



# Characterization of size-differentiated inorganic composition of aerosols in Mexico City

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## Abstract

Size-differentiated atmospheric aerosol particles were collected during December 2000–October 2001 in Mexico City (19°N, 99°W) using a micro-orifice uniform deposit impactor. Sulfate and ammonium, which were correlated, were major features of the size distributions. The more predominant mode was at  $0.32 \pm 0.1 \mu\text{m}$ , aerodynamic diameter. This peak of concentration is likely the result of condensation of secondary aerosol components from the gas phase. During part of the rainy season (April and June), a larger mode was found at  $0.56 \pm 0.2 \mu\text{m}$ , aerodynamic diameter. This peak of concentration, identified as a droplet mode, is probably the result of aqueous-phase reactions (i.e., oxidation of sulfur dioxide in liquid droplets). During August, the peak of concentration was observed at both size ranges of the accumulation mode. Overall, ion balances were achieved with a small deficit of cations, except for the April and June samples, where a significant amount of excess sulfate was present as a result of moderate–high activity of the neighboring volcano Popocatepetl, as well as ambient conditions that favored production of sulfate (moderate–high relative humidity values). Based on the analysis of the ammonia/sulfate molar ratios, the ammonia concentrations were sufficient to fully neutralize sulfate concentrations, except for the April and June samples. During these months, ammonium bisulfate, letovicite and  $\text{H}_2\text{SO}_{4(\text{aq})}$  (or a solution of the corresponding ions) were the dominant form of sulfate present in both fine and coarse modes. The acidic nature of these particles (with  $\text{NH}_3/\text{H}_2\text{SO}_4$  molar ratio less than 2) is potentially important in assessing health effects of inhaled particles.

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## 1. Introduction

Atmospheric pollution in the Mexico City basin, mainly due to high levels of ozone ( $\text{O}_3$ ) and aerosols (particulate matter, PM), has become a significant issue for its nearly 20 million inhabitants. This pollution problem, favored by high insolation due to Mexico City's elevation of 2.2 km above sea level and its location in a basin surrounded by mountains, is the result of significant high emissions by mobile (around 3 million

vehicles) and fixed sources. Both  $\text{O}_3$  and PM levels exceed the Mexican  $\text{O}_3$  and  $\text{PM}_{10}$  (PM with aerodynamic diameter  $\leq 10 \mu\text{m}$ ) 24-h standard on most days of the year (Edgerton et al., 1999). Although there is no Mexican standard for  $\text{PM}_{2.5}$  (PM with aerodynamic diameter  $\leq 2.5 \mu\text{m}$ ), the  $\text{PM}_{2.5}$  levels in the valley are routinely well above acceptable limits, using as a reference the US 24-h average standard of  $65 \mu\text{g m}^{-3}$ . Atmospheric aerosols reduce the local visibility and have adverse effects on human health (Dockery et al., 1992, 1993; Spengler et al., 1990; Shuetzle, 1983). Inorganic species typically comprise 25–50% of the aerosol mass (Gray et al., 1986) with sulfates, ammonium and nitrates

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as major components. Understanding the formation, transport and removal of atmospheric aerosols requires detailed information on their size and physical and chemical properties. Relatively few observational and modeling studies have addressed the inorganic aerosol chemical composition of this metropolitan area (e.g., Edgerton et al., 1999; Moya et al., 2001). These studies did not consider the differences in composition of different particles in detail, but mainly addressed the chemical composition (measured or modeled) of the “bulk” particulate phase (e.g.,  $PM_{2.5}$  and  $PM_{10}$ ). Recently, Baumgardner et al. (2000) reported measurements of size-resolved aerosol composition (from 0.01 to  $0.7\ \mu\text{m}$  size range) obtained during a 2-week period in November 1997 at a mountain site 400 m above the southwest sector of the Mexico City basin. The present study extends the earlier work with characterization of size distributions (from 0.18 to  $10\ \mu\text{m}$  size range) for major inorganic ions, at a research site located in the southwest (Ciudad Universitaria, CU) of the Mexico City basin, through a year. Complementary goals of this work are: (1) determine the annual variability of the aerosol size distributions at the CU site; (2) determine the number of modes defining the inorganic aerosol size distributions and (3) determine how prevalent these modes are through the sampled year.

