



## VARIATIONS OF NITRATE AND SULFATE IN THE ATMOSPHERE ON DAYS OF HIGH AND LOW PARTICULATE MATTERS

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**Abstract**—Particulate matters with aerodynamic diameter less than 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ) were collected with high-volume samplers for four periods of consecutive samplings. Each period included a high  $\text{PM}_{10}$  (defined as  $\text{PM}_{10} \geq 110 \mu\text{g}/\text{m}^3$ ) episode. The concentrations of all ionic species of high  $\text{PM}_{10}$  day (HPD) samples were higher than those of low  $\text{PM}_{10}$  (defined as  $\text{PM}_{10} < 110 \mu\text{g}/\text{m}^3$ ) d (LPD) samples. Using the ionic concentrations of HPD samples at each station divided by those of LPD samples at respective stations, the results showed that  $\text{NO}_3^-$  increased most from LPD to HPD among the eight ionic species examined. A high mean value (3.15) of  $\text{NO}_3^-/\text{elemental carbon (EC)}$  ratio of HPD divided by that of LPD indicates that concentration variations due to chemical formation and nonchemical factors apparently were higher than those of the concentration variations due to nonchemical factors alone. The  $\text{NO}_3^-/\text{SO}_4^{2-}$  ratio of HPD divided by that of LPD ranged from 1.62 to 3.92 for the four periods. The results indicate that more nitrate than sulfate had formed during high  $\text{PM}_{10}$  episodes. Multiple linear regression analysis showed that the percentage of  $\text{NH}_4^+$  associated with nitrate and sulfate decreased and the percentage that could be explained by  $\text{Ca}^{2+}$  and  $\text{Na}^+$  increased on HPD. The reactions of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  with sea salt particles and with aqueous carbonates on soil particles during HPD were considered the main causes leading to these variations.

**Keywords**—High particulate matter    Low particulate matter    Ionic species

### INTRODUCTION

Atmospheric aerosols can cause many environmental problems, including reduction in visibility, solar radiation transfers, cloud formations, and acidification of rains. Therefore, atmospheric aerosols currently have aroused a great deal of concern. Most research has put special emphasis on the seasonal variations, size distribution, aerosol transportation, and source of contributions [1–4]. The results reveal the existence of temporal and spatial variability and, as a consequence, high  $\text{PM}_{10}$  (defined as  $\text{PM}_{10}$  concentration more than  $110 \mu\text{g}/\text{m}^3$ ) episodes occurred in both polluted and unpolluted areas. Some highly concentrated chemical species occasionally have been found in unpolluted areas. Although chemical formations for ionic species of aerosols for long-range transport have been observed [5], they have not been well reported for local variations in short time periods and, as a result, the real variations of ionic species for aerosol change on a short timescale still are unclear. Some articles have described in detail the chemical mechanism of aerosol formation for diurnal variations [6]. However, little reliable data in the field has been reported exploring the chemical variations during the occurrence of pollution events on a short timescale.

In order to understand the variation mechanism of local aerosols, we compared the chemical composition of aerosol samples collected during both high  $\text{PM}_{10}$  days (HPD) and low  $\text{PM}_{10}$  days (LPD). The aerosols collected on both HPD and LPD provide important information about aerosol formation during pollution events, and assist us in understanding what rapid species changes occur in the atmosphere during pollution episodes. In addition, the results will help us to understand

what the possible pathways of aerosol formation are during pollution episodes. In this study, four periods of consecutive sampling were carried out with each sampling period lasting 4 to 5 d and including a pollution event.

### MATERIALS AND METHODS

#### *Sampling scheme*

In this study, a total of ten sites in the Taichung area of central Taiwan and in the vicinity of air quality monitoring stations were selected for sampling (Fig. 1). The four sampling periods were September 13 through 17, 2000 (period 1, sample number  $n = 54$ ), August 21 through 25, 2001 (period 2,  $n = 45$ ), December 10 through 13, 2001 (period 3,  $n = 32$ ), and March 6 through 10, 2002 (period 4,  $n = 45$ ). Each sampling period covered a  $\text{PM}_{10}$  pollution episode that had been forecast using the current continuous incoming data of variation trends of  $\text{PM}_{10}$  (data from the air quality monitoring stations) and meteorological conditions. Continuous sample collections were alternated between 8:00 AM to 5:00 PM one day and from 5:30 PM to 7:30 AM the following day. A total of 115 samples from LPD and 61 samples from HPD were collected for analysis.

