



## Chemical Characterization of Fine and Coarse Particles in Gosan, Korea during Springtime Dust Events

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### ABSTRACT

Particulate matter was collected at Gosan, Korea, a remote location in the East China Sea, from late-March through May, 2007. Two sizes of particles, fine (PM<sub>2.5</sub>) and coarse (PM<sub>10-2.5</sub>) modes, were analyzed for chemical composition. Samples were analyzed by mass, elemental and organic carbon, and inorganic ions. Organic molecular markers were also measured using solvent-extraction gas chromatography mass spectrometry in order to identify different pollution sources. Two major dust events were captured, occurring on 31 March and 26 May, and were characterized by high concentrations of coarse particles, calcium, and secondary inorganic ions. A major pollution event occurred on 26 April with elevated fine particle concentrations and markers of combustion-related and secondary aerosols. Non-event periods in April and May were used to provide context in the interpretation of extreme events. This study demonstrates that carbonaceous aerosols from biomass burning, coal combustion, and motor vehicles containing organic and elemental components that are typically found in fine particles were included in coarse particle mass during dust events. Primary and secondary carbonaceous particles were found to become internally mixed with dust, which is expected to have implications on the dust's chemical composition and surface properties.

**Keywords:** Aerosol; Dust; Gosan; Korea; PAC-DEX; Molecular markers.

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### INTRODUCTION

East Asian dust storms have been characterized as regional air masses polluted with massive amounts of dust and soil mixed with anthropogenic pollution. Dust storms have multi-faceted impacts on the earth's radiative balance by causing surface cooling and atmospheric warming, while contributing to indirect forcing as dust and associated components can be hygroscopic (Seinfeld *et al.*, 2004). Gosan, Korea located on Cheju Island in the East China Sea is a super-site for meteorological and atmospheric measurements and has been utilized for many studies of dust storms and pollution transport in recent decades. It has been a primary ground-based monitoring site during the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) (Kim *et al.*, 2005), Atmospheric Brown Cloud (ABC) field campaigns (Ramanathan *et al.*, 2007), and the PACific Dust EXperiment (PAC-DEX) (Stith *et al.*, 2009) that coincides with this study.

The springtime months (particularly April) at Cheju Island are associated with the highest aerosol loadings caused by dust events originating over the Asian mainland (Carmichael *et al.*, 1997). This period is prone to dust events because of the combination of dry atmospheres (low rainfall), strong winds, and agricultural tilling (Seinfeld *et al.*, 2004). Polluted air masses typically travel to Cheju from the northern part of China and contain a combination of dust and anthropogenic sources (Carmichael *et al.*, 1996; Takamura *et al.*, 2007). The dust in the region is thought to originate primarily in the Gobi desert and has been called Kosa or Yellow Sand. In recent decades, dust storms have been becoming more frequent in East Asia (Kim, 2008), while future climatic change scenarios suggest further increases in emissions of dust to the atmosphere (IPCC, 2007).

Mineral dust alters the chemistry atmosphere, most notably due to its alkaline composition and high surface area for chemical reactions and adsorption of gases. Dust particles are typically in the coarse particle size range with aerodynamic diameters of 1–10  $\mu\text{m}$ . It is primarily comprised of crustal elements, such as silicon, aluminum, iron, calcium, magnesium, and others (Seinfeld *et al.*, 2004; Lee *et al.*, 2007; Duvall *et al.*, 2008). The alkaline nature of dust makes it a key player in atmospheric acid-base

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reactions and in determining the chemical composition of particles. Secondary acids, including sulfuric and nitric acids, are attracted to the coarse mode's alkali metals and alkaline earth metals. The aging of mineral dust involves the inclusion of secondary inorganic species, like sulfate and nitrate, and the release of more volatile inorganic dust components, like carbonate and bicarbonate (Song and Carmichael, 1999). Single-particle mass spectrometry has shown oxalic and malonic acids to be internally mixed with mineral dust and sea salt particles. Their enrichment in mineral dust over carbonaceous particles is consistent with photochemical production, with preferential partitioning of organic acids to alkaline dust (Sullivan *et al.*, 2007).

During atmospheric aging, mineral dust becomes internally mixed with secondary and other species. Pathways leading to internal mixing include heterogeneous uptake, cloud processing, and/or coagulation with secondary particles (Sullivan *et al.*, 2007). Previous studies have suggested that dust particles hydrate and serve as a surface that enhances the formation of secondary compounds like sulfate and nitrate (Hirai *et al.*, 1991; Carmichael *et al.*, 1996; Seinfeld *et al.*, 2004). The aging of mineral dusts can either enhance or decrease the surface reactivity of particles, depending on the chemistry of the aging process (Usher *et al.*, 2003). The inclusion of acidic species that increase particle hygroscopicity are expected to enhance aerosol-cloud interactions and indirect radiative forcing (Sullivan *et al.*, 2007).

Carbonaceous aerosol, including organic and elemental carbon (OC and EC) tend to increase during dust storms and have been shown to increase in size from fine to coarse particles (Lim *et al.*, 2003). The carbonaceous fraction of PM at Gosan has been less comprehensively studied than the inorganic portion, but is expected to be important in aerosol radiative forcing. Mochida *et al.* (2007) measured organic carboxylic acids in fine and coarse particles and concluded that secondary organic aerosol (SOA) formation during dust and anthropogenic pollution events may play an important role in regulating cloud formation. Other studies have suggested that dust may play a role in SOA formation, similar to secondary ions, based on increases of organic acid concentrations during periods of long-term transport (Simoneit *et al.*, 2004; Wang *et al.*, 2009) and water-soluble organic carbon measurements (Duvall *et al.*, 2008).

Highly-specific organic compounds that come from different aerosol source categories, hereby called molecular markers, have been used extensively for the identification of sources and apportionment of ambient aerosol (Simoneit, 1999; Schauer and Cass, 2000). In an April 2001 study at Gosan, Simoneit *et al.* (2004) used particle-phase organic compounds in total suspended particles (TSP) to identify sources of organic matter as fossil fuel use, biomass burning, soil, natural terrestrial, natural marine, and secondary. Several years later, Wang *et al.* (2009) observed markers for similar sources in TSP.

This study combines the characterization of organic and inorganic aerosol composition in size-resolved samples

collected during springtime dust events, a high-pollution event (unrelated to dust), and non-event periods. We focus on understanding the relative concentrations of OC, EC, and organic species in fine (PM<sub>2.5</sub>) and coarse (PM<sub>10-2.5</sub>) size fractions. The organic species of interest are molecular markers and carboxylic acids, which have only previously been measured at Gosan in a single size fraction (TSP). The assessment of the distribution of organic compounds in fine and coarse particles provided for an understanding of how aerosol from different sources behaved during different pollution events.

## METHODS

### Sample Collection

The samples discussed in this paper were collected in Gosan, South Korea (33.68°N, 126.17°E, 73 m above sea level), located on Cheju Island in the East China Sea. Cheju Island is a well-established air pollution measurement site, utilized in previous ABC and ACE-Asia field campaigns (Lim *et al.*, 2003; Seinfeld *et al.*, 2004; Kim *et al.*, 2007; Ramanathan *et al.*, 2007). The island is distanced from the surrounding land areas by a minimum of 100 km. The major use of Cheju is tourism and it contains no large industrial sources, such that the island is considered to be remote for the purpose of atmospheric studies.