## 2. Experimental

### 2.1. Sampling site description

The CU site is located in the southwest of Mexico City (Fig. 1), within University Campus ( $19^{\circ}19'50''\text{N}$ ,  $99^{\circ}11'03''\text{W}$ ) characterized by academic buildings interspersed among park-like vegetation, with very few anthropogenic emissions in the immediate vicinity of the sampling site. As seen in Fig. 1, the neighboring volcano, Popocatepetl (elevation of 3000 m above the level of the city) is located approximately 30 and 60 km SE of Mexico City and the CU site, respectively. Recirculating flows are a common feature of the local dynamics and may provide a mechanism for transporting air from upper levels into the city (Fast and Zhong, 1998).

### 2.2. Atmospheric conditions during the study

The nominal elevation of the Valley of Mexico is 2.240 m above mean sea level. Although its elevation is high, Mexico City's location at  $19^{\circ}\text{N}$  latitude provides it with a temperate climate throughout the year. The mean annual temperature was  $16^{\circ}\text{C}$  over the year sampled (2000–2001). Two seasons are commonly present in the

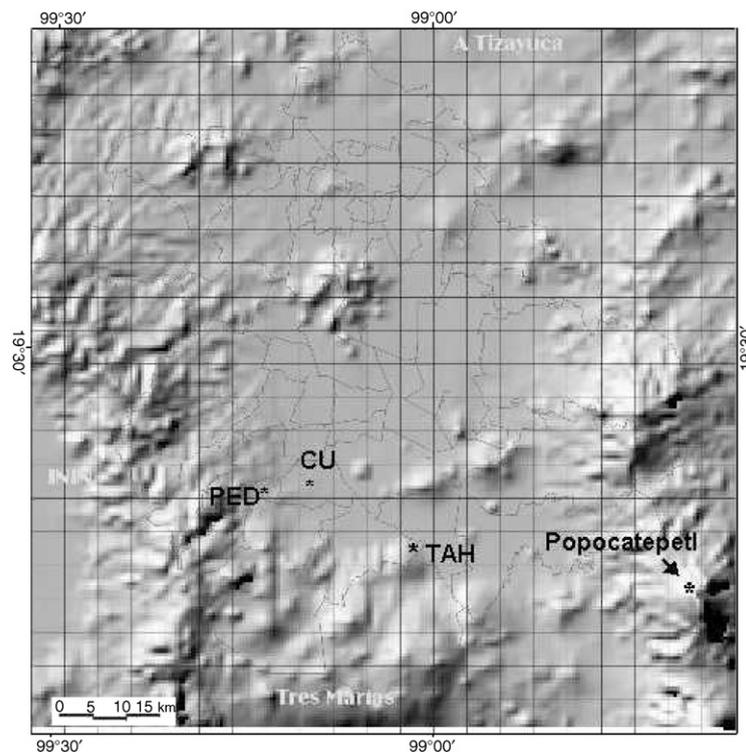


Fig. 1. The research site CU for the inorganic aerosol characterization study. Pedregal (PED) and Tláhuac (TAH) are RAMA (Atmospheric Monitoring Automated Network of Mexico City) sampling sites.

valley. The dry season is from November through April. The wet season is from late April through October. Winters are slightly cooler than summers.

### 2.3. Sampling

Aerosol particles were collected with a cascade micro-orifice uniform deposit impactor (MOUDI), MSP Model 100 (Marple et al., 1991) from December 2000 through October 2001. Specifically, the days sampled were 16–20 December 2000 along with 17–21 January, 21–25 February, 29 March–3 April, 25–29 April, 27 June–1 July, 22–26 August and 3–7 October 2001. The impactor flow rate was  $301\text{min}^{-1}$ . The 50% cutoff for stages 1–8 were 0.18, 0.32, 0.56, 1.0, 1.78, 3.16, 5.62 and  $10\mu\text{m}$ , aerodynamic diameter, respectively. Aerosol samples were taken from air brought through a chimney. The effective inlet height above the ground was about 15 m.

