. Then several ratios of species combining EC, OC,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$  and PAH compounds were used to identify potential sources of carbonaceous materials.

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**Results:** Quite different characteristic in the chemical composition of fine particles was observed by regional groups of backward trajectories. Concentrations of ion components including secondary aerosol such as  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  were relatively high when air masses were originated from north China. Concentrations of OC and gaseous PAHs were higher when they transported from Japan than from other source regions. High concentrations of secondary aerosols as well as particulate PAHs were observed in the air mass from north China with a higher correlation between them. Elemental carbon had a better correlation in this case not only with secondary aerosols, but also with OC and CO, implying that carbonaceous materials were originated from long-distance combustion sources. Especially positive correlation with benzo(ghi)perylene suggested that they also had a vehicular origin.

**Conclusion:** The results showed that biomass burning and vehicular emissions mainly influenced ambient fine particles when they derived from north China and the Korea peninsula while fossil fuel combustion chiefly affected them when they originated in south China during six intensive measurement periods.

*Keywords: PM<sub>2.5</sub>; carbonaceous aerosol; PAHs; backward trajectory; source estimation.*

## 1. INTRODUCTION

Particulate matter in atmosphere is mainly composed of water-soluble inorganic salts, insoluble mineral dust, and carbonaceous materials. Most previous aerosol measurements have concentrated on sampling and analyzing inorganic components, such as sulfate, nitrate and ammonium, which have relatively well-known physical and chemical properties. On the other hand, in spite of the potential importance of carbonaceous components in atmospheric chemistry, available information is relatively rare in terms of concentrations, sources, mechanisms of formation, and chemical properties.

Carbonaceous components, composed of organic (OC) and elemental carbon (EC), constitute a significant fraction of the fine aerosol mass. Organic carbon is usually very abundant component of fine aerosol after sulfate and several ion components. It may be directly introduced into the atmosphere in particulate form or may condense by gas-to-particle conversion of volatile anthropogenic and biogenic precursors [1]. However, it is extremely difficult to make a complete characterization of OC because it covers a very wide range of molecular forms, solubilities, reactivities, and physical properties [2]. On the other hand, EC is only produced by incomplete combustion of fossil and biomass fuels. Therefore, it is used as a tracer for combustion source [3].

Asian aerosol sources are distinguished from those in other regions in various points of view. By burning much coal and biomass, atmospheric aerosol contains more absorbing

soot and organic compounds [4]. In addition, according to the economic expansion in Asia, it is difficult to effectively reduce emissions of  $\text{SO}_2$ , organic matter, and soot into atmosphere in spite of the decrease of sulfur emission from China [5].

In this paper, the chemical composition of fine aerosols (aerodynamic diameter < 2.5  $\mu\text{m}$ ) collected at Gosan, Korea is discussed. Concentrations of major ion components, trace elements, EC, OC, and polycyclic aromatic hydrocarbons (PAHs) are presented. Tracers for fossil fuel and biomass burning are selected and used to identify probable sources. The distribution of sources around the sampling site is estimated based on backward trajectories by comparing the composition of tracers according to the routes of air masses.

## 2. METHODS

### 2.1 Sampling Site and Period

The sampling site is Gosan, located at the western tip of Jeju Island. Latitude is 33°17' N, longitude is 126°10' E, and elevation is 70 m above sea level. Gosan is the representative background site in Korea and was a major research location of many previous studies on the long range transport in Asia [6,7]. In addition, it has been concerned as a super site of ACE-Asia (Asia-Pacific Regional Aerosol Characterization Experiment [4] and ABC (Atmospheric Brown Clouds) [8]. Sampling was conducted during six intensive measurement periods for 3 years. They were from 13 to 25 Nov. 2001, from 29 Mar. to 11 Apr. 2002, from 27

**Table 1. List of PAHs analyzed and their abbreviation in present work**

Naphthalene (Nap) <sup>a,b</sup>	Fluoranthene (Flt)	Benzo(a)pyrene (BaP)
Acenaphthylene (Acy)	Pyrene (Pyr)	Benzo(e)pyrene (BeP) <sup>b</sup>
Acenaphthene (Ace)	Benzo(a)anthracene (BaA)	Benzo(g,h,i)perylene (BghiP)
Fluorene (Flu)	Chrysene (Chry)	Indeno(1,2,3-cd)pyrene (Ind)
Anthracene (Anthr)	Benzo(b)fluoranthene (BbF)	Dibenz(a,h)anthracene (DbahA)
Phenanthrene (Phen)	Benzo(k)fluoranthene (BkF)	

<sup>a</sup>Abbreviation used in this paper<sup>b</sup>Measured from the 3rd measurement period, that is, from the summer of 2002.

Aug. to 11 Sep. 2002, from 14 to 26 Feb 2003, from 6 to 22 Jun. 2003, and from 18 Aug. to 1 Sep. 2003.

## 2.2 Sampling and Analysis

Three sets of low volume air samplers with PM<sub>2.5</sub> cyclone were used with 47mm Teflon membrane filter (Gelman, Zefluor) and 47mm pre-fired quartz filter (URG-2000-30UB) at a flow rate of 16.7 L min<sup>-1</sup> for measuring ion, trace elements and carbonaceous materials. In order to measure PAHs in the particulate and gas phases, TSP high volume air sampler (Sibata DHV-1000s) was used with pretreated quartz filter (Whatman, QM-A) and polyurethane foam (Sibata 8013-0941A) at a flow rate of 700 L min<sup>-1</sup>.

Samples were regularly collected for 24 hours. After sampling, Teflon membrane filters were extracted with 20 mL of distilled and deionized water for 120 min by shaker, and filtrated using a 1 μm cellulose filter (Toyo, 5C). Then anions of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup> were analyzed by ion chromatography (Dionex, DX-500) with an AS4A-SC separate column, and cations of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>, were analyzed by atomic absorption spectroscopy (PerkinElmer, Analyst 800). NH<sub>4</sub><sup>+</sup> was determined by UV/VIS spectrometer (PerkinElmer, Lambda 20) using the indo-phenol colorimetric method.

Quartz filters were analyzed for carbon components and trace elements. Elemental and organic carbons were determined by thermal/optical reflectance (TOR) system (Atmoslytic, DRI Model 2001) using the protocol adopted by the IMPROVE program [9]. Twenty-one species of trace elements, such as Na, K, Mg, Ca, S, Si, Al, Fe, Ti, V, Mn, Co, Cu, Zn, Sr, Ni, Cd, Ba, Pb, Cr and As, are measured by ICP/AES (PerkinElmer, Optima 4300DV) and

ICP/MS (ThermoElemental, X7) after digestion with acid solution (HNO<sub>3</sub> : HCl=3:1).

As shown in Table 1, seventeen PAHs were analyzed using GC/MSD (HP, 6890/5973N). The Concentrations of criteria pollutants and meteorological data were obtained from co-located background air pollution monitoring station and upper air station, respectively.