Samples were collected from 31 March to 26 May on Tuesdays, Thursdays, and Saturdays beginning at 09:00 local time and lasting for 24-h. A medium-volume PM<sub>2.5</sub> and PM<sub>10</sub> sampling apparatus (URG3000-ABC) was located on a platform approximately 3m above ground. PM<sub>10</sub> particles were selected using a PM<sub>10</sub> inlet followed by a cyclone at a flow rate of 32 liters per minute (L/min). PM<sub>2.5</sub> was collected through one of two cyclones operating at flows of 16 L/min. Air flow was initiated by a vacuum pump, controlled by critical orifices, and measured before and after sampling with a calibrated Rotameter. Particulate matter was collected on Teflon and quartz fiber filters (47 mm, Pall Life Sciences) and the latter substrate was pre-cleaned in the laboratory by baking at 550°C for a minimum of 18-h. Filters were stored in Petri dishes sealed with Teflon tape and were stored frozen after sample collection.

### Chemical Analysis

Fine and coarse particle mass was measured gravimetrically using a robot (Bohdon Automation) and a calibrated high-precision scale (Mettler Toledo 5). Particulate mass was measured as the difference between pre- and post-sampling tare weights of Teflon filters. Filters were allowed to equilibrate for a minimum of 24 hours in a controlled environment with constant temperature (21 ± 2°C) and humidity (35 ± 3%) prior to weighing. OC and EC were measured on quartz filters by a thermal-optical instrument (Sunset Laboratories) following the ACE-Asia base case protocol (Schauer *et al.*, 2003).

To measure water-soluble ions, Teflon filters were pre-wetted with 0.3 mL isopropanol (99.9%, Fisher Scientific) and then extracted in 30mL of high-purity water (MilliQ)

by shaking for three hours. The decanted liquid was analyzed by ion-exchange chromatography with conductivity detection (Dionex Corporation) for potassium, sodium, ammonium, calcium, sulfate, nitrate, and chloride. Standard analyte solutions (Accustandard) were analyzed along with samples and five-point calibration curves were used for quantification.

Organic species were measured in filter composites that are listed in Table 1. The basis for forming these composites is discussed in the following section. Composites of filters were spiked with isotopically-labeled recovery standards that included benz(a)anthracene-D<sub>12</sub>, coronene-D<sub>12</sub>, cholestane-D<sub>4</sub>, eicosane-D<sub>42</sub>, triacontane-D<sub>62</sub>, dotriacontane-D<sub>66</sub>, eicosanoic acid-D<sub>39</sub>, tetracosanoic acid-D<sub>59</sub>, and levoglucosan-<sup>13</sup>C<sub>6</sub>. Samples were extracted by Soxhlets with dichloromethane followed by methanol, each for 24-h. The solvent extract was subsequently reduced to a volume of 100  $\mu\text{L}$  by means of rotary and nitrogen evaporation. Prior to analysis, extracts were derivatized first by methylation using diazomethane and then by silylation (Nolte *et al.*, 2002). Samples were analyzed using gas chromatography mass spectrometry (GCMS, Agilent Technologies) with negative electron impact ionization. To assist with instrument sensitivity, 30  $\mu\text{L}$  of sample was injected into the GC using programmable temperature vaporization (PTV). The PTV-GCMS conditions used in this study are described in detail elsewhere (von Schneidmesser *et al.*, 2008). Standard solutions containing target analytes and internal standards were analyzed alongside samples to create calibration curves for quantification. Additional details about filter extraction and GCMS analysis may be found in other publications (Sheesley *et al.*, 2004).

For all analytical measurements quality control procedures were followed. At a minimum, one field blank was analyzed for every five samples. For some analyses, laboratory blanks, filter spikes, and external check standards were also analyzed. The uncertainty of chemical measurements was propagated from the standard deviation of field blank values and a percentage of the measurement that represented the range of acceptable recoveries from spiked filters. The concentrations of analytes in the coarse mode (PM<sub>10-2.5</sub>) were calculated by taking the difference of PM<sub>10</sub> and PM<sub>2.5</sub> measurements.

## RESULTS AND DISCUSSION

### Particulate Mass and Carbon

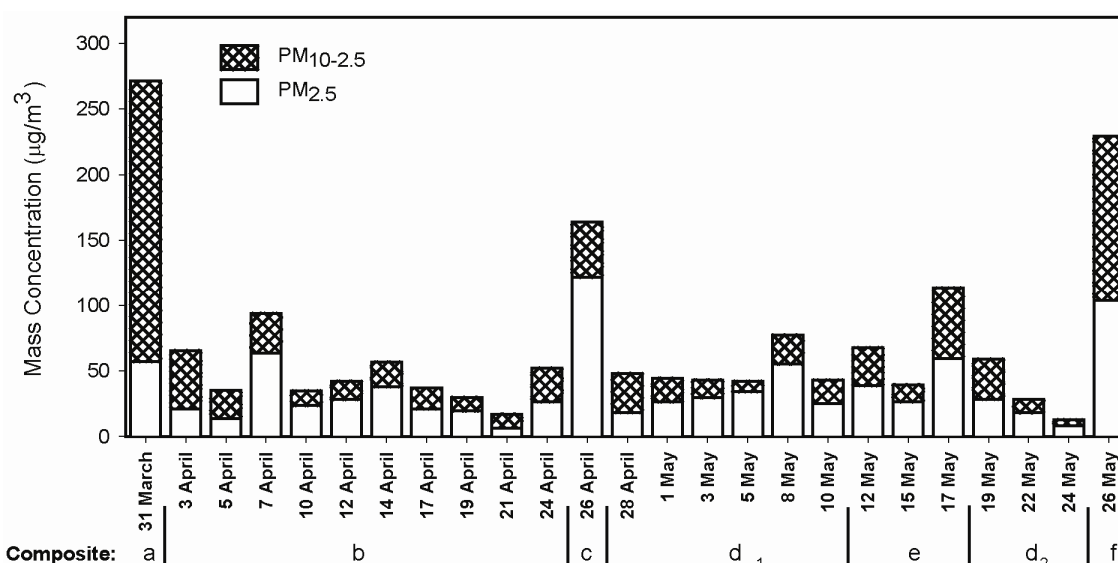
The period of study, ranging from 31 March to 26 May 2007, encompassed the springtime Asian dust season and corresponded to the intensive PACific Dust EXperiment (PAC-DEX) field campaign. At Gosan, Korea the ground-based 24-h average PM<sub>2.5</sub> concentration ( $\pm$  one standard deviation) was  $36 \pm 26 \mu\text{g}/\text{m}^3$ , while PM<sub>10</sub> was  $68 \pm 59 \mu\text{g}/\text{m}^3$ . Coarse-mode aerosol, defined as PM<sub>10-2.5</sub>, had concentrations in the range of 4.3 to 214  $\mu\text{g}/\text{m}^3$  and averaged  $31 \pm 41 \mu\text{g}/\text{m}^3$ . On two sampling days, 31 March and 26 May, the coarse PM concentrations exceeded 100  $\mu\text{g}/\text{m}^3$ , as shown in Fig. 1, and were identified as dust events based on corresponding chemical measurements (discussed in the following section). On 12, 15, and 17 May, coarse PM concentrations were elevated relative to PM<sub>2.5</sub> and exhibited chemical characteristics of dust events. However, the 12–17 May period did not have extreme dust loadings and were consequently treated separately from the major dust events. On 26 April, a maximum PM<sub>2.5</sub> concentration of 122  $\mu\text{g}/\text{m}^3$  occurred while coarse aerosol concentrations were near the average value; consequently, this day was identified as a high PM event unrelated to dust.