The collection of inorganic compounds (sulfate, nitrate, ammonium and potassium) was done by placing an aluminum foil in each one of the stages of the MOUDI. Prior to sampling, the aluminum foils (47 mm, MSP) were heated (at  $450^\circ\text{C}$ ) in a furnace for 8 h to eliminate impurities. The aluminum foils ensured particle collection by impaction without particle losses through the filter by filtration (Venkataraman et al., 2002). All the aluminum filters were weighed before and after sampling on a micro-balance accurate to  $15\mu\text{g}$  (Model 210S, Sartorius, Germany). Before weighing, the filters were conditioned for about 24 h in the weighing room at a relative humidity (RH) of  $40\pm 5\%$  and at about  $20^\circ\text{C}$ . Each sample was collected for 24 h (on the aforementioned days), then stored in a cool ( $+5^\circ\text{C}$ ), dark room until analysis.

### 2.4. Analytical procedures

The aluminum filters were analyzed for nitrate, sulfate, potassium, and ammonium using high-performance liquid chromatography methods. Nitrate and sulfate were analyzed by non-suppressed ion chromatography, and ammonium and potassium by suppressed chromatography with a Perkin-Elmer chromatograph. A Hamilton PRP-X100 column was used for nitrate and sulfate analysis. The injection volume was  $100\mu\text{l}$ . The mobile phase was phthalic acid 2 mmolar in 10% acetone and  $2\text{mlmin}^{-1}$  of flow rate. The details are given elsewhere (Báez et al., 1997). For ammonium and potassium ions, the injection volume was  $50\mu\text{l}$ . The analytical conditions were as follows: Hamilton PRP-X200 analytical column; Alltech 335SPCS suppressor module; Alltech cation suppressor cartridge. The mobile phase was a solution of nitric acid, 4 mmolar in 7:3 (water:methanol) and  $2\text{mlmin}^{-1}$  of flow rate.

## 3. Results and discussion

### 3.1. Particle size distributions

A total of 40 (five for each one of the months sampled) size distributions of major ions (sulfate, nitrate, ammonium and potassium) were obtained during the study at the CU sampling site. Figs. 2 and 3 show the monthly averaged particle size distributions of major ions measured at the CU site. As shown, sulfate and ammonium, which were correlated, were major features of the size distributions. The more predominant mode was at  $0.32\pm 0.1\mu\text{m}$ , aerodynamic diameter, except for the April and June samples, where a larger mode was observed at  $0.56\pm 0.2\mu\text{m}$ , aerodynamic diameter. During August, the peak of concentration was observed at both size ranges of the accumulation mode (nitrate and sulfate/ammonium at 0.32 and  $0.56\mu\text{m}$ , aerodynamic diameter, respectively). The smaller mode ( $\sim 0.3\mu\text{m}$ ) is probably a condensation mode containing gas-phase reaction products (Seinfeld and Pandis, 1998). The larger mode ( $\sim 0.6\mu\text{m}$ ) seen in late April and June is indicative of aqueous-phase reactions (i.e., oxidation of sulfur dioxide in liquid droplets), and is consistent with the fact that these months are part of the rainy season in Mexico City. During the sampling periods of these 2 months, and also for the month of August, the average 24-h RH was around 60–70% while for the rest of the months sampled it was 30–50% (according to measurements from the *Atmospheric Monitoring Automated Network* of Mexico City, also called RAMA).

Two important findings related to these aerosol size distributions are: (1) Overall, there was not a significant presence of coarse particles at the CU site during the year sampled (although small peaks of concentration were observed in the  $1.8\text{--}5.6\mu\text{m}$  size range for particulate nitrate and sulfate). (2) There were significantly higher sulfate concentrations during April and June (two-, three-fold higher than that measured from the rest of the months). Regarding the first finding, although there are no size-differentiated coarse aerosol distributions reported in the literature for this metropolitan area, a comparison was made between the size-differentiated coarse inorganic concentrations obtained in this study and “bulk” coarse ( $\text{PM}_{10}\text{--}\text{PM}_{2.5}$ ) inorganic observations obtained during the IMADA study in March 1997 (Chow et al., 2002). Average concentrations of coarse ammonium and sulfate measured in this study at the CU site (March 2001) were very similar with those obtained during IMADA at the Pedregal (PED) site (located  $\sim 5\text{km}$  SW from the CU site, see Fig. 1). Regarding the coarse-nitrate concentrations obtained at the CU site (March 2001), these were comparable with the average concentration of non-volatilized nitrate obtained at the PED site (March 1997). Although