## 2.3 Backward Trajectory Analysis

In this study, backward trajectory is used to estimate the location of probable sources. Three-day air mass backward trajectories were computed using the Hybrid Single-Particle Lagrangian Integrated Trajectories model (HYSPLIT4, Version 4.7) developed in the Air Resource Laboratory (ARL), National Oceanic and Atmospheric Administration (NOAA) [10,11,12]. The arrival elevation is set up at a height of 1,500m, which is similar with the average mixed height during the measurement periods. NCEP/NCAR reanalysis data with 6 hours temporal resolution on a 2.5° X 2.5° global grid have been used as meteorological input data to the trajectory model. Vertical velocity model was applied to calculate the vertical profiles of backward trajectories.

## 3. RESULTS AND DISCUSSION

### 3.1 Atmospheric Condition and Backward Trajectories

Meteorological conditions at the sampling site are summarized in figure 1 and figure 2. In late winter, fall and spring, winds were mainly from the north. On the other hand, in summer southerly winds were more common. Wind speed was faster in spring and winter than in other seasons. In spring, a huge Asian dust storm

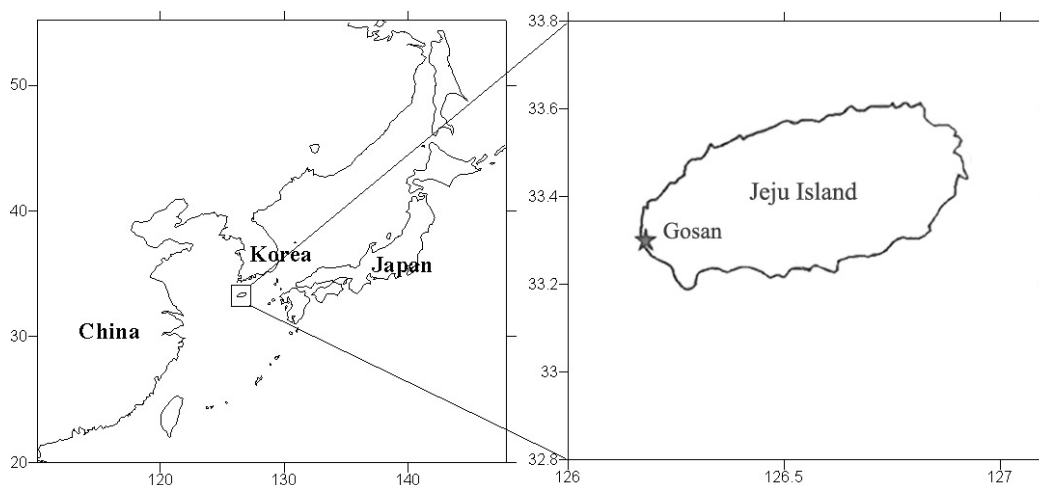


Fig. 1. Location of Gosan sampling site in Jeju, Korea

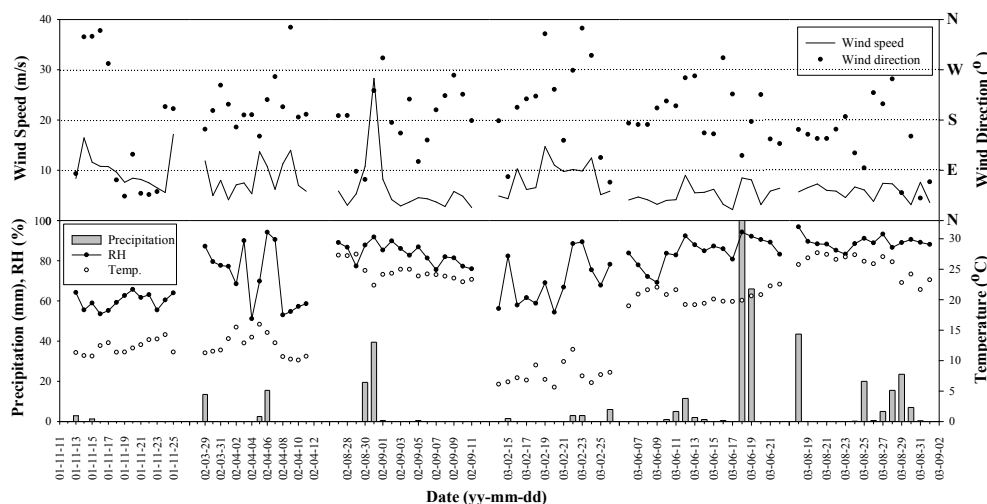


Fig. 2. Meteorological condition at Gosan during six intensive measurement periods

passed between 8 and 10 April 2002. Furthermore, in summer, rainfall was frequent associated with the Asian monsoon and also due to typhoons. The data during the Asian dust period are excluded from the following analysis, because high soil contents could greatly influence the composition of fine particles. Especially, the data collected at 7 April 2002 also eliminated from analysis by reason of the partial include of Asian dust period.

Fig. 3(a) shows backward trajectories from Gosan during the six measurement periods. It reveals that the routes of air masses were extensively changed over the periods. The sources and chemical composition of fine particles could be different with the routes of air

masses. In order to investigate the influence of outside source regions, such as China, Korea, and Japan, the windward side of Gosan is divided into five sectors as shown in figure 3(b). At this time, three-day backward trajectories were calculated eight times a day at 01, 04, 07, 10, 13, 16, 19, and 22 UTC during the measurement periods. 576 trajectory endpoints were then used to classify the dominant sector in each day. The sector including more than 75% of the endpoints were decided as a major source area of a day. If one area was not dominantly occupy the endpoints, two sectors, which includes them more than criteria, selected as source areas. Table 2 shows the distribution of backward trajectories and the mean concentrations of criteria pollutants observed at

the background monitoring station by sectors. About 40% of the trajectories passed through Sector II, north China along with the highest concentrations of SO<sub>2</sub>, NO<sub>2</sub>, CO and PM<sub>10</sub>. On the other hand, air mass originated from Sector IV, North Pacific Ocean, had the lowest concentration of almost all pollutants except SO<sub>2</sub>. It is interesting to note that O<sub>3</sub> was the highest when air mass was transported from the Korea Peninsula. By seasons, in late winter, fall and spring, the flows were mainly from north including Sectors I and II, while in summer, the southwest-south-southeast windward including Sectors III, IV and V was dominant.

### 3.2 Chemical Composition of Fine Particles

As shown in Table 3, average PM<sub>2.5</sub> concentration was 23.14 µg/m<sup>3</sup>. SO<sub>4</sub><sup>2-</sup> was the highest followed by OC, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>. As a result, secondary ion components, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, occupied 37% of total PM<sub>2.5</sub> mass concentration. Figure 4 shows the daily variation of major aerosol components. Except the Asian dust period, almost anthropogenic components, such as secondary ion components, trace elements and carbonaceous materials had high

concentration in November 2001 and February 2003, while in June and August 2003, these reveals the lowest concentration. At first, the concentration of secondary ion components was the highest in February 2003. On the other hand, K<sup>+</sup> and carbonaceous materials were higher in September 2001 than other periods.