Back trajectory analysis was performed to gain insight to the origins of air masses impacting Gosan from 31 March to 26 May. The NOAA Hybrid Single Particle Lagrangian Trajectory (HYSPLIT) model used six-hour meteorological data provided by the US National Centers for Environmental Prediction Global Data Assimilation System (Draxler and Rolph, 2003). Air masses impacting Gosan were modeled over a five-day backward trajectory. Starting altitudes of 500, 1000, and 1500 m were considered and the isentropic vertical motion option was employed. Trajectories started at 00 UTC of each day; at Gosan, a dust event occurred at 12 UTC on 31 March, hence the backward trajectory on 1 April was analyzed. Trajectories were classified for each composite sample based on a previous study of dust events in Gosan (Kim *et al.*, 2007) and are summarized in Supplemental Table S1. Trajectories confirmed that samples classified as dust events were impacted by long-range transport from the Gobi desert and Inner Mongolia regions of China. The

**Table 1.** Summary of composite samples from Gosan, Korea and their average chemical characteristics.

Composite	Dates in 2007 <sup>a</sup>	Description	Fine Particulate Matter (PM <sub>2.5</sub> )			Coarse Particulate Matter (PM <sub>10-2.5</sub> )		
			Mass ( $\mu\text{g}/\text{m}^3$ )	Organic Carbon (% PM)	Elemental Carbon (% PM)	Mass ( $\mu\text{g}/\text{m}^3$ )	Organic Carbon (% PM)	Elemental Carbon (% PM)
a	March 31	Dust Event	57.0	4.4	0.5	214.2	1.9	0.1
b	April 3–21	Non-Event	26.1	9.2	1.2	19.6	1.7	< 0.1
c	April 26	PM Event	122.0	8.8	0.7	41.8	3.0	0.8
d	May 1–10, 19–24	Non-Event	28.1	7.1	0.8	15.5	2.6	0.3
e	May 12–17	Small Dust Events	41.5	2.7	0.2	32.0	4.7	1.1
f	May 26	Dust Event	103.9	4.0	0.8	125.4	1.0	0.3

<sup>a</sup> Composite b includes April 3, 5, 7, 10, 12, 14, 17, 18 and 21; Composite d includes May 1, 3, 5, 8, 10, 18, 22, and 24; Composite e includes May 12, 15, and 17.



**Fig. 1.** Ambient concentrations of fine (PM<sub>2.5</sub>) and coarse (PM<sub>10-2.5</sub>) particles measured at Gosan, Korea in 2007 at a sampling rate of three days per week. The markings “a–f” correspond to composite samples, further described in Table 1.

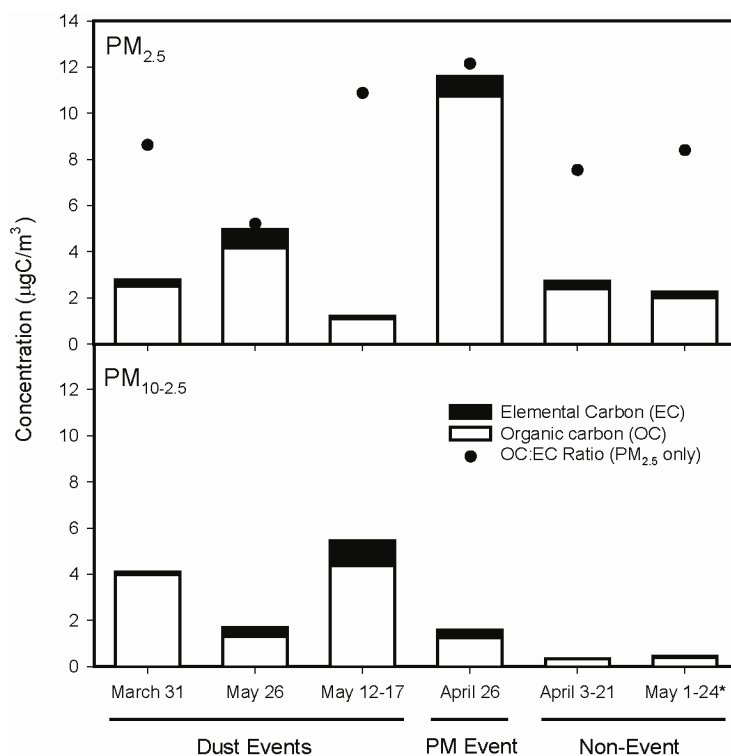
air mass associated with the PM event originated over Northeastern China. Non-event periods were characterized by spatial variability in air masses that included origins over Northeastern China, the Korean peninsula, and the East China Sea.

Filter samples were separated into composites, summarized in Table 1, that correspond to individual dust or PM events or non-event periods. The PM mass for each composite is shown in Supplemental Fig. S1. The purpose of dividing the samples into composites was to compile enough organic material to conduct detailed composition measurements while preserving the ability to compare across dust and non-dust periods.

OC and EC were measured in each 24-h sample and composite average concentrations are shown in Fig. 2 and summarized in Table 1. For this study, the average OC and EC concentrations in PM<sub>2.5</sub> were 2.54 and 0.31 µg/m<sup>3</sup> while concentrations in PM<sub>10-2.5</sub> were smaller at 0.75 and 0.15 µg/m<sup>3</sup>. Carbonaceous aerosol (OC plus EC) accounted for an average of 8.2% of PM<sub>2.5</sub> and 5.8% of PM<sub>10</sub> mass. Maximum PM<sub>2.5</sub> OC and EC concentrations occurred on 26 April during the PM event and were 10.7 and 0.9 µg/m<sup>3</sup>, respectively. During dust events, higher levels of OC and EC were observed in the coarse mode compared to non-event levels, a finding also observed during ACE-Asia (Lim *et al.*, 2003; Mochida *et al.*, 2007). Since EC is formed only by combustion processes, it is expected to be present primarily in the PM<sub>2.5</sub> size fraction. The enhancement of EC in the coarse fraction during dust events suggested that dust conditions facilitated atmospheric processes that caused PM<sub>2.5</sub> to increase in size. Examples of such processes include coagulation, in which smaller particles combine to form larger ones, or coating of PM<sub>2.5</sub> particles with semi-volatile compounds, secondary aerosols, or other materials (Seinfeld *et al.*, 2004). These physical changes also cause changes in particle mixing state and morphology, which have

significant impacts on light-absorbing properties of aerosols (Fuller *et al.*, 1999). The ratios of OC to EC observed in this study ranged from 5.2–12. The 26 May dust event had the lowest OC to EC ratio compared to the other samples. The shift in OC relative to EC may have been related to the longer aerosol residence times associated with the dust event, during which OC may be removed more quickly than EC, as was observed by Lim *et al.* (2003). The OC to EC ratios observed during the 31 March dust event and 12–17 May minor dust events were comparable to background periods, suggesting that the selective removal of OC was not a consistent phenomenon.

The aerosol composition observed in Gosan during this study was comparable to previous springtime measurements when considering the caveats introduced by measuring different aerosol size fractions across various studies. The average PM<sub>2.5</sub> mass concentration in this study (36.5 µg/m<sup>3</sup>) was moderately higher than in the ABC East Asian Regional EXperiments (EAREX) field campaign from 13–30 March 2005 when the average was 27.3 µg/m<sup>3</sup> (Lee *et al.*, 2007), but were comparable to April 2001 levels observed by Duvall *et al.* (2008) in PM<sub>1.0</sub> during the ACE-Asia study. The PM<sub>10</sub> mass concentrations observed in this study were expectedly lower than springtime TSP concentrations, since the PM<sub>10</sub> fraction omits particles greater than 10 µm that are included in TSP. The concentrations of carbonaceous species were slightly lower in this study compared to EAREX when Lee *et al.* (2007) observed an average PM<sub>2.5</sub> OC and EC concentrations of 4.2 and 1.0 µg/m<sup>3</sup>, respectively and ACE-Asia when Simoneit *et al.* (2004) observed higher concentrations in TSP. The ratios of OC to EC were also slightly higher in this study than observed in either of the previous studies (Lim *et al.*, 2003). The differences between carbonaceous aerosol composition between this and previous studies may have been caused by changes to its sources over time or by differences in measurement techniques.