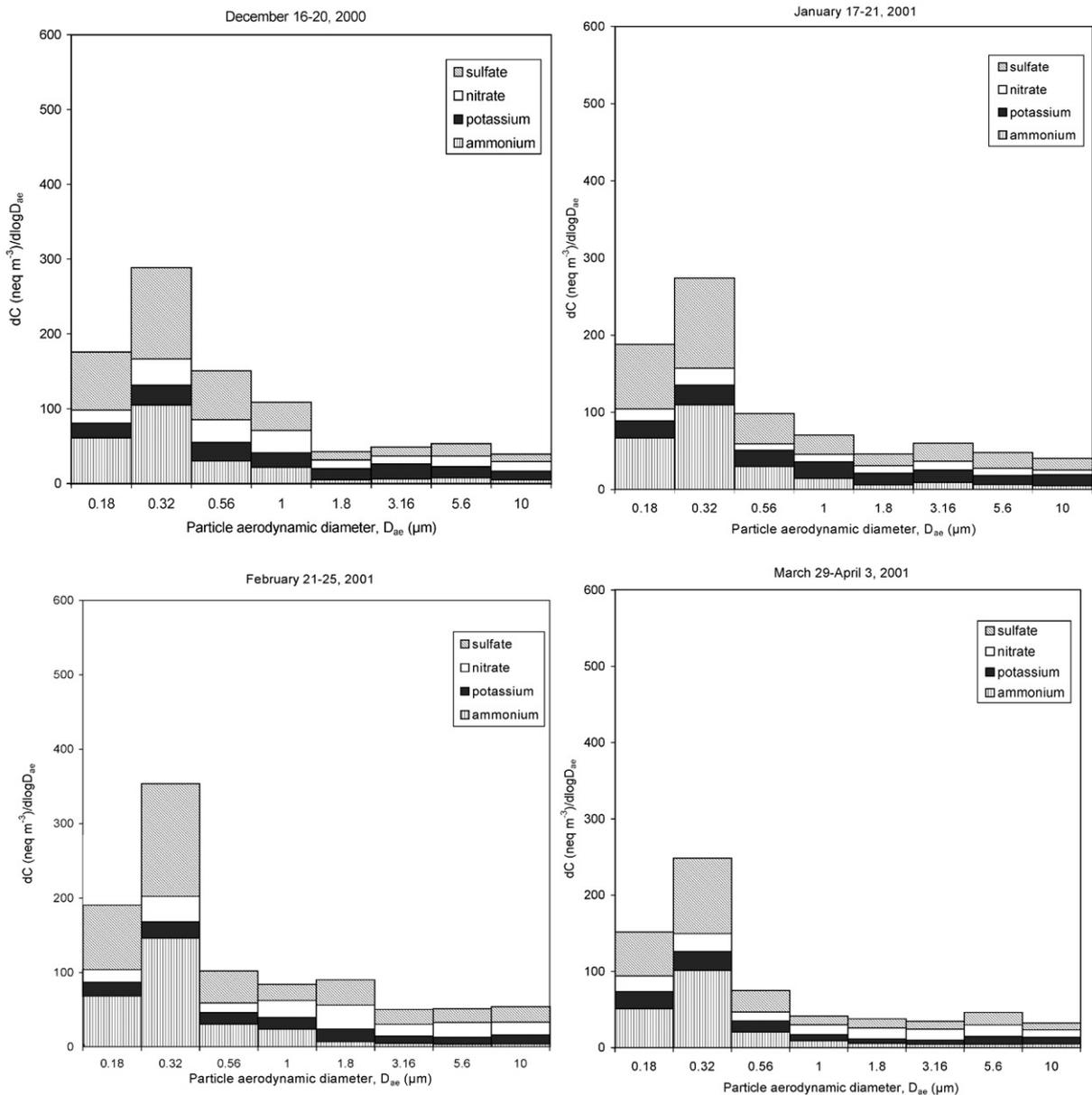


Fig. 2. Size distributions of major ions measured at the CU site during the months of December 2000 and January, February and March 2001. Concentration ( $C$ ) of major ions is given in nanoequivalents per cubic meter ( $\text{neq m}^{-3}$ ).