In order to assess the influence of regional anthropogenic sources, the mean concentration of each component for the five cases described above was compared in figure 5. Most components had higher concentration in the case of sector II. Especially, metal was remarkably elevated. However, OC were as high or higher in sector V than sector II. Considering the fact that the case of sector V predominantly happened in summer, it is inferred that long-range transported pollutants mainly originated from north China while primary OC was mainly transported from relatively close Japan on account of high temperature in summer. As shown in figure 5, the influence of anthropogenic pollutants was revealed when air masses were originated not only from north China but also from the mainland of Korea and south China. On the contrary, relatively clean air masses were moved in Gosan from North Pacific Ocean.

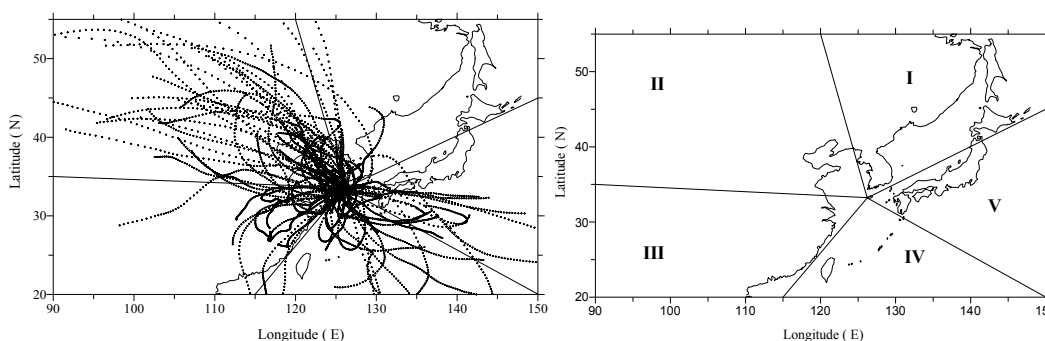


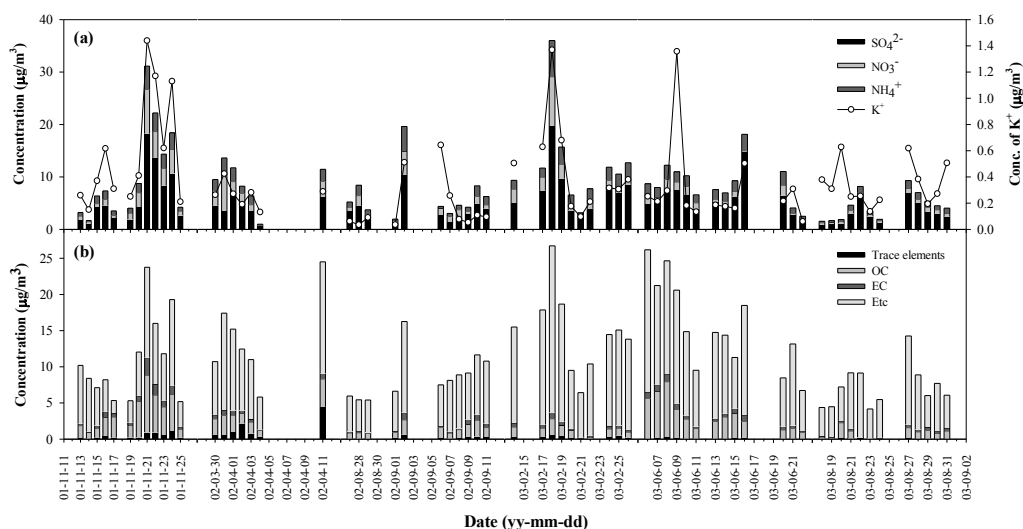
Fig. 3. Spatial distribution of 3-day air mass trajectories arrived at Gosan during the measurement periods

Table 2. Frequency of backward trajectories and mean concentrations of criteria pollutants classified by regional groups

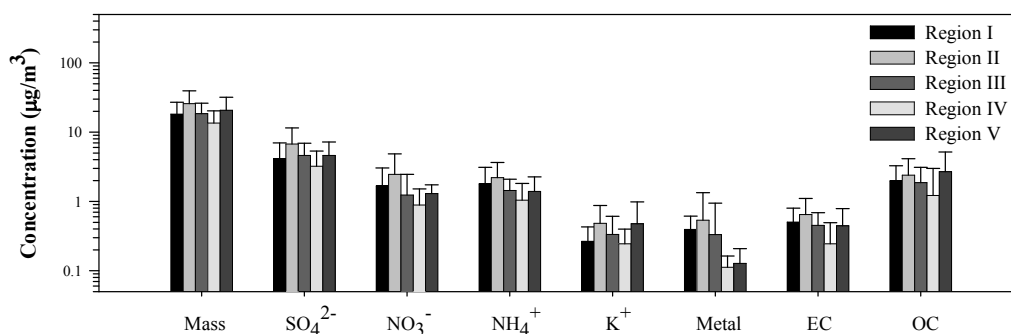
Sector	Major area	Frequency	SO <sub>2</sub> (ppb)	NO <sub>2</sub> (ppb)	O <sub>3</sub> (ppb)	CO (ppm)	PM <sub>10</sub> (µg m <sup>-3</sup> )
I	Korean Peninsula	13 (13.4%)	1.78	3.77	45.1	0.33	41.3
II	North China	37 (40.2%)	2.57	3.96	41.2	0.41	52.6
III	South China	17 (17.5%)	1.57	3.64	33.3	0.38	38.3
IV	North Pacific Ocean	14 (14.4%)	1.28	2.69	19.9	0.29	29.1
V	Japan	11 (11.3%)	1.18	4.62	34.3	0.32	41.4
Total		97 (100%)	1.65	3.70	34.9	0.35	43.9

**Table 3. Mean concentrations of major components of fine particles during the measurement periods**

Species	PM <sub>2.5</sub> mass	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Trace elements	EC	OC
Average (mass %)	20.66	5.13 (24.9%)	1.69 (8.2%)	1.68 (8.1%)	0.39 (1.9%)	0.36 (1.7%)	0.48 (2.3%)	2.01 (9.7%)
Standard deviation	11.84	3.89	1.83	1.21	0.34	0.62	0.39	1.75
Maximum	64.28	19.71	9.41	6.89	1.54	4.46	2.39	7.89
Minimum	6.29	0.74	0.06	0.19	0.04	0.01	0.04	0.01
Number of samples	65							



**Fig. 4. Daily variation of (a) major ion components, (b) metal and carbonaceous materials in PM<sub>2.5</sub>**



**Fig. 5. Concentration of major components in PM<sub>2.5</sub> by regional groups**

**3.3 Particulate and Gaseous PAHs**

In this study, the PAH fraction of TSP was shown in Table 4. The concentration of particulate PAHs ranged from 0.03 to 14.81 ng

m<sup>-3</sup>, and gaseous PAHs varied from 0.26 to 7.27ng m<sup>-3</sup>.