**Fig. 2.** Ambient concentrations of organic and elemental carbon and their relative ratios observed in fine and coarse particles by composite.

### Water-Soluble Ions

Previous studies at Gosan have reported water-soluble ion concentrations during dust events; their key findings are briefly discussed in the context of this study, to demonstrate that the dust events observed in this study are representative of other events in the region. In this study, calcium, ammonium, potassium, sodium, sulfate, nitrate, and chloride were measured in 24-h samples and ambient concentrations are summarized in Table 2 and presented in Supplemental Figs. S1–S4 by composite. The vast majority of calcium was found in the coarse particle fraction (average  $\pm$  one standard deviation,  $80 \pm 18\%$ ). The highest calcium concentrations in coarse PM occurred during the dust events on 31 March at  $4.3 \mu\text{g}/\text{m}^3$  and 26 May at  $4.5 \mu\text{g}/\text{m}^3$ , while springtime non-event levels averaged  $0.6 \pm 0.4 \mu\text{g}/\text{m}^3$ . During previous dust events, elevated levels of water-soluble calcium were observed (Carmichael *et al.*, 1996; Seinfeld *et al.*, 2004) and attributed to high concentrations of calcium in surface soils (e.g. 2.8% by mass in Gobi Desert soil) (Carmichael *et al.*, 1997).

Sodium and chloride are associated with aerosols generated by sea spray (Friedlander, 1973) and are abundant in coastal areas like Gosan. In this study,  $82 \pm 9\%$  of sodium and  $89 \pm 16\%$  of chloride were found in the coarse fraction. During non-event periods, the mass contribution of sodium and chloride was  $16 \pm 13\%$  of coarse particle mass, on average, compared to dust events when it contributed less than 2%. For all days, the abundance of chloride relative to sodium was smaller than predicted by the composition of seawater; an observation noted in a previous study that was suggested to be caused

chlorine-liberating reactions in the atmosphere or on filter (Carmichael *et al.*, 1997).

Sulfate was the most abundant ion species measured, with the highest concentration occurring on 26 April during the PM event when  $\text{PM}_{2.5}$  concentrations reached  $55 \mu\text{g}/\text{m}^3$  and accounted for 45% of particle mass. On average,  $98 \pm 2\%$  of sulfate was from non-sea salt origins and more than  $88 \pm 8\%$  was found in the fine fraction, which supported the conclusion that sulfate was formed in the atmosphere via secondary reactions. Sulfate was enriched during dust periods compared to non-event periods, by a factor of 2.4 for  $\text{PM}_{2.5}$  and 4.0 for coarse aerosol. Nitrate, also considered to be formed via secondary reactions, was highest during the PM event; it was also elevated during dust events, by factors of 1.5 for  $\text{PM}_{2.5}$  and 3.5 for coarse aerosol. In contrast to sulfate, nitrate demonstrated less of a preference towards the fine fraction, in which an average of  $38 \pm 12\%$  of the observed concentration was found; these size distributions were also noted during ACE-Asia (Seinfeld *et al.*, 2004). High concentrations of inorganic ions typically of secondary origin—sulfate and nitrate—were also enhanced in previously studied dust events (Carmichael *et al.*, 1996), as discussed in the introductory section. Ammonium was the most abundant cation measured; its concentrations were greatest during the PM event and the 26 May dust event. It was found almost entirely in the fine fraction ( $> 95 \pm 9\%$ ) and was frequently not detected in the coarse fraction. Mochida *et al.* (2007) also found that ammonium was excluded from coarse particles and attributed it to the preferential neutralization of acids by alkaline metals over ammonium.

**Table 2.** Summary of elemental carbon and organic species observed in fine and coarse particulate matter in Gosan, Korea during dust events (an average of March 31 and May 26) and PM event (April 26) compared to the non-event periods (averages from April and May). Inorganic ions refer to the water-soluble fraction only. Note that units vary by species.

Aerosol Component	Fine Particulate Matter (PM <sub>2.5</sub> )			Coarse Particulate Matter (PM <sub>10-2.5</sub> )		
	Dust Events	PM Event	Non-Event Periods	Dust Events	PM Event	Non-Event Periods
Mass (µg/m <sup>3</sup> )	80.4	122.0	27.1	169.8	41.8	17.5
Organic Carbon (µg/m <sup>3</sup> )	3.33	10.73	2.21	2.64	1.26	0.37
Elemental Carbon (µg/m <sup>3</sup> )	0.54	0.88	0.28	0.25	0.31	0.05
Sulfate (µg/m <sup>3</sup> )	22.86	55.12	9.57	4.10	2.58	0.99
Nitrate (µg/m <sup>3</sup> )	1.78	8.41	1.22	6.95	11.14	2.01
Chloride (µg/m <sup>3</sup> )	0.07	0.06	0.15	0.99	0.23	1.52
Calcium (µg/m <sup>3</sup> )	1.05	0.24	0.10	4.42	1.62	0.43
Ammonium (µg/m <sup>3</sup> )	6.31	18.30	3.33	< 0.2	0.90	0.21
Potassium (µg/m <sup>3</sup> )	0.74	1.43	0.33	0.26	0.12	0.09
Sodium (µg/m <sup>3</sup> )	0.48	0.35	0.36	1.35	1.34	1.51
Polyaromatic Hydrocarbons (ng/m <sup>3</sup> )						
Benzo(b)fluoranthene	0.42	0.86	0.19	0.13	0.13	0.04
Benzo(k)fluoranthene	0.20	0.37	0.07	< 0.03	< 0.03	< 0.03
Benzo(e)pyrene	0.33	0.74	0.10	0.04	< 0.03	< 0.03
Benzo(a)pyrene	0.14	0.36	0.05	< 0.03	< 0.03	< 0.03
Perylene	0.03	0.04	0.01	0.05	0.04	< 0.03
Picene	0.05	0.07	0.03	< 0.02	< 0.02	< 0.02
Hopanes (ng/m <sup>3</sup> )						
17α(H)-22,29,30-Trisnorhopane	0.018	0.028	0.007	0.005	0.011	0.003
17β(H)-21α(H)-30-Norhopane	0.056	0.152	0.023	0.010	0.015	0.008
17α(H)-21β(H)-Hopane	0.103	0.203	0.024	0.022	0.016	0.011
Levoglucosan (ng/m <sup>3</sup> )	5.83	10.05	10.26	11.25	2.42	0.37
<i>n</i> -Alkanes (ng/m <sup>3</sup> )						
Heptacosane	3.05	5.38	1.24	3.13	2.70	0.54
Octacosane	1.43	3.40	0.63	0.40	0.07	0.09
Nonacosane	5.31	4.70	1.19	5.05	5.22	0.69
Triacontane	1.69	2.70	0.49	0.55	< 0.05	0.14
Hentriacontane	2.94	5.43	0.99	4.01	1.89	0.45
<i>n</i> -Alkanoic Acids (ng/m <sup>3</sup> )						
Docosanoic acid	4.88	21.52	2.62	4.28	< 0.30	2.60
Tricosanoic acid	1.62	9.51	1.28	0.42	< 0.30	0.37
Tetracosanoic acid	4.42	18.51	2.94	4.38	< 0.30	0.83
Pentacosanoic acid	0.76	3.46	0.73	0.31	< 0.30	< 0.30
Hexacosanoic acid	3.26	8.58	1.50	2.11	< 0.30	< 0.30
Heptacosanoic acid	0.64	2.80	0.47	0.49	< 0.30	< 0.30
Octacosanoic acid	4.11	10.81	2.07	1.57	< 0.30	< 0.30
Aromatic Acids (ng/m <sup>3</sup> )						
1,2,4-Benzenetricarboxylic acid	0.36	0.20	0.05	< 0.02	< 0.02	0.22
1,2,3-Benzenetricarboxylic acid	0.13	0.65	< 0.02	0.06	< 0.02	< 0.02
1,2,4,5-Benzenetetracarboxylic acid	0.10	0.13	< 0.02	0.10	0.04	< 0.02

#### Organic Molecular Markers and Carboxylic Acids

The organic composition of PM<sub>2.5</sub> and PM<sub>10-2.5</sub> was studied for dust and PM events and compared to non-event periods. The measured species were molecular markers for primary sources and included PAH, hopanes, levoglucosan, C<sub>27</sub>–C<sub>31</sub> *n*-alkanes, and C<sub>22</sub>–C<sub>28</sub> *n*-alkanoic acids. Carboxylic acid species were used as tracers of SOA. The selected set of organic compounds allowed for assessment of how PM from different primary and secondary sources behaved during dust, high-PM, and non-event periods and how dust events impacted the size distribution of organic

species. The ambient concentrations of organic molecules in PM<sub>2.5</sub> and PM<sub>10-2.5</sub> are discussed by compound classes and in the context of their sources.