Sampling instruments were deployed on the rooftops of buildings that were about 15 m above the ground.  $\text{PM}_{10}$  aerosols were collected on quartz fiber filters at a flow rate of 1,200 L/min using high-volume samplers (Kimoto model-121FT, Osaka, Japan) equipped with cyclone separators (Kimoto model-120A). Quartz fiber filters (Pallflex Tissuquartz 2500QAT-UP, MI, USA) were pretreated in a furnace at  $900^\circ\text{C}$  for 4 h to remove carbonaceous contaminants.

#### *Sample analysis*

After collection filters were conditioned at a constant temperature of  $(23 \pm 3^\circ\text{C})$  and at a level of humidity  $(45 \pm 5\%)$ ,

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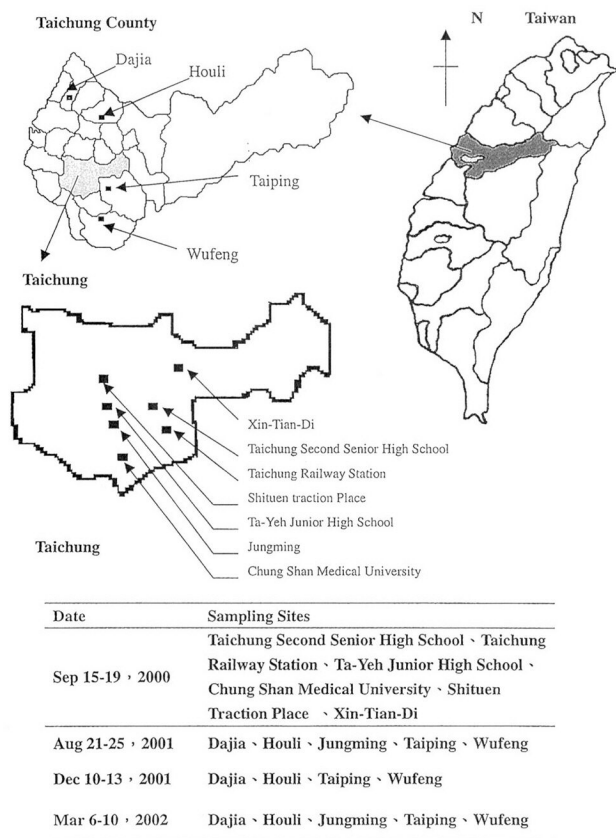


Fig. 1. The location of the sampling sites were in the Taichung area of central Taiwan.

the PM<sub>10</sub> levels were measured by weighing the filters with a Mettler AT261 balance (Mettler-Toledo AG, Greifensee, Switzerland), both before and after a sampling run. The differences in the two totals were divided by the collected sampling volumes to obtain the corresponding concentrations. Before weighing, the filters were passed through a StaticMasters (VWR, Scientific Products, Plainfield, NJ, USA) to eliminate the static electricity. The aerosols deposited on the filters were collected from high-volume samples and were further extracted ultrasonically with 10 ml of deionized water for analyzing the water-soluble ionic components. The extracts were analyzed

by ion-chromatography (Dionex-120, Sunnyvale, CA, USA) to determine concentrations of anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) and cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>). The concentrations of elemental carbon (EC) were determined with a total organic carbon analyzer (Shimadzu SSM-5000A, Kyoto, Japan). The filters were heated in advance at 340°C under a pure oxygen flow of 2 L/min for 2 h to expel the organic carbon [7]. The remaining carbon content was then determined with a total organic carbon analyzer to obtain the EC content.

#### Statistical methods

Data analyses were performed using the SAS 8.0 software package (Cary, NC, USA). A comparison between LPD and HPD for measured indicators was made using the Wilcoxon rank-sum test. Comparison between stations for ionic concentrations in the four periods was made by using the Kruskal-Wallis test. Subsequently, a multiple linear regression was applied to NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> on HPD and LPD separately using Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and Ca<sup>2+</sup> as independent variables. Using Mg<sup>2+</sup> as an independent variable was not considered in this study because the concentrations of Mg<sup>2+</sup> were very low in the atmosphere of Taichung and probably would have led to an incorrect interpretation. Finally, putting the spatial variability effects into consideration, we added stations in random order as independent variables to the data set for performing multiple linear regressions. The coefficient of determination (*r*<sup>2</sup>), % of *r*<sup>2</sup>-value, and partial correlation coefficients were obtained in this study. A probability of 0.05 or less was considered to be significant.