In aerosol phase, PAHs with four rings including Fluoranthene, Pyrene, Benzo(a)anthracene and

Chrysene, had the highest concentration, and Fluoranthene was the most abundant four rings PAH. Moreover, the high concentrations of PAH with five and six rings, such as benzo(k+b)fluoranthene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, benzo(a)pyrene, dibenz(a,h)anthracene, were observed. On the other hand, in gas phase, the concentrations of PAHs with two and three rings, such as Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Anthracene and Phenanthrene, were much higher than other PAHs, and PAHs with five and six rings were rarely existed. These results correspond to the fact that the lower molecular weight (LMW) PAHs with three rings tend to be more concentrated in the vapor phase while the higher molecular weight ones are often associated with particulates [13,14].

Fig. 6 shows the daily variation of PAHs in aerosol and gas phase. Particulate PAHs increased in November 2001 and February 2003. At the same time, gaseous PAHs were decreased in inverse proportion to particulate PAHs. The opposite case was also observed in September 2002. Generally, PAHs were transported as a form of aerosol from a long distance. However, the distribution of PAHs between the gas and aerosol phase mainly depends on temperature [15]. Especially, for intermediate PAHs with four rings, which had high concentrations in both phase, temperature

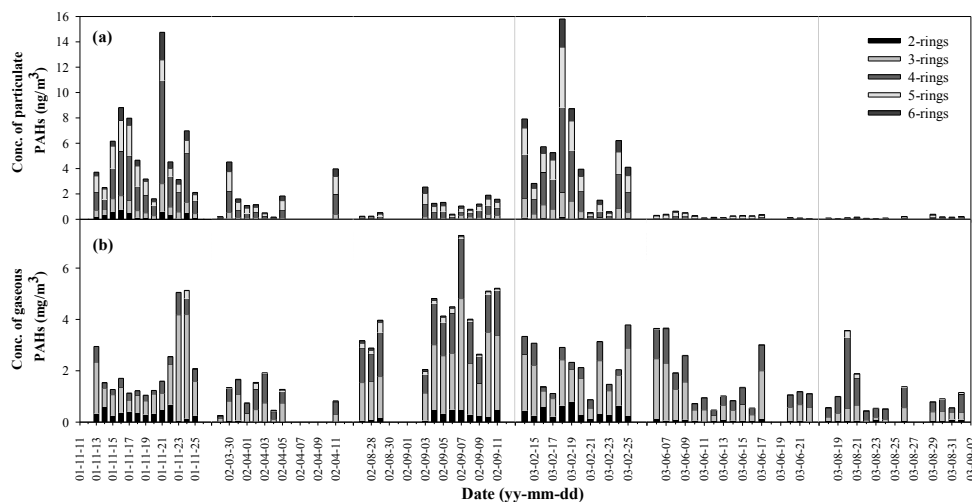
significantly influences to the type of them in the ambient air. Therefore, it is inferred that in September 2002, the high concentration of gaseous PAHs was caused by the evaporation of particulate PAHs influenced by the high temperature in this period as shown in Fig. 2. In addition, the reverse correlations between particulate and gaseous PAHs imply the vapor-solid equilibrium state of PAHs.

Fig. 7 represents the mean concentration of PAHs in aerosol and gas phase by regional groups. In aerosol phase, most PAHs components predominantly existed in sector II. In addition, the influence of sector I was also larger than the rest three regions. Therefore, it is inferred that PAHs in aerosol phase were chiefly transported from north China and Korea peninsula. On the other hand, in gas phase, PAHs had high concentration in sector V influenced by the high temperature in summer. Especially, the high molecular weight PAHs such as Dibenz(a,h)anthracene, Indeno(1,2,3-cd)pyrene and Benzo(g,h,i)perylene remarkably existed in this region. Overall, particulate PAHs mainly influenced by the emission sources in north China, and gaseous PAHs predominantly affected by the sources in Japan. Moreover, the impact from the mainland of Korea and south China was also significantly larger in both phases.

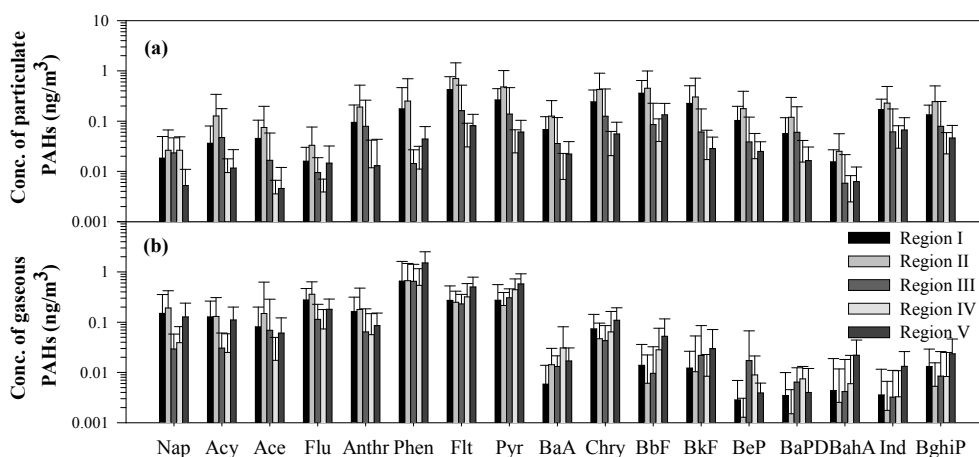
**Table 4. Concentrations of individual PAHs at Gosan**

(Unit : ng m<sup>-3</sup>)

	Particulate PAHs					Gaseous PAHs				
	Avg.	Std.	Max.	Min.	No.	Avg.	Std.	Max.	Min.	No.
Nap	0.022	0.031	0.154	0.000	60	0.119	0.171	0.775	0.000	60
Acy	0.068	0.157	0.746	0.000	73	0.099	0.143	0.685	0.005	73
Ace	0.043	0.092	0.476	0.000	73	0.091	0.331	2.708	0.000	73
Flu	0.02	0.033	0.217	0.000	73	0.236	0.242	1.209	0.004	73
Anthr	0.106	0.244	1.613	0.000	73	0.127	0.222	1.368	0.000	73
Phen	0.135	0.326	1.731	0.001	73	0.708	0.81	3.696	0.000	73
Flt	0.381	0.600	2.986	0.000	73	0.289	0.223	1.05	0.004	73
Pyr	0.264	0.427	2.493	0.001	73	0.317	0.265	1.162	0.015	73
BaA	0.068	0.105	0.575	0.000	73	0.017	0.026	0.194	0.000	73
Chry	0.234	0.377	2.245	0.000	73	0.061	0.07	0.39	0.000	73
BbF	0.266	0.421	2.757	0.000	73	0.016	0.036	0.186	0.000	73
BkF	0.177	0.329	1.666	0.000	73	0.012	0.034	0.248	0.000	73
BeP	0.086	0.156	0.955	0.000	60	0.007	0.025	0.19	0.000	60
BaP	0.069	0.132	0.785	0.000	73	0.004	0.006	0.024	0.000	73
Ind	0.135	0.204	1.091	0.000	73	0.004	0.008	0.034	0.000	73
DBahA	0.014	0.024	0.141	0.000	73	0.006	0.015	0.056	0.000	73
BghiP	0.138	0.205	1.136	0.000	73	0.009	0.016	0.064	0.000	73
Total	2.207	3.127	14.812	0.033	73	2.099	1.483	7.269	0.257	73