Five PAH measured in this study—benzo(b) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, and perylene—are used as tracers for emissions from fossil fuel combustion, which includes an array of sources such as gasoline motor vehicles, diesel engines, fuel oil combustion, and coal combustion (Simoneit, 1999; Lough *et al.*, 2007), and in source apportionment of organic aerosol (Sheesley *et al.*, 2007). These PAH were selected

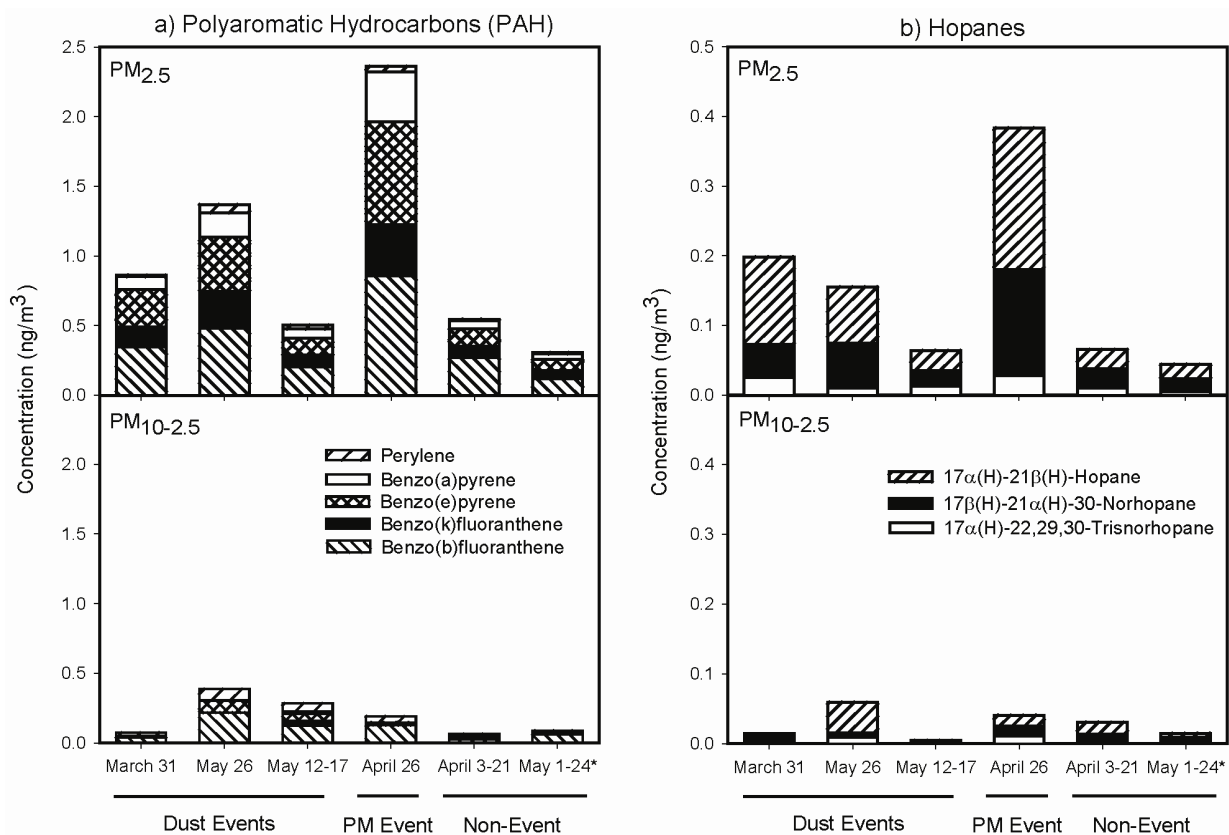
for their high molecular weights ( $\geq 252$  amu) and low vapor pressures, such that they are found in the particle phase at ambient temperatures. As shown in Fig. 3a and Table 2, the majority of PAH was observed in the fine fraction and for many samples PAH were not observed in the coarse fraction. These findings are consistent with PAH originating from combustion sources, which are known generate fine particulate matter. The  $PM_{2.5}$  concentration of these five PAH was greatest on 26 April at a total concentration of  $2.4 \text{ ng/m}^3$ , indicating that PM related to fossil fuel burning had the greatest impact during the PM event. PAH concentrations in  $PM_{2.5}$  were elevated during major dust events ( $0.9\text{--}1.4 \text{ ng/m}^3$ ) compared to non-event concentrations ( $0.3\text{--}0.6 \text{ ng/m}^3$ ). This result suggested that dust events were also associated with transport of anthropogenic pollutants, an observation made during previous studies at Gosan (Carmichael *et al.*, 1997; Lee *et al.*, 2007; Duvall *et al.*, 2008). The coarse-mode PAH concentrations were elevated above non-event levels during the 26 May dust event and the dust-impacted period in mid-May, but not the 31 March event, indicating that dust may, but does not necessarily contribute to growth of  $PM_{2.5}$  to form particles in the  $PM_{10-2.5}$  fraction. The  $PM_{10}$  levels of PAH (sum of five species) observed in this study during dust and PM events ranged from  $0.8\text{--}2.5 \text{ ng/m}^3$  and were similar to 48-h concentrations measured by Simoneit *et al.* (2004) in the springtime of 2001 ( $1.0\text{--}2.4 \text{ ng/m}^3$ ) and the mean concentration ( $1.4 \text{ ng/m}^3$ ) observed in the spring of 2005 by Wang *et al.* (2009), where both measurements used for comparison correspond to TSP. The results of this study were also comparable to fine particle PAH measurements made by Moon *et al.* (2008), where similarly measured PAH concentrations averaged  $0.07\text{--}0.27 \text{ ng/m}^3$  individually.

Picene is a highly-specific PAH found only in the emissions from coal combustion (Oros and Simoneit, 2000; Zhang *et al.*, 2008). As shown in Table 2, this compound was observed only in the  $PM_{2.5}$  fraction. Picene followed a similar trend as other PAH, where the ambient picene concentration peaked on 26 April (at  $0.07 \text{ ng/m}^3$ ) and was elevated during dust events ( $0.04\text{--}0.05 \text{ ng/m}^3$ ) compared to non-event levels ( $0.02\text{--}0.03 \text{ ng/m}^3$ ). The coal combustion profiles developed by Zhang *et al.* (2008) report picene-to-OC ratios of  $72\text{--}430 \text{ pg}/\mu\text{g}$  for small-scale, residential boilers burning five different types of coal. Using this range of conversion factors, the estimated coal contribution to OC on 26 April range was  $0.16\text{--}0.97 \mu\text{g/m}^3$  or  $1.5\text{--}9.1\%$  of total OC. These data indicate that coal combustion contributed to the anthropogenic pollution impacting Gosan during the PM event and had similar influence on the air masses carrying dust from the Asian mainland. It is not possible to draw conclusions about how that particle-phase OC from coal combustion behaved during dust events, since picene was not detectable in the coarse fraction.