## RESULTS AND DISCUSSION

The meteorological conditions of four periods are shown in Table 1. Wind velocities on HPD were lower than those on LPD for most periods, except for period 2. Wind directions made only a very slight difference in HPD and LPD, showing that the pollutants in HPD and LPD mostly came from the same directions as the pollution sources. Moreover, temperature and humidity in the atmosphere were higher on HPD than those on LPD, which might have effects on ionic concentration between HPD and LPD. Detailed descriptions about the relationship between meteorological conditions and variation of ionic concentrations will be given later.

The concentrations of all ionic species of HPD samples

Table 1. Meteorological conditions. Values are mean ± standard deviation

	Period 1	Period 2	Period 3	Period 4
Wind velocity (m/s)				
LPD <sup>a</sup>	1.98 ± 1.15	1.57 ± 0.64	3.46 ± 2.49	2.93 ± 1.62
HPD <sup>b</sup>	0.91 ± 0.63	1.79 ± 0.74	2.24 ± 1.25	1.80 ± 1.40
Wind direction <sup>c</sup>				
LPD	S <sup>c</sup>	S	SW <sup>c</sup>	S
HPD	SSW <sup>c</sup>	SSW	WSW <sup>c</sup>	SSE <sup>c</sup>
Temperature (°C)				
LPD	25.53 ± 2.18	30.41 ± 1.38	20.46 ± 2.72	17.24 ± 2.97
HPD	25.56 ± 2.03	30.42 ± 1.59	24.06 ± 2.32	20.73 ± 1.98
Humidity (%)				
LPD	55.07 ± 9.36	72.38 ± 7.63	82.43 ± 8.85	47.29 ± 9.65
HPD	61.20 ± 8.14	76.18 ± 7.84	81.43 ± 9.42	61.58 ± 11.57

<sup>a</sup> LPD = Low particulate matter (diameter less than 10 μm) (PM<sub>10</sub>) days.

<sup>b</sup> HPD = High PM<sub>10</sub> days.

<sup>c</sup> S = South; SW = Southwest; SSW = South-southwest; WSW = West-southwest; SSE = South-southeast.

Table 2. Concentrations ( $\mu\text{g}/\text{m}^3$ ) of the measured species in aerosols on low  $\text{PM}_{10}$  days (LPD) and high  $\text{PM}_{10}$  days (HPD)<sup>a</sup>

	LPD ( $n = 115$ )			HPD ( $n = 61$ )			$p$ value <sup>b</sup>
	Arithmetic mean	Standard deviation	Geometric mean	Arithmetic mean	Standard deviation	Geometric mean	
EC <sup>c</sup>	5.37	2.79	4.71	6.83	2.82	6.26	0.0002
Na <sup>+</sup>	0.40	0.24	0.34	0.44	0.28	0.39	0.5118
NH <sub>4</sub> <sup>+</sup>	3.36	1.70	2.98	5.50	2.60	4.86	0.0001
K <sup>+</sup>	0.53	0.26	0.48	0.67	0.36	0.60	0.0028
Mg <sup>2+</sup>	0.04	0.03	0.04	0.09	0.09	0.08	0.0001
Ca <sup>2+</sup>	0.19	0.17	0.15	0.30	0.23	0.24	0.0001
Cl <sup>-</sup>	0.77	0.49	0.61	0.96	1.20	0.67	0.7701
NO <sub>3</sub> <sup>-</sup>	1.90	2.50	0.91	6.92	5.81	4.45	0.0001
SO <sub>4</sub> <sup>2-</sup>	7.10	3.19	6.42	9.94	3.50	9.38	0.0001

<sup>a</sup> See Table 1 for definition of acronyms.

<sup>b</sup> Comparison between LPD and HPD.