**Fig. 6. Daily variation of (a) particulate, and (b) gaseous PAHs components; PAHs with 3 rings are Ace, Flu, Anthr and Phen, and PAHs with 4 rings are Flt, Pry, BaA and Chry. Finally, PAHs with 5 rings are BbF, BkF, BaP, BeP and DBahA, and PAHs with 6 rings are BghiP and Ind**



**Fig. 7. Concentration of (a) particulate and (b) gaseous PAHs by regional groups**

### 3.4 Correlation between Chemical Components

As shown in Table 5 and figure 8, correlation and relationship between several index components including carbonaceous materials were considered in order to estimate the anthropogenic source and the influence of long-range transport.

First of all, aerosol  $SO_4^{2-}$  has been used for the indicator of secondary aerosols transported from remote region [16]. In addition, Sulfur species,

such as  $SO_2$  and aerosol  $SO_4^{2-}$ , can be used as tracers of anthropogenic pollution because sulfur gases, which are oxidized to the secondary ion component  $SO_4^{2-}$  in the atmosphere, are mainly produced by industrial activities and fossil fuel burning [17], and only small quantities are emitted during biomass burning [18,19]. On the other hand, Potassium ( $K^+$ ) is a useful marker for biomass burning [3]. It is released in large amounts during the combustion process because it is a major electrolyte in the cytoplasm of plants. But it is not emitted in significant quantities by combustion of fossil fuels. In addition to soluble



potassium  $K^+$ , K, OC and EC are also known as the marker component of biomass burning [20], [21]. Carbon monoxide (CO) is another gaseous tracer for combustion, especially biomass burning [18]. Its global production from biomass burning is much higher than its production from fossil fuel.

Overall, carbonaceous materials and special ion components in  $PM_{2.5}$  had good correlations. Among them,  $SO_4^{2-}$  and EC ( $R=0.75$ ), EC and OC ( $R=0.85$ ) revealed relatively high correlation coefficient. Therefore, it was estimated that most carbonaceous materials in  $PM_{2.5}$  were transported from a remote region and their origins involved with biomass burning as well as fossil fuel emission. Better correlations between K and EC in sector II, III, V ( $R=0.86, 0.90, 0.87$ ) mean that the influence of biomass burning predominantly revealed when air masses transported from north and south China and the mainland of Korea. Especially, the impact was higher in sector II, which showed partially linear distribution with high concentration of K and EC as shown in Fig. 8 (c).

In the case of PAHs in aerosol phase, the association of benzo(ghi)perylene with vehicle exhaust has long been established [14]. Generally, benzo(ghi)perylene have higher concentration when influenced by the vehicular emission than originated by fossil fuel combustion. Therefore, the positive correlation with benzo(ghi)perylene suggest the vehicular origin. For the measured samples, BghiP had partially positive correlation with EC in region I and II, and had high correlation coefficient ( $R=0.96$ ) with particulate PAHs implying the influence of vehicular emission. On the other hand, it is known that Benzo(a)pyrene and other PAHs on a variety of aerosol substrates react with gaseous  $NO_2$  to form nitro-PAHs. As a result, negative correlation between particulate BaP and gaseous  $NO_2$  as shown in Fig. 8(i),

indicate the chemical transformations of PAHs in aerosol phase leading to formation of products more polar than the parent PAHs.

### 3.5 Ratios of Chemical Components

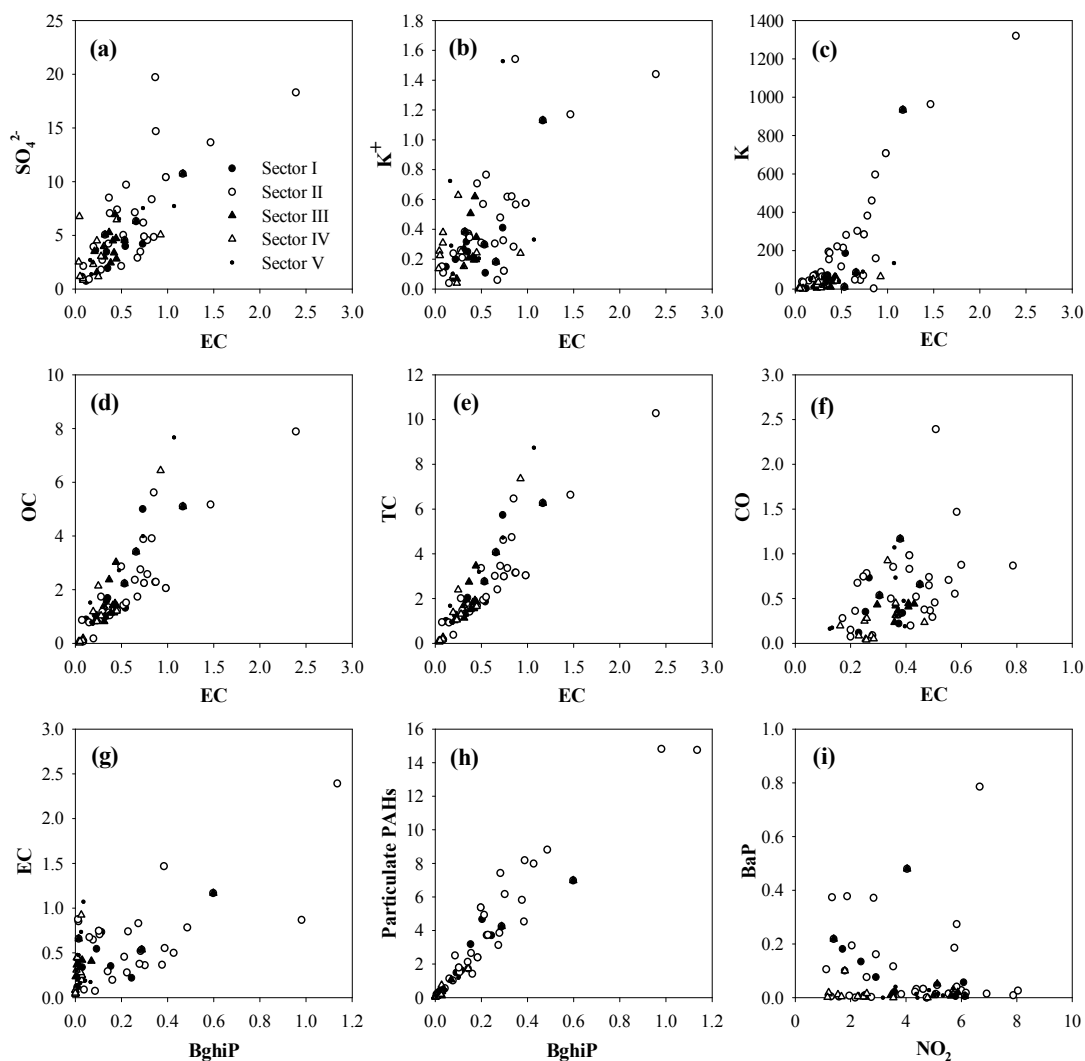
Several chemical components of aerosol are predominantly emitted by a special source. Therefore, the ratios of these constituents can be used to identify the individual source of aerosol. In this study, in order to assess the influence of more detail sources, the ratios of several indicators on anthropogenic sources were calculated in Table 6.