during our sampling study volatilized nitrate concentrations were not measured, John et al. (1990) have reported volatilization losses of ammonium nitrate around 10% using a nine-stage Berner cascade impactor, under hot ( $35^{\circ}\text{C}$ ), dry conditions. The lack of volatilized nitrate measurements in our study might introduce some errors in the size-differentiated nitrate concentrations reported here (Chang et al., 2000).

Regarding the second finding, i.e., the high sulfate concentrations observed during April and June, these

are explained by the influence of volcanic emissions (particularly  $\text{SO}_2$ ) from the neighboring volcano, Popocatepetl, to the sampling site. During the sampling periods of April and June, the CENAPRED (National Center for the Prevention of Disasters) reported moderate–high activity at the Popocatepetl. Although during our study  $\text{SO}_2$  concentrations were not measured at the CU site, strong correlations were found (see Fig. 4) between our sulfate measurements and  $\text{SO}_2$  concentrations observed at the TAH site (located

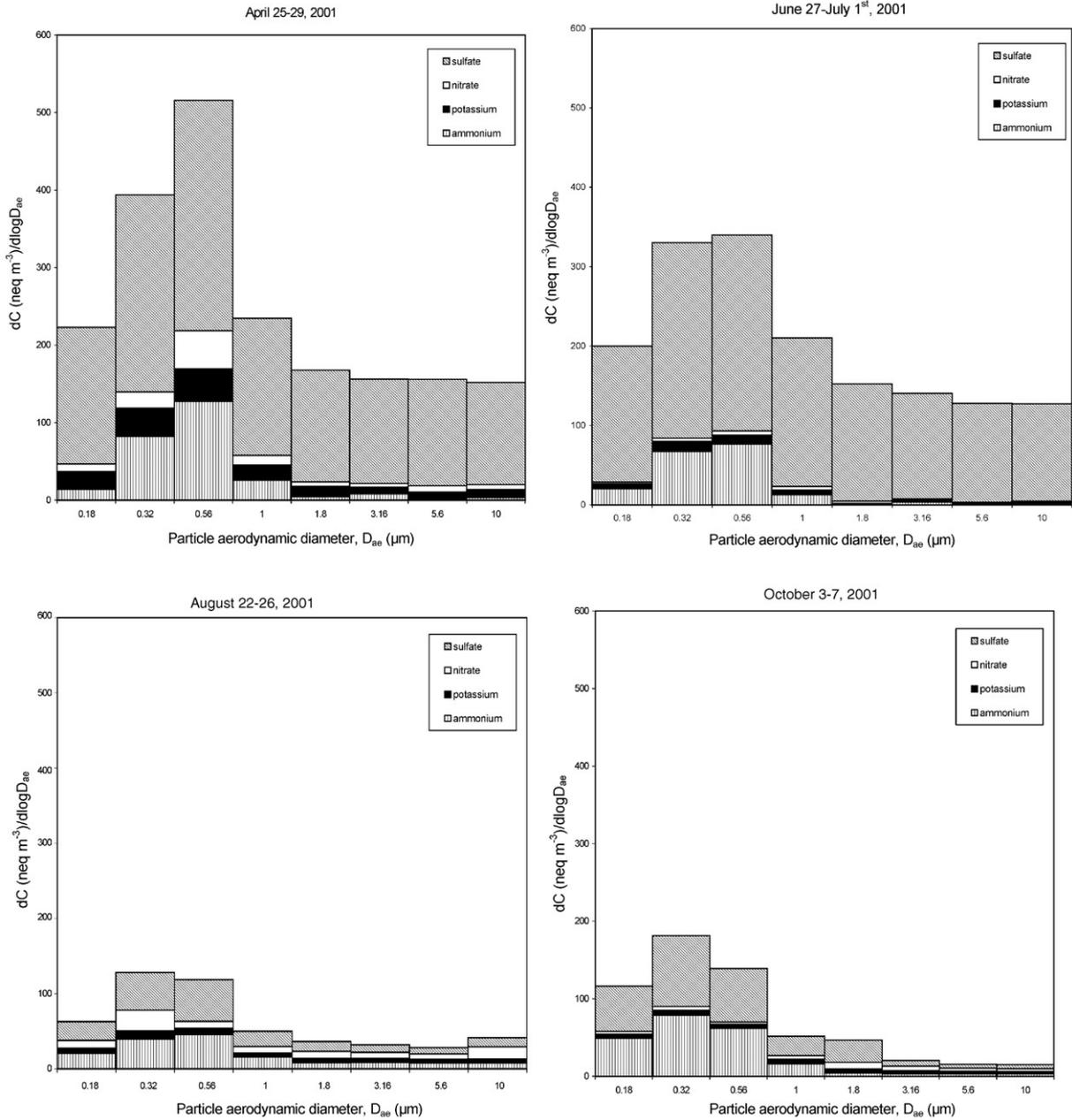


Fig. 3. Size distributions of major ions measured at the CU site during the months of April, June, August and October 2001. Concentration ( $C$ ) of major ions is given in nanoequivalents per cubic meter ( $\text{neq m}^{-3}$ ).

~40 km from the volcano, see Fig. 1). Thus, it is evident that the high sulfate levels observed during these months were not only due to faster oxidation associated with higher RH and aqueous chemistry (as evidenced by the shift of the mode from 0.32 to 0.56  $\mu\text{m}$ ), but also due to a higher atmospheric burden of total sulfur. We also note that during the sampling periods of April and June predominant easterly winds were observed, supporting