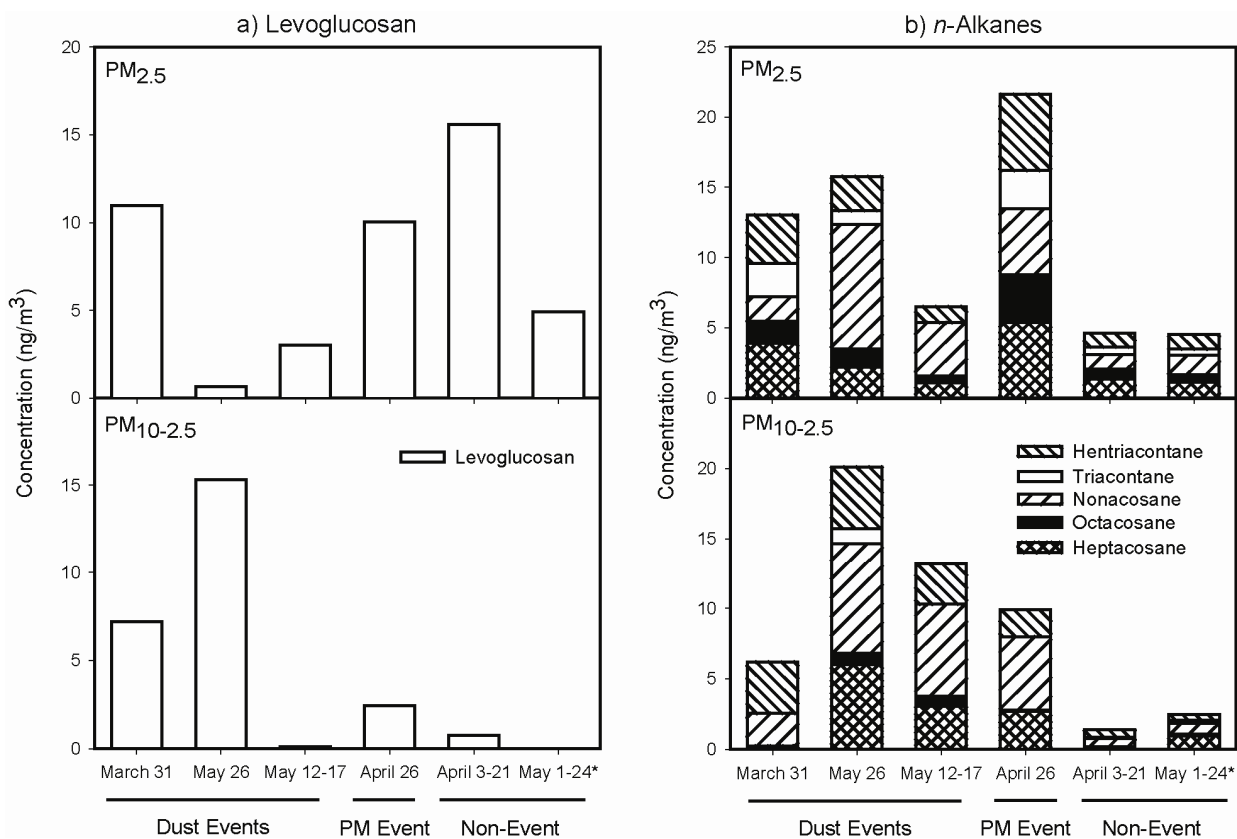
Hopanes in atmospheric aerosols are indicators of fossil uses, as they are formed in appreciable levels only on geologic time scales (Simoneit, 1999). They are known to be emitted from gasoline- and diesel-powered motor vehicles (Lough *et al.*, 2007) primarily through use of

motor oils (Zielinska *et al.*, 2008), from coal (Zhang *et al.*, 2008), and fuel oil (Rogge *et al.*, 1997) combustion. They appear in a homologous series of pentacyclic triterpanes, in which the three hopanes reported in this study— $17\alpha(\text{H})\text{-}21\beta(\text{H})\text{-hopane}$ ,  $17\beta(\text{H})\text{-}21\alpha(\text{H})\text{-}30\text{-norhopane}$ , and  $17\alpha(\text{H})\text{-}22,29,30\text{-trisorhopane}$ —are among the most abundant. As shown in Fig. 3b, hopanes were most abundant in the fine fraction and were observed at total levels that ranged from  $0.04\text{--}0.07 \text{ ng/m}^3$  for non-event periods and  $0.16\text{--}0.20 \text{ ng/m}^3$  for major dust events. The maximum concentration was observed during the 26 April PM event at  $0.38 \text{ ng/m}^3$ . The relative abundance of the hopanes was consistent across  $PM_{2.5}$  samples and averaged  $1.00:0.76:0.25$  ( $17\alpha(\text{H})\text{-}21\beta(\text{H})\text{-hopane}:17\beta(\text{H})\text{-}21\alpha(\text{H})\text{-}30\text{-norhopane}:17\alpha(\text{H})\text{-}22,29,30\text{-trisorhopane}$ ). If ratios had greatly differed across samples, this would have suggested that sources of hopanes in Gosan were temporally irregular and that multiple hopane sources (with different relative abundances of hopanes) had impacted the site. The amount of hopanes in the coarse fraction accounted for an average of only 10% of the total concentration. The  $PM_{10-2.5}$  hopane concentrations were elevated during the 26 May dust event compared to non-event periods, but not in the 31 March major dust event or the 12–17 May minor events. This trend is analogous to that of PAH and secondary inorganic ions, and supporting the ACE-Asia observation that dust events may carry anthropogenic pollution to Gosan (Seinfeld *et al.*, 2004).

Levoglucosan is a well-known biomarker for the combustion of modern biomass that is formed by the pyrolysis of cellulose at temperatures greater than  $300^\circ\text{C}$  (Simoneit *et al.*, 1999). While the exact concentrations of levoglucosan in biomass burning emissions vary with fuel type and burn condition, it accounts for an average of 21% of organic carbon (Schauer *et al.*, 2001; Fine *et al.*, 2004a, b; Lee *et al.*, 2005). The levoglucosan concentrations observed in Gosan are shown in Fig. 4a.  $PM_{2.5}$  levoglucosan concentrations ranged from  $0.7\text{--}15.6 \text{ ng/m}^3$  while  $PM_{10-2.5}$  concentrations ranged from below detection to  $15.3 \text{ ng/m}^3$ . These are considerably lower than areas heavily impacted by biomass burning emissions where levoglucosan concentrations have reached  $500 \text{ ng/m}^3$  (Sheesley *et al.*, 2007) to more than  $1000 \text{ ng/m}^3$  (Schauer and Cass, 2000). Rather, the levels observed in this study were in the same range as those observed in Hanimaadhoo, Maldives during a polluted, dry period impacted by a regional haze (Stone *et al.*, 2007) and were of the same order of magnitude as previous measurements in Gosan (Simoneit *et al.*, 2004; Wang *et al.*, 2009). Using a levoglucosan-to-OC ratio of 0.21, it is estimated that maximum biomass contributions to  $PM_{2.5}$  occurred during the April non-event period at levels around  $70 \text{ ng/m}^3$  and accounted for 3% of OC while for other periods, biomass burning contributions to  $PM_{2.5}$  OC ranged from  $0.4\text{--}2.1\%$ . The maximum contribution to  $PM_{10-2.5}$  observed on the 26 May dust event at  $70 \text{ ng/m}^3$  and accounted for 6% of OC. The relatively small biomass burning influence at Gosan was also noted by Moon *et al.* (2008) who estimated that this source contributed an average of 0.2% of fine particle



**Fig. 3.** Ambient concentrations of a) polyaromatic hydrocarbons (PAH) and b) hopanes in fine and coarse particles by composite.