First of all, EC/TC ratio was used to address the contributions of biofuel and fossil fuel because the relative mass concentrations of EC and OC depend on the sources of the carbonaceous aerosol material and on the efficiency of the combustion process. In general, the concentration of EC produced by fossil fuel combustion can be as high as that of OC while during biofuel burning, the emissions of OC are much higher than that of EC.

Therefore, EC/TC and EC/OC ratios in particles from biofuel burning ( $0.11\pm0.5, 0.15\pm0.22$ ) can be significantly lower than in aerosol derived from fossil fuel combustion ( $0.5\pm0.05, 1.0$ ) as shown in Table 6. As a result of measurement, the relatively constant ratios of EC/TC ( $0.23\pm0.11$ ) and EC/OC ( $0.34\pm0.42$ ) and the good correlation between TC and EC ( $R=0.86$ ) suggest that fine carbonaceous aerosol at Gosan is affected by both biofuel and fossil fuel combustion. Contributions of biofuel and fossil fuel combustion calculated from both source index and measured ratio, were about 70% and 30%. The values of this ratio were lower than those in major urban and industrial pollution sources around Gosan, and enriched OC implies the present of secondary OC.

**Table 5. Correlation coefficient between marker species**

	Sector I	Sector II	Sector III	Sector IV	Sector V	Overall
$SO_4^{2-}$ vs. EC	0.86	0.74	0.84	0.44	0.91	0.75
$K^+$ vs. EC	0.59	0.74	0.79	0.00	0.31	0.64
K vs. EC	0.81	0.86	0.90	0.81	0.87	0.80
OC vs. EC	0.57	0.89	0.90	0.95	0.98	0.85
TC vs. EC	0.70	0.93	0.93	0.96	0.98	0.90
CO vs. EC	0.22	0.39	0.15	0.37	0.47	0.45
EC vs. BghiP	0.04	0.63	0.86	0.53	-0.1	0.65
Particulate PAHs vs. BghiP	0.87	0.95	0.99	0.95	0.98	0.96
BaP vs. $NO_2$	-0.8	-0.1	-0.2	-0.1	0.16	-0.03



**Fig. 8. Correlations between the major components of carbonaceous aerosols by regional group ((a)  $\text{SO}_4^{2-}$  vs. EC, (b)  $\text{K}^+$  vs. EC, (c) K vs. S, (d) OC vs. EC, (e) TC vs. EC, (f) CO vs. EC, (g) BghiP vs. EC, (h) Bghi vs. Particulate PAHs, (i)  $\text{NO}_2$  vs. BaP)**

The aerosol  $\text{SO}_4^{2-}$  and EC were correlated well ( $R=0.74$ ), and the averaged  $\text{SO}_4^{2-}/\text{EC}$  ratio was  $14.2 \pm 18.6$ . Generally, aerosol  $\text{SO}_4^{2-}$  is known as the indicator for long-range transported secondary aerosols as well as the tracer of anthropogenic pollution, such as industrial activities and fossil fuel burning [16,17]. In this study, the ratio of  $\text{SO}_4^{2-}/\text{EC}$  ( $14.2 \pm 18.6$ ) was very high implying that fossil fuel burning significantly contributed to the ambient aerosol at Gosan. The result of calculation showed that only about 30% of  $\text{SO}_4^{2-}$  was originated from biofuel and about 70% of that was emitted from fossil fuel combustion.

If an area strongly influenced by biomass burning, the ratio of  $\text{K}^+/\text{EC}$  should be higher, since  $\text{K}^+$  and CO are emitted in high concentrations during most types of biomass burning while EC is released in lower concentrations [22]. Andreae and Merlet [23] showed that the  $\text{K}^+/\text{EC}$  ratio is highly dependent on the type of biomass burned. The  $\text{K}^+/\text{EC}$  ratio from the burning of wood fuel is about 0.09 and non-wood biomass is about 0.63. The ratio of  $\text{K}^+/\text{EC}$  calculated for measured data ( $1.14 \pm 1.13$ ) was much higher than 0.63 implying measured  $\text{K}^+$  mainly originated from non wood biomass burning.

Table 6. Ratios of chemical components as an indicator for various anthropogenic sources