<sup>c</sup> Elemental carbon.

were higher than those of LPD samples (Table 2). In that the wind directions only showed a slight variation, the difference in ionic concentrations between LPD and HPD is deemed not to have resulted primarily from winds prevailing from pollution sources variation (Table 1). Taichung Electrical Power Plant is located about 40 km to the west of Taichung City. In this plant, coal is used as fuel, which might contribute larger amounts of  $\text{SO}_2$  and  $\text{NO}_x$  to the Taichung atmosphere. For further accurate comparisons, it is necessary to assess the spatial variability of ionic concentrations. Statistical analysis by the Kruskal-Wallis test showed that no significant differences between stations were found for most ionic species except for  $\text{Mg}^{2+}$  on LPD for period 1 ( $p = 0.0002$ ) and  $\text{Ca}^{2+}$  on LPD for period 2 ( $p = 0.0083$ ). These results showed that the spatial variability of concentrations for the major ions ( $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) were consistent in this study. Moreover, LPD and HPD readings occurred randomly during the day and night of each sampling period (chi-square test,  $p = 0.160$ ), indicating that the difference in ionic concentrations between HPD and LPD did not originate from day and night variation.

The formation of nitric acid by the oxidation of  $\text{NO}_2$  with OH and the formation of sulfuric acid by the oxidation of  $\text{SO}_2$  with OH both are important reactions in the atmosphere.



The concentrations of  $\text{NO}_x$  ( $p = 0.19$ ) and  $\text{SO}_2$  ( $p = 0.45$ ) on HPD had no significant difference with those on LPD. Therefore, the possibility that the increase of concentrations of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  is due to the high  $\text{NO}_x$  and  $\text{SO}_2$  concentration need not be taken into account during these four episodes.

In addition to the homogeneous gas-phase reactions, nitrate and sulfate could form in the atmosphere through heterogeneous reactions. The heterogeneous aqueous-phase reactions of nitrate formation include the absorption of  $\text{NO}_2$  or  $\text{NO}_3$  radicals in water, and the reaction of  $\text{NO}_2$  or nitric acid on existing ambient particles [8]. However, according to model studies, nitrate production via aqueous-phase oxidation of  $\text{NO}_x$  probably is of minor importance in the atmosphere [9]. For sulfate, the heterogeneous reactions occur in the aqueous sur-

face layer of pre-existing particles where  $\text{SO}_2$  reacts with  $\text{O}_3$  or  $\text{H}_2\text{O}_2$  to produce sulfate [10,11]. Previous studies found that sulfate might slowly form by the oxidation of  $\text{SO}_2$  with  $\text{O}_3$  in the gas phase, but in the liquid phase the reaction is rapid [12,13]. Except for period 3, the relative humidity was higher on HPD than it was on LPD. Consequently, higher amounts of sulfate were formed by these heterogeneous aqueous-phase reactions on HPD than those on LPD. Russell and Cass [14] have indicated that transport of nitric acid to the surface of particles is the governing factor for nitrate salt formation. This phenomenon also is applied to sulfate salt formation on particles. The wind velocities for the four sampling periods on HPD were lower than those on LPD except for period 2. This provided a longer contact time for nitric acid and sulfuric acid with particles on HPD.

In order to compare the variations for different ionic species during high  $\text{PM}_{10}$  episodes, a simple indicator (HPD/LPD) was employed. Ratios of HPD/LPD for each period (Table 3) were calculated by using the ionic concentrations of HPD samples at each station divided by those of LPD samples at respective stations. The results showed that  $\text{NO}_3^-$  had the highest ratios among all species in each sampling period, implying that  $\text{NO}_3^-$  increased most from LPD to HPD among the eight ionic species examined during high  $\text{PM}_{10}$  episodes. This phenomenon has been reported in previous literature [15,16]. However, the authors did not explain why  $\text{NO}_3^-$  increased most from LPD to HPD among those species during high  $\text{PM}_{10}$  episodes.

Ratios of  $\text{NO}_3^-/\text{PM}_{10}$ ,  $\text{NO}_3^-/\text{EC}$ , and  $\text{NO}_3^-/\text{SO}_4^{2-}$  between dif-

Table 3. Comparison of the ratios of high  $\text{PM}_{10}$  days (HPD)/low  $\text{PM}_{10}$  days (LPD) for eight ionic species in four periods. Italic numerals represent the highest ratio in each column. Values are mean  $\pm$  standard deviation<sup>a</sup>