**Fig. 4.** Ambient concentrations of a) levoglucosan and b) *n*-alkanes observed in fine and coarse particles by composite.



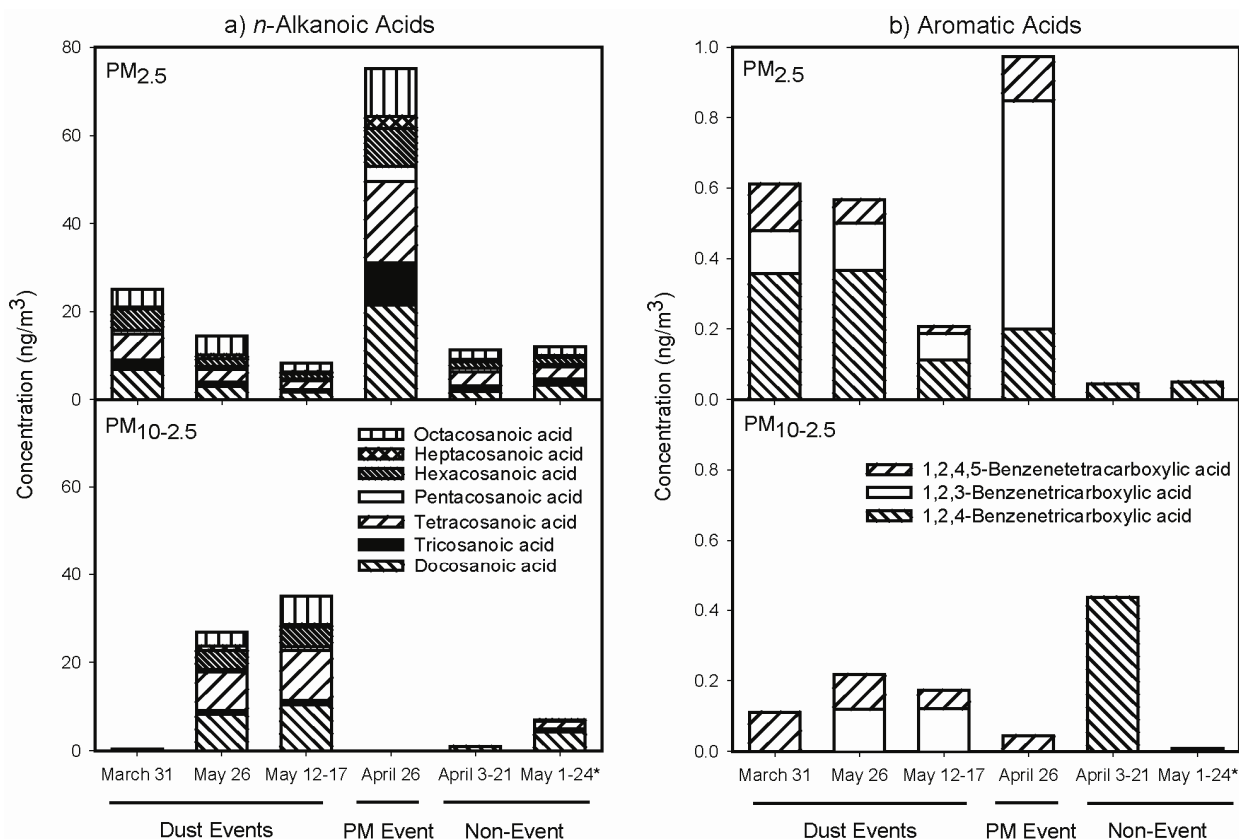
mass at Gosan during the springtime of 2002 using multivariate analysis. Other studies have already shown that dust events at Gosan can be impacted by biomass burning events, as was the case in the study of Wang *et al.* (2009) who observed increased levoglucosan concentrations during a dust storm and linked this to biomass burning events in Siberia and northeastern China. In this study, there is a clear trend that levoglucosan was enhanced in the coarse fraction during the two major dust events compared to non-event periods. In particular, an excess of 95% of observed levoglucosan was found in the coarse fraction on 26 May. These results indicated that biomass burning emissions underwent physical changes in the presence of dust that caused them to increase in size.

Particle-phase *n*-alkanes come from several sources that can be differentiated based on chemical signatures. Alkanes from plant waxes fall into the range of C<sub>16</sub>–C<sub>40</sub> with a distinct odd-carbon preference. A lack of carbon preference in alkanes ranging from C<sub>14</sub>–C<sub>22</sub> is associated with petroleum components and anthropogenic fossil fuel use (Simoneit, 1999). In this study, we focused on the *n*-alkanes ranging from C<sub>27</sub>–C<sub>31</sub> shown in Fig. 4b. The carbon preference index (CPI) is defined as the sum of odd-carbon species concentrations divided by the sum of even-carbon species concentrations. In all PM<sub>2.5</sub> and PM<sub>10–2.5</sub> composites, an odd-carbon preference with CPI greater than one was observed, which indicated biogenic matter as the primary origin of *n*-alkanes. In fact, the coarse fraction had consistently higher CPI indices than the fine fraction and a stronger influence from plant waxes. This result was consistent with plant wax aerosols being generated from leaf-abrasion, a mechanical process that preferentially forms particles in the coarse mode. It was not expected that *n*-alkanes in Gosan were associated with vegetative detritus suspended during biomass combustion due to the low impacts from this source. For the 31 March dust event the *n*-alkane observed at highest abundance across measured size fractions was hentriacontane (C<sub>31</sub>), whereas for all other composites maxima occurred at heptacosane (C<sub>29</sub>). This slight divergence implied differences in the source regions of the biogenic matter affecting the 31 March sample (Simoneit *et al.*, 2004). The absolute concentrations of measured *n*-alkanes in PM<sub>10</sub> as part of this study ranged from 7–36 ng/m<sup>3</sup> and encompassed the average concentration of 17 ng/m<sup>3</sup> observed in an earlier study of TSP in Gosan (Wang *et al.*, 2009).

A homologous series of *n*-alkanoic acids in the range of C<sub>22</sub>–C<sub>28</sub> were also measured. The *n*-alkanoic acids in this size range typically originate in plant waxes and demonstrate an even-carbon preference (Simoneit, 1999). Of the compound classes measured, *n*-alkanoic acids contributed the greatest amount of OC; their mass concentrations are shown in Fig. 5a and are summarized in Table 2. The total concentrations of these compounds ranged from 14–25 ng/m<sup>3</sup> during dust events, 11–12 ng/m<sup>3</sup> during non-event periods, and peaked at 75 ng/m<sup>3</sup> during the 26 April pollution event. Similar concentrations were observed by Simoneit *et al.* (2004) and Wang *et al.* (2009) in earlier studies. The calculated CPI indices for *n*-alkanoic

acids averaged 3.3 for PM<sub>2.5</sub>, confirming their biogenic origin. For the three composites in May, when the full homologous series were observed in the coarse fraction, the PM<sub>10–2.5</sub> CPI indices were consistently two times higher than the fine fraction. For the May dust periods, 65–81% of *n*-alkanoic was observed the coarse mode. Although *n*-alkanoic acids and *n*-alkanes have similar sources, their concentrations did not track together across the different samples. The main similarity between the biogenically-derived markers is their enhancement during May dust events. Yet, differences suggest that *n*-alkanoic exhibited more temporal seasonality since concentrations were higher in May compared to earlier periods.