Source	EC/TC	EC/OC	SO <sub>4</sub> <sup>2-</sup> /EC	K <sup>+</sup> /EC	Bep/Bap	Phen/ (Phen+Anthr)	BaP/BghiP	Ind/ (Ind+BghiP)	BaA/ (BaA+Chry)	BeP/ (BeP+BaP)	Flt/(Flt+Pry)	BkF/BbF	References
Gosan, Korea, Total	0.23±0.11	0.34±0.42	14.2±18.6	1.14±1.13	4.68±7.74	0.69±0.41	0.67±0.95	0.51±0.13	0.34±0.30	0.54±0.35	0.55±0.10	0.80±1.04	This study
Gosan, Korea, R-I	0.20±0.08	0.27±0.13	8.57±3.72	0.66±0.37	5.10±7.11	0.46±0.42	0.44±0.35	0.54±0.11	0.19±0.14	0.58±0.40	0.59±0.05	0.84±0.81	This study
Gosan, Korea, R-II	0.24±0.10	0.34±0.25	11.6±6.0	0.84±0.46	8.88±10.4	0.56±0.45	0.49±0.40	0.49±0.16	0.23±0.19	0.57±0.39	0.59±0.06	0.95±1.26	This study
Gosan, Korea, R-III	0.21±0.05	0.27±0.07	10.6±3.70	0.72±0.39	1.69±1.44	0.77±0.39	1.04±1.33	0.51±0.11	0.43±0.26	0.51±0.25	0.54±0.06	0.71±0.61	This study
Gosan, Korea, R-IV	0.30±0.19	0.62±0.88	28.3±41.4	2.26±2.01	0.95±1.06	0.90±0.26	1.08±1.70	0.54±0.07	0.65±0.40	0.45±0.35	0.43±0.10	0.34±0.31	This study
Gosan, Korea, R-V	0.16±0.04	0.19±0.05	11.6±3.35	1.42±1.50	1.37±0.57	0.92±0.18	0.56±0.62	0.59±0.03	0.25±0.19	0.65±0.22	0.57±0.05	0.22±0.03	This study
Biofuel	0.11±0.5	0.15±0.22	0.70±0.10	0.09±0.3	-	-	-	0.67 <sup>c</sup>	-	-	-	-	Andreae and Merlet [23]
Rice straw	-	-	-	-	0.5	-	2	0.5	0.46	0.33	0.51	1	Sheesley et al. [24]
Biomass briquettes	-	-	-	-	0.48	-	1.4	0.52	0.45	0.32	0.48	1.14	Sheesley et al. [24]
Fossil fuel <sup>a</sup>	0.5±0.05	1	19.0 <sup>b</sup>	0	-	>0.70 <sup>e</sup>	0.9~0.66 <sup>d</sup>	0.56 <sup>c</sup>	-	-	-	-	Andreae and Merlet [23]
Gasoline vehicle	-	-	-	-	1.05	0.77~0.89	0.3~0.4	0.18 <sup>f</sup>	0.33~0.44	0.51	0.44~0.61	0.69~1.07	Rogge et al. [25]
Diesel truck	-	-	-	-	2	0.88	0.81	0.37 <sup>f</sup>	0.12	0.67	0.37	0.93	Rogge et al. [25]
Road dust	-	-	-	-	1.14~1.33	0.82	0.28~1.10	0.36	0.13~0.47	0.53~0.57	0.17~0.42	1.25~1.48	Rogge et al. [26]
Charboilers and-Meat Cooking	-	-	-	-	1	-	0.79	-	0.17	0.50	0.32~0.59	1.29~1.5	Rogge et al. [27]
Seoul, Korea, URB	0.43±0.05	0.76±0.1	-	-	-	-	-	-	-	-	-	-	Kim et al. [7]
Sapporo, Japan, URB	0.49	0.97	1.1	0.04	-	-	-	-	-	-	-	-	Kaneyasu et al. [28]
Kyoto, Japan, URB	0.21	0.26	-	-	-	-	-	-	-	-	-	-	He et al. [29]
Beijing, China, URB	0.3	0.44	-	-	-	-	-	-	-	-	-	-	He et al. [29]
Hongkong, China, URB	0.38	0.61	-	-	-	-	-	-	-	-	-	-	Ho et al. [30]
Pacific Ocean (coast of Japan)	0.38	0.61	-	-	-	-	-	-	-	-	-	-	Chung and Seinfeld [31]

Source	EC/TC	EC/OC	SO <sub>4</sub> <sup>2-</sup> /EC	K <sup>+</sup> /EC	Bep/Bap	Phen/ (Phen+Anthr)	BaP/BghiP	Ind/ (Ind+BghiP)	BaA/ (BaA+Chry)	BeP/ (BeP+BaP)	Flt/(Flt+Pry)	BkF/BbF	References
ACE-2 (submicron), URB	0.38±0.12	0.58±0.22	15.2±7.2	-	-	-	-	-	-	-	-	-	Novakov et al. [32]
EXPRESSO Africa, BB	0.20±0.06	0.22	0.44	0.085	-	-	-	-	-	-	-	-	Ruellan et al. [33]
SCAR-B, Brazil, BB	0.10±0.03	0.12±0.03	0.28±0.13	0.52±0.11	-	-	-	-	-	-	-	-	Ferek et al. [34]
<sup>a</sup> Assumed from diesel, household coal dominated [35]													
<sup>b</sup> Reddy and Venkataraman [36]													
<sup>c</sup> Gogou et al. [37]													
<sup>d</sup> Simcik et al. [38]													
<sup>e</sup> Sicre et al. [39]													
<sup>f</sup> Kavouras et al. [40]													
							- = not available or not measured						
							R-I~V = Region I~V						
							URB=urban and industrial pollution						
							MIX=mixed emission sources of both biomass burning and fossil fuel combustion						
							BB=biomass burning						
							EXPRESSO (Experiment for Regional Sources and Sinks of Oxidants), Africa, savanna in the boundary layer, aircraft measurements.						

#### 4. CONCLUSION

The analysis of fine carbonaceous aerosol was conducted at Gosan in Jeju, Korea during six intensive measurement periods, from November 2001 to September 2003. This research is aimed to characterize the carbonaceous materials in fine aerosol and identify the possible emission sources, which impact on the ground level fine aerosol. Overall, gaseous and particulate pollutants have different concentration level according to the source regions classified by using three-day backward trajectories. Especially, when air masses were originated from north China, most secondary anthropogenic components, such as secondary ion components and PAHs in aerosol phase, have the highest concentration. In addition, considerable amounts of these pollutants were transported from the Korea peninsula and south China. On the other hand, primary pollutants, such as PAHs in gas phase and primary OC, were mainly originated from relatively close Japan in summer, influenced by Asian monsoon and high temperature in this season. In order to identify more detailed anthropogenic sources, the ratios of several source indicators in aerosol phase were calculated. As a result, anthropogenic pollutants exhausted from biofuel burning and vehicular emissions were mainly transported from north China and the Korea peninsula while pollutants associated with fossil fuel combustion were chiefly originated from south China. Furthermore, these anthropogenic pollutants had better correlation to each other and showed relatively stable form by the chemical transformation during long-range transport.

In present work, the possibility of long-range transport of anthropogenic pollutants was suggested, and sources were estimated considering the dominant characteristics of several major sources. In order to identify more various and exact anthropogenic sources, further work is needed not only to collect much more data but also to combine emission and measurement.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### REFERENCES

- Jacobson MC, Hansson HC, Noone KJ, Charlson RJ. Organic atmospheric aerosols: Review and state of the science. *Rev Geophys*. 2000;38(2):267-294.
- Turpin BJ, Saxena P, Andrews E. Measuring and simulating particulate organics in the atmosphere: Problem and prospects. *Atmos Environ*. 2000;34:2983-3031.
- Mayol Bracero OL, Gabriel R, Andreae MO, Kirchstetter TW, Novakov T, Ogren J et al. Carbonaceous aerosols over the Indian Ocean during the Indian Ocean Experiment (INDOEX): Chemical characterization, optical properties, and probable sources. *J Geophys Res*. 2002; 107(D19):8030.
- Huebert BJ, Bates T, Russel PB, Shi G, Kim YJ, Kawamura K et al. An overview of ACE-Asia: Strategies for quantifying the relationships between Asian aerosols and their climatic impacts. *J Geophys Res*. 2003;108(D23):9633.
- Carmichael G, Streets D, Calorie G, Amann M, Jacobson M, Hansen J, et al. Changing trends in sulfur deposition in Asia: Implications for acid deposition, air pollution and climate. *Environ Sci Technol*. 2002;36:4704-4713.
- Han JS, Moon KJ, Kim YJ. Identification of potential sources and source regions of fine ambient particles measured at Gosan background site in Korea using advanced hybrid receptor model combined with positive matrix factorization. *J Geophys Res*. 2006;111:D22217.
- Kim YP, Moon KC, Lee JH, Baik NJ. Concentrations of carbonaceous species in particles at Seoul and Cheju in Korea. *Atmos Environ*. 1999;33:2751-2758.
- Ramanathan V, Carmichael G, Crutzen PJ, Holben B, Prather K, Prospero J et al. Regional aerosol-chemistry-climate observatories for the Indo-Asia-Pacific Region. Proposal submitted to NOAA; 2003.
- Chow JC, Watson JG, Pritchett LC, Pierson WR, Frazier CA, Purcell RG. The DRI thermal/optical reflectance carbon