	Period 1	Period 2	Period 3	Period 4
	HPD/LPD	HPD/LPD	HPD/LPD	HPD/LPD
Na <sup>+</sup>	1.25 $\pm$ 0.42	1.12 $\pm$ 0.54	2.57 $\pm$ 0.69	1.11 $\pm$ 0.32
NH <sub>4</sub> <sup>+</sup>	2.96 $\pm$ 0.49	1.52 $\pm$ 0.27	1.75 $\pm$ 0.49	2.05 $\pm$ 1.01
K <sup>+</sup>	1.76 $\pm$ 0.55	1.27 $\pm$ 0.32	1.73 $\pm$ 0.28	0.95 $\pm$ 0.21
Mg <sup>2+</sup>	2.48 $\pm$ 2.69	1.15 $\pm$ 0.22	3.11 $\pm$ 1.39	1.83 $\pm$ 0.81
Ca <sup>2+</sup>	2.00 $\pm$ 0.84	1.19 $\pm$ 0.23	3.04 $\pm$ 1.39	0.85 $\pm$ 0.22
Cl <sup>-</sup>	2.16 $\pm$ 1.71	1.12 $\pm$ 0.55	2.11 $\pm$ 0.92	1.45 $\pm$ 0.55
NO <sub>3</sub> <sup>-</sup>	8.88 $\pm$ 4.37	3.32 $\pm$ 1.29	3.98 $\pm$ 2.67	3.00 $\pm$ 1.20
SO <sub>4</sub> <sup>2-</sup>	1.97 $\pm$ 0.27	1.45 $\pm$ 0.31	2.41 $\pm$ 1.21	1.09 $\pm$ 0.20

<sup>a</sup> See Table 1 for definition of acronyms.

Table 4. Comparison of the ratios of NO<sub>3</sub><sup>-</sup>:PM<sub>10</sub>, NO<sub>3</sub><sup>-</sup>:EC, and NO<sub>3</sub><sup>-</sup>:SO<sub>4</sub><sup>2-</sup> increased from low PM<sub>10</sub> days (LPD) to high PM<sub>10</sub> days (HPD) in four periods<sup>a</sup>

	NO <sub>3</sub> <sup>-</sup> :PM <sub>10</sub>	NO <sub>3</sub> <sup>-</sup> :EC	NO <sub>3</sub> <sup>-</sup> :SO <sub>4</sub> <sup>2-</sup>
Period 1			
LPD (n = 42)	0.03 ± 0.01	0.15 ± 0.04	0.25 ± 0.04
HPD (n = 12)	0.13 ± 0.03	1.03 ± 0.30	0.98 ± 0.28
HPD/LPD	4.33	6.87	3.92
Period 2			
LPD (n = 35)	0.04 ± 0.02	0.34 ± 0.20	0.16 ± 0.06
HPD (n = 10)	0.07 ± 0.03	0.62 ± 0.37	0.29 ± 0.12
HPD/LPD	1.75	1.82	1.81
Period 3			
LPD (n = 26)	0.09 ± 0.02	0.68 ± 0.10	0.53 ± 0.20
HPD (n = 6)	0.12 ± 0.05	1.36 ± 0.85	0.86 ± 0.11
HPD/LPD	1.33	2.00	1.62
Period 4			
LPD (n = 12)	0.04 ± 0.01	0.49 ± 0.12	0.23 ± 0.10
HPD (n = 33)	0.10 ± 0.02	0.94 ± 0.49	0.62 ± 0.10
HPD/LPD	2.50	1.92	2.7

<sup>a</sup> See Table 1 for definition of acronyms.

ferent stations were analyzed by the Kruskal-Wallis statistical test. The results showed no significant differences in spatial variability for the three ratios. The values of NO<sub>3</sub><sup>-</sup>/PM<sub>10</sub> shown in Table 4 clearly indicated that NO<sub>3</sub><sup>-</sup> in PM<sub>10</sub> increased during high PM<sub>10</sub> episodes, especially for period 1 (HPD/LPD = 4.33). A higher value of 0.09 for the NO<sub>3</sub><sup>-</sup>/PM<sub>10</sub> ratio was found in LPD samples for period 3, which probably was caused by the smaller loss of NH<sub>4</sub>NO<sub>3</sub> at low temperatures during winter. Therefore, a high NO<sub>3</sub><sup>-</sup>/PM<sub>10</sub> ratio (0.12) was found in HPD samples for period 3 and a low HPD/LPD ratio (1.33) still was observed for period 3. A high mean ratio (HPD/LPD) of 2.48 for all four periods indicates that nitrates could contribute more to the PM<sub>10</sub> particles during HPD. Tsai and Cheng [16] found that nitrate ion was the only species in which the percentage of ionic species/PM<sub>10</sub> increased during high PM<sub>10</sub> episodes. In this study, we also found that the percentage of NO<sub>3</sub><sup>-</sup>/PM<sub>10</sub> increased significantly on HPD. Hence, we suggest that the new formation of nitrate salt during high PM<sub>10</sub> episodes is one of the important factors resulting in the concentrations of PM<sub>10</sub> over the regulatory values of the Taiwan Environmental Protection Agency.