Aromatic polycarboxylic acids in ambient atmospheres have been established as tracers for SOA (Fine *et al.*, 2004c; Sheesley *et al.*, 2004) and have been used as markers of SOA in a seasonal haze in South Asia (Stone *et al.*, 2007). Although aromatic acids may be emitted from primary sources (Simoneit, 1985), it is expected that secondary reactions are primarily responsible for their presence in the atmosphere (Fraser *et al.*, 2003). Secondary species that form through photochemical reaction appear predominantly in the fine fraction where nucleated particles accumulate. This study focuses on three aromatic acids: 1,2,4-benzenetricarboxylic acid, 1,2,3-benzenetricarboxylic acid, and 1,2,4,5-benzenetetracarboxylic acid. While dicarboxylic and other tricarboxylic isomers were observed, emphasis was placed on the selected compounds because they were most consistently observed above the limit of detection. As shown in Fig. 5b, the majority of these compounds were observed in the PM<sub>2.5</sub> fraction, at an average of 79%. Similar results were observed during the ACE-Asia experiment, when Mochida *et al.* (2007) observed 77–98% of 1,2-benzenedicarboxylic acid in the submicron fraction. An exception to this size distribution was the April non-event period when only 9% was found in the PM<sub>2.5</sub> size mode; however, the unique presence of 1,2,4-benzenetricarboxylic acid in this sample may signify the presence of a point source that produced this compound or its precursors. The 1,2,4-benzenetricarboxylic acid isomer was frequently the most abundant in the fine fraction, except for the 26 April pollution event when 1,2,3-benzenetricarboxylic acid was greatest. For the three dust periods observed in this study, the average concentration of aromatic acids was enhanced compared to non-event levels for both fine and coarse modes. This result was also observed during ACE-Asia for aliphatic dicarboxylic acids associated with SOA (Mochida *et al.*, 2007). Carboxylic acids and SOA contribute to water-soluble OC in the atmosphere, which has previously been shown to be elevated during dust storms at Gosan (Duvall *et al.*, 2008). Similarly, carboxylic acids were observed at highest concentrations in Maldives during polluted periods when aerosol masses had long residence times and were transported over long distances (Stone *et al.*, 2007). Aromatic carboxylic acids concentrations in Gosan may have been elevated during dust events because of long aerosol residence times causing aging of gas and particle phase organics species.



**Fig. 5.** Ambient concentrations of a) *n*-alkanoic acids and b) aromatic carboxylic acids observed in fine and coarse particles by composite.

While the absolute concentrations of various aerosol components and molecular markers varied considerably during different pollution events, their relative contributions to particulate mass did, too. Table 3 compares the relative contribution of major inorganic ions and organic molecular markers by compound class in the  $PM_{2.5}$  and  $PM_{10-2.5}$  size fractions across dust and non-event periods. Such a comparison is valuable in that it highlights the aerosol components that were most strongly influenced by dust events, evidenced by increased relative contributions to coarse particle mass. Using this method of comparison, coarse particle mass was 29% greater during dust events compared to the non-event periods. Carbonaceous aerosol contributions to  $PM_{10-2.5}$  also increased; OC was enhanced by 30% and EC by 16%. Since dust is not a source of carbonaceous aerosol and EC is formed only through combustion, this result implies that major dust events cause physical transformations to carbonaceous aerosols and increase their particle sizes. Sulfate contributed an average of 6% more of coarse particle mass during dust events, while other secondary ions did not demonstrate such distinct differences. The conversion of sulfur dioxide to sulfate was likely to have occurred on the surface of dust particles (Seinfeld *et al.*, 2004).

The comparison of the relative distribution of molecular markers in fine and coarse particles provided information about the effects of dust events on carbonaceous aerosol from different sources. Primary combustion tracers—PAH,

hopanes, and levoglucosan—emitted in the  $PM_{2.5}$  size range, were enriched in the coarse mode during select dust events. Their enrichment suggested that primary combustion particles became internally mixed with dust particles during transport, likely through coagulation processes. The inclusion of primary OC and EC with dust are expected to have significant impacts on the radiative properties of particles, by increasing their radiative forcing potential (Fuller *et al.*, 1999) and changing their surface chemistry (Usher *et al.*, 2003). The enrichment of secondary organic acids in coarse aerosol during dust events implicates dust as playing an important role in aerosol aging. As with secondary inorganic acids, the dust may provide a surface upon which reactions occur and/or participate in chemical reaction.

## CONCLUSIONS

The previous sections have outlined the differences in the chemical composition in fine and coarse mode aerosol measured in Gosan, Korea during the springtime dust season. These data demonstrate that several different types of pollution events occurred: a) the 31 March dust event with the highest dust loadings observed in this study and a strong crustal component to the aerosol mixed with anthropogenic pollution and biomass burning, b) the 26 May dust event impacted by biomass burning, secondary, and anthropogenic sources, c) the 12–17 May period of minor dust events, with

**Table 3.** Average aerosol composition during dust events compared to non-event periods for fine (PM<sub>2.5</sub>) and coarse (PM<sub>10-2.5</sub>) modes, with the distribution of components between the two modes. Components in the coarse mode enhanced during dust events by greater than 50% are shown in bold. Organic compounds are presented relative to organic carbon (OC).

Aerosol Component	PM <sub>2.5</sub> (%)		PM <sub>10-2.5</sub> (%)		Fraction in Coarse Mode (PM <sub>10-2.5</sub> ) (%)	
	Dust Events	Non-Event Period	Dust Events	Non-Event Period	Dust Events	Non-Event Period
Mass	–	–	–	–	<b>68</b>	39
Organic Carbon	4.1	8.1	1.6	2.1	<b>44</b>	14
Elemental Carbon	0.7	1.0	0.1	0.3	<b>32</b>	16
Sulfate	28.4	35.3	2.4	5.6	<b>15</b>	9
Nitrate	2.2	4.5	4.1	11.5	80	62
Calcium	1.3	0.4	2.6	2.4	81	81
Ammonium	7.8	12.3	bd	1.2	bd	6
Potassium	0.9	1.2	0.2	0.5	26	21
Organic Compounds (% OC)						
Levoglucosan	1.75	4.65	4.26	1.00	<b>66</b>	3
PAH <sup>a</sup>	0.12	0.09	0.05	0.12	28	57
Hopanes	0.018	0.008	0.005	0.020	18	30
<i>n</i> -Alkanes <sup>b</sup>	0.95	0.46	1.19	1.20	<b>45</b>	28

bd = below detection; <sup>a</sup> estimated by benzo(b)fluoranthene; <sup>b</sup> estimated by heptacosane, octacosane, nonacosane, and hentriacontane.

impacts from dust, seaspray, and anthropogenic pollution and little biomass burning, d) the 26 April pollution event with very high concentrations of fine particles from motor vehicles, biogenic materials, biomass burning, and secondary sources that contributed inorganic ions and SOA. These events were put into context by comparison to low-pollution atmospheres that included: e) the April non-event period with below-average secondary inorganic ion concentrations, but above-average markers for fossil fuels and biomass burning and f) the May non-event period with very low concentrations of nearly all measured species. Overall, this study demonstrates that dust events play an important role in determining the size distribution of OC, EC, and molecular markers and, in turn, that primary and secondary carbonaceous particles change the composition and surface properties of dust particles.

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#### SUPPLEMENTARY MATERIALS

Concentrations of aerosol components are shown for fine and coarse fractions by composite. Table S1: Summary of

composite samples from Gosan, Korea and the air mass origins summarized from back trajectory analysis; Fig. S1: Particulate mass and water-soluble calcium; Fig. S2: Sulfate and nitrate; Fig. S3: Water-soluble ammonium and potassium; Fig. S4: Sodium and chloride. Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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