- analysis system: Description, evaluation and applications in US air quality studies. *Aerosol Environ.* 1993;27A:1185-1201.
10. Stein AR, Draxler RR, Rolph GD, Stunder BJB, Cohen MD, Ngan F. NOAA's HYSPLIT Atmospheric transport and dispersion modeling system. *American Meteorological Society*; 2015. Available:<https://doi.org/10.1175/BAMS-D-14-00110.1>
  11. Draxler RR. HYSPLIT\_4 User's Guide (Online Version). NOAA Technical Memorandum ERL ARL-230; 2002. (Assessed March 2004)
  12. Draxler RR, Hess GD. NOAA technical memorandum ERL ARL-224: Description of the HYSPLIT\_4 modeling system. Silber Spring, Meryland: Air Resources Lab. 1998;28. Available:[http://www.arl.noaa.gov/data/web/models/hysplit4/win95/user\\_guide.pdf](http://www.arl.noaa.gov/data/web/models/hysplit4/win95/user_guide.pdf)
  13. Zheng M, Fang M, Wang F, To KL. Characterization of the solvent extractable organic compounds in PM<sub>2.5</sub> aerosols in Hong Kong. *Atmos Environ.* 2000;34:2691-2702.
  14. Baek SO, Field RA, Goldstone ME, Kirk PW, Lester JN, Perry R. A review of atmospheric polycyclic aromatic hydrocarbons: Sources, fate and behavior. *Water Air Soil Poll.* 1991;60:279-300.
  15. Seinfeld JH, Pandis SN. *Atmospheric chemistry and physics from air pollution to climate change*. New York: John Wiley & Sons; 1998.
  16. Han JS, Moon KJ, Ahn JY, Hong YD, Kim YJ, Ryu SY, et al. Characterization of ion components and trace elements of fine particles at Gosan, Korea in spring time from 2001 to 2002. *Environ Monit Assess.* 2004;92:73-93.
  17. Spiro PA, Jacob DJ, Logan JA. Global inventory of sulfur emissions with 1°×1° resolution. *J Geophys Res.* 1992;97:6023-6036.
  18. Crutzen PJ, Andreae MO. Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles. *Science.* 1990;250:1669-1978.
  19. Reddy MS, Venkataraman C. Inventory of aerosol and sulphur dioxide emissions from India, II. Biomass combustion. *Atmos Environ.* 2002b;36:697-710.
  20. US EPA. Protocol for applying and validating the CMB model. EPA-450/4-87-010; 1987.
  21. Hopke PK, Song XH, Polissar AV. Sources of fine particle composition in the northeastern US, *Atmos Environ.* 2001;35: 5277-5286.
  22. Andreae MO, Andreae TW, Annegarn H, Beer J, Cachier H, Iecanut P, et al. Airborne studies of aerosol emissions from savanna fires in southern Africa: 2. Aerosol chemical composition. *J Geophys Res.* 1998;103:32119-32128.
  23. Andreae MO, Merlet P. Emission of trace gases and aerosols from biomass burning. *Global Biogeochem Cy.* 2001;15:955-966.
  24. Sheesley RJ, Schauer JJ, Chowdhury Z, Cass GR, Simoneit BRT. Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia. *J Geophys Res.* 2003; 108(D9):4285.
  25. Rogge WF, Hildemann LM, Mazurek MA, Cass GR. Sources of fine organic aerosol. 2. noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ Sci Technol.* 1993a;27:636-651.
  26. Rogge WF, Hildemann LM, Mazurek MA, Cass GR. Sources of fine organic aerosol. 3. road dust, tire debris, and organometallic brake lining dust: Roads as sources and sinks. *Environ Sci Technol.* 1993b;27:1892-1904.
  27. Rogge WF, Hildemann LM, Mazurek MA, Cass GR. Sources of fine organic aerosol. 1. charbroilers and meat cooking operations. *Environ Sci Technol.* 1993c;25: 1112-1125.
  28. Kaneyasu N, Ohta S, Murao N. Seasonal variation in the chemical composition of atmospheric aerosols and gaseous species in Sapporo, Japan. *Atmos Environ.* 1995;29(13):1559-1568.
  29. He Z, Kim YJ, Ogunjobi KO, Kim JE, Ryu SY. Carbonaceous aerosol characteristics of PM<sub>2.5</sub> particles in Northeastern Asia in summer 2002. *Atmos Environ.* 2004; 38:1795-1800.
  30. Ho KF, Lee SC, Yu JC, Zou SC, Fung K. Carbonaceous characteristics of atmospheric particulate matter in Hong Kong. *Sci Total Environ.* 2002;300:59-67.
  31. Chung SH, Seinfeld JH. Global distribution and climate forcing of carbonaceous aerosols. *J Geophys Res.* 2002;107(D19): 4407.
  32. Novakov T, Bates TS, Quinn PK. Shipboard measurements of concentrations and properties of carbonaceous

- aerosols during ACE-2. *Tellus Ser B.* 2000; 52:228-237.
33. Ruellan S, Cachier H, Gaudichet A, Masclet P, Lacaux JP. Air-borne aerosols over central Africa during experiment for regional sources and sinks of oxidants (EXPRESSO). *J Geophys Res.* 1999; 104:30673-30690.
  34. Ferek RJ, Reid JS, Hobbs P, Blake DR, Liousse C. Emission factors of hydrocarbons, halocarbons, trace gases and particles from biomass burning in Brazil. *J Geophys Res.* 1998;103:32107-32118.
  35. Kleeman MJ, Schauer JJ, Cass GR. Size and composition of fine particulate matter emitted from motor vehicles. *Environ Sci Technol.* 2000;34:1132-1143.
  36. Reddy MS, Venkataraman C. Inventory of aerosol and sulphur dioxide emissions from India, I. Fossil fuel combustion. *Atmos Environ.* 2002a;36:677-697.
  37. Gogou A, Stratigakis N, Kanakidou M, Stephanou E. Organic aerosols in Eastern mediterranean: Components source reconciliation by using molecular markers and atmospheric back trajectories. *Org Geochem.* 1996;25:79-96.
  38. Simcik MF, Eisenreich SJ, Liou PJ. Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmos Environ.* 1999;33:5071-5079.
  39. Sicre MA, Marty JC, Saliot A, Aparicio X, Grimault J, Albaiges J. Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean sea: occurrence and origin. *Atmos Environ.* 1987;21:2247-2259.
  40. Kavouras IG, Lawrence J, Koutrakis P, Stephanou EG, Oyola P. Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago do Chile: source reconciliation and evaluation of sampling artifacts. *Atmos Environ.* 1999; 33:4977-4986.