Elemental carbon is an inert constituent in the atmosphere, and its concentration is not affected by chemical reactions during the transition from LPD to HPD. The ratio of NO<sub>3</sub><sup>-</sup>/EC, therefore, can be used as an index to show the degree of concentration variations due to chemical reactions (e.g., oxidation of NO<sub>2</sub> to nitrate). For all sampling periods, mean ratios of NO<sub>3</sub><sup>-</sup>/EC for HPD samples were higher than those for LPD samples (Table 4). For quantitative comparison, the NO<sub>3</sub><sup>-</sup>/EC ratio of HPD was divided by that of LPD. The quotients ranged from 1.82 to 6.87 for the four periods. The NO<sub>3</sub><sup>-</sup>/EC ratios had a very high mean value of 3.15, which indicated that concentration variations due to chemical formation plus nonchemical (e.g., mixing layer of air mass) factors apparently were higher than those due to nonchemical factors alone. The contribution to atmospheric aerosols from chemical formation, especially nitrate on HPD, cannot be ignored.

Mean concentrations of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in LPD samples were 1.90 and 7.10 μg/m<sup>3</sup> (Table 1), respectively, and the mean ratios of NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> for LPD samples ranged from 0.16 to 0.53

(Table 4). These concentrations and ratios are similar to previous studies [3,17]. However, mean ratios of NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> for each HPD sample were higher than those of corresponding LPD samples (*p* < 0.0001). The NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> ratio of HPD divided by that of LPD ranged from 1.62 to 3.92 for the four periods. These results indicate that more nitrate than sulfate formed during high PM<sub>10</sub> episodes. Hewitt [18] has indicated that the reaction rate of nitrate formation is approximately ten times that of the sulfate formation. Additionally, the mean annual concentration of NO<sub>x</sub> in the atmosphere of the Taichung area is about 3.8 times that of SO<sub>2</sub>. Theoretically, both these factors will lead to higher nitrate formations than that of sulfate on LPD. However, the ratios of NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> were less than unity, especially in LPD samples (Table 4). Ammonium nitrate is the major component of airborne nitrate salt. It easily evaporates back to the gas phase, which in turn results in relatively low concentrations of nitrate on LPD. Because nitrate has a relatively high formation rate, when meteorological or chemical conditions are more favorable, and/or when reactive pollutants (e.g., sea salt or soil particles, OH, NH<sub>3</sub>) are increased, large amounts of nitrate form rapidly during HPD. Sulfate, on the other hand, has a very low vapor pressure, so it remains in the particulate phase once formed in the atmosphere. Sulfate has a relatively low formation rate and, therefore, less sulfate forms during HPD. As a result, perceptibly higher ratios of NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> for each HPD sample were found in this study.

Although noticeable changes of ionic species in atmospheric aerosols during high PM<sub>10</sub> episodes were observed, relatively minor errors resulted from chemical or physical changes during or after sample collection, causing some problems. Tsai and Perng [19] recently pointed out that the percentage of artifacts of a species (determined by high-volume PM<sub>10</sub> samplers) over the actual concentrations of that species (determined by Annular Denuder Systems, University Research Glassware, NC, USA) are +11 and -16% for sulfate and nitrate species, respectively. Compared to the varying amounts during the formation of high PM<sub>10</sub> episodes, these artifacts were small. In our sampling process, no additional denuder was used to eliminate the artifact. Thus, the sampling artifact is possible, and such artifacts can modify slightly NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> ratios.

Previous studies indicated that nitric and sulfuric acid react rapidly with alkaline substances, such as ammonium, sodium, and calcium, in the atmosphere to produce nitrate and sulfate salts, respectively [8,9,20,21]. To understand what the major pathway of the salt formation is, it is necessary to know what kinds of nitrate and sulfate salts in aerosols predominantly formed during high PM<sub>10</sub> episodes. Similar to the previous result, multiple linear regressions also suggest that the spatial effect on the data were minor (<2.3%). Data of coefficient of determination (*r*<sup>2</sup>) show that 74% of SO<sub>4</sub><sup>2-</sup> was associated with these cations on LPD, and only about 39% of NO<sub>3</sub><sup>-</sup> could be explained by these cations. Compared to the results of Karakas and Tuncel [3], more SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were associated with these cations in this study. The coefficients of determination between SO<sub>4</sub><sup>2-</sup> and these cations on HPD (57%) were lower than those on LPD (74%). Due to the semivolatile nature of sulfuric acid, these data imply that higher percentage (43%) of SO<sub>4</sub><sup>2-</sup> probably was associated with H<sup>+</sup> on HPD than that on LPD (26%). The coefficient of determination between NO<sub>3</sub><sup>-</sup> and these cations on HPD (53%) was higher than that on LPD (39%). This means that higher percentage of NO<sub>3</sub><sup>-</sup> on HPD than on LPD could be

explained by these cations. Moreover, from the data of partial correlation coefficients (% of  $r^2$  explained by three cation and sites), we found that the forms of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  on LPD and HPD were quite different. The percentages of partial correlation coefficients show that 59% of  $\text{SO}_4^{2-}$  was associated with  $\text{NH}_4^+$  on LPD, and only 36% of  $\text{SO}_4^{2-}$  was associated with  $\text{NH}_4^+$  on HPD. Sodium ion and  $\text{Ca}^{2+}$  neutralized the remaining 16% and 2.3% on HPD, respectively. Nitrates primarily were associated with  $\text{NH}_4^+$  (36%) on LPD, and 40% of  $\text{NO}_3^-$  was associated with  $\text{NH}_4^+$  on HPD. The percentage of  $\text{NO}_3^-$  neutralized by  $\text{Ca}^{2+}$  was 0.8% on LPD, and the percentage neutralized by  $\text{Ca}^{2+}$  was 7.4% on HPD.

Both  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were present predominately in the form of ammonium salts on LPD. This was due to much higher concentrations of  $\text{NH}_4^+$  than  $\text{Ca}^{2+}$  and  $\text{Na}^+$  in the atmosphere on LPD (Table 1). The concentrations of  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  increased markedly on HPD, while  $\text{Na}^+$  only increased slightly on HPD. The percentage that could be explained by  $\text{NH}_4^+$  showed a decrease, and the percentage that could be explained by  $\text{Ca}^{2+}$  and  $\text{Na}^+$  showed an increase on HPD. These results indicate that much of the calcium and sodium salts were newly formed and/or that relatively fewer of the ammonium salts were newly formed during  $\text{PM}_{10}$  episodes.

Sulfate can form by the reactions of  $\text{H}_2\text{SO}_4$  with sea salt particles [21].

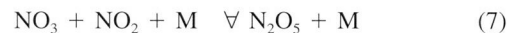


In addition, Sievering et al. [22] found that the heterogeneous reaction of  $\text{SO}_2$  by  $\text{O}_3$  proceeds rapidly in freshly formed, coarse sea salt aerosol when it contains water because of the initial alkaline nature of the particles. They further indicated that the conversion is strongly dependent on the volume of sea salt aerosol water. We pointed out previously that the relative humidity and the concentrations of  $\text{Na}^+$  on HPD were higher than those on LPD. The percentage of  $\text{Na}^+$  associated with  $\text{SO}_4^{2-}$  on HPD increased about 1.8 times higher than that of LPD. These reactions of  $\text{H}_2\text{SO}_4$  with sea salt particles and/or  $\text{SO}_2$  with  $\text{O}_3$  in sea salt particles may form sodium sulfate, which would explain these results. In addition, other studies pointed out that  $\text{H}_2\text{SO}_4$  can react with aqueous carbonates, such as dissolved  $\text{CaCO}_3$  on soil particles to form sulfate [21].



Higher concentrations of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  on HPD than those on LPD show the probability of newly formed  $\text{CaSO}_4$  during high  $\text{PM}_{10}$  episodes. However, the percentage of  $\text{Ca}^{2+}$  associated with  $\text{SO}_4^{2-}$  on HPD (2.3%) shows no significant difference with that of LPD (2.2%). These results suggest that sodium sulfate formed on sea salt particles was the predominant pathway of sulfate formation during high  $\text{PM}_{10}$  episodes.

Usually,  $\text{Na}^+$  is assumed to be mainly from sea salt aerosols, though  $\text{Ca}^{2+}$  is assumed to be mainly from soil aerosols. Hence,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  were used as tracers of sea salt and soil components, respectively, for comparing the relative abundance of sea salt and soil particles. Higher equivalent ratios of  $\text{Ca}^{2+}/\text{Na}^+$  on HPD (0.79) than those on LPD (0.56) show that a larger abundance of soil particles were present on HPD. Wolff [23] pointed out that it appears that the  $\text{HNO}_3$  soil reaction becomes important when there is appreciable  $\text{H}_2\text{SO}_4$ , or when  $\text{NH}_4\text{NO}_3$  tends to be quite unstable. During the day, nitrate is formed by the reaction of  $\text{HNO}_3$  with airborne soil. At night, nitrate is formed directly on the soil particles by the following reaction:



Parmar et al. [24] further indicated that soil particles might absorb water and form droplets. Aerosol nitrate, thus, may be formed by the absorption and subsequent reaction of  $\text{NO}_2$  on the soil aerosol droplets or by the dissolution of gaseous  $\text{HNO}_3$ . Studies by Zhuang et al. [21] showed that nitric acid can react with calcium carbonate on soil particles to form nitrate.



Clarke and Karani [25] found that calcium carbonate was a major constituent in the atmosphere, which provides the evidence for the formation of calcium nitrate through reaction 9. The percentage of  $\text{Ca}^{2+}$  associated with  $\text{NO}_3^-$  on HPD increased about nine times higher than that of LPD. The increased percentages of  $\text{Ca}^{2+}$  associated with  $\text{NO}_3^-$  during HPD show that a great deal of nitrate was formed on airborne soil particles during those high  $\text{PM}_{10}$  episodes. Nitric acid in the atmosphere can react with sea salt particles ( $\text{NaCl}$ ) to form sodium nitrate. However, negative partial correlation coefficients between  $\text{NO}_3^-$  and  $\text{Na}^+$  were found on both LPD and HPD. In sea salt particles,  $\text{Na}^+$  is the most abundant ion, whereas the concentration of  $\text{NO}_3^-$  is negligible. As a result, the measured concentrations of  $\text{Na}^+$  in the aerosols contributed by  $\text{NaCl}$  are much higher than those contributed by  $\text{NaNO}_3$ . This would explain these negative correlation phenomena. In addition, results of higher equivalent ratios of  $\text{Ca}^{2+}/\text{Na}^+$  on HPD than those on LPD suggest that calcium nitrate formed on airborne soil particles was the predominant pathway of nitrate formation during high  $\text{PM}_{10}$  episodes.

## CONCLUSION

Mean concentrations of all ionic species of HPD samples were higher than those of LPD samples. Wind directions showed only a slight variation during HPD and LPD, suggesting that the pollutants primarily came from the same sources and, thus, were not an influencing factor in ionic concentrations between HPD and LPD. Among the eight ionic species, the concentrations of  $\text{NO}_3^-$  increased most from LPD to HPD. In addition, the very high mean value (3.15) of  $\text{NO}_3^-/\text{EC}$  ratio of HPD divided by that of LPD indicates that concentration variations due to chemical formation and nonchemical factors apparently were higher than those of the concentration variations due to nonchemical factors alone. Using multiple linear regression analysis, we found that both  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  mostly were associated with  $\text{NH}_4^+$  on LPD. The percentage of  $\text{Na}^+$  associated with  $\text{SO}_4^{2-}$  on HPD increased about 2.3 times higher than that of LPD, whereas the percentage of  $\text{Ca}^{2+}$  associated with  $\text{SO}_4^{2-}$  on HPD shows no significant difference with that of LPD. These results suggest that sodium sulfate formed on sea salt particles was the predominant pathway of sulfate formation during high  $\text{PM}_{10}$  episodes. However, the percentage of  $\text{Ca}^{2+}$  associated with  $\text{NO}_3^-$  on HPD increased about nine times higher than that of LPD. Higher equivalent ratios of  $\text{Ca}^{2+}/\text{Na}^+$  on HPD (0.79) than those on LPD (0.56) imply that a larger abundance of soil particles were present on HPD. This evidence suggests that a great deal of calcium nitrate was formed on airborne soil particles during those high  $\text{PM}_{10}$  episodes.

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