the hypothesis that the elevated  $\text{SO}_2$  concentrations have been transported from the volcano into the city. The relative influence of volcanic emissions versus conditions of high humidity on the production of sulfate at the sampling site can be analyzed by comparing the April–June cases to the August case. Moderate–high RH conditions and moderate–high activity of the volcano characterized the April and June cases. Moderate–high

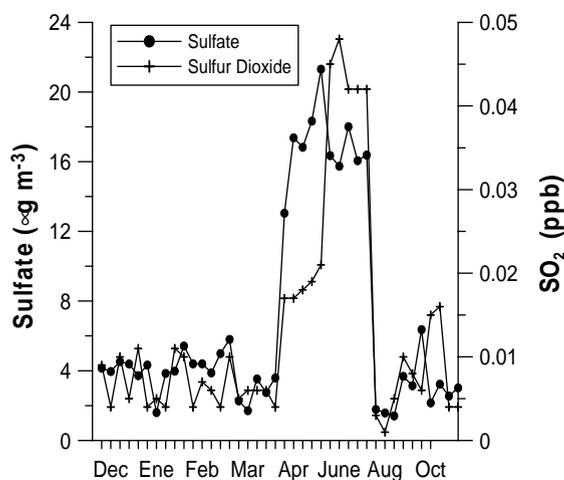


Fig. 4. Correlation between sulfate (measured at the CU site) and sulfur dioxide (measured at the TAH site) concentrations during the period of study. Sulfate and sulfur dioxide concentrations are represented in 24-h averages.  $\text{SO}_2$  measurements for two sampling periods were not available at the TAH site and we plotted those corresponding to the PED site instead.

humidity conditions but low volcanic activity characterized the August case. As seen in Fig. 4, the influence of volcanic emissions (particularly  $\text{SO}_2$ ) during April and June led to more particulate sulfate production at the CU site ( $\sim 2$ – $3$  times higher than that observed during August). The existence of a link between elevated  $\text{SO}_2$  concentrations (due to volcanic emissions) and sulfate mass in the southwest sector of the Mexico City Basin is in agreement with findings reported by Raga et al. (1999).

### 3.2. Ion balances

Figs. 5 and 6 show the sum of the cations (ammonium and potassium) plotted versus the sum of the anions (sulfate and nitrate) for each one of the months sampled. Overall, the slopes for these ion balances (except for the months of April and June) were within 15% of unity (see Fig. 7a), with a small deficit of cations. It is important to mention that crustal species such as calcium and water-soluble organic compounds were not measured for this sampling study. Although some improvement in ion balances would be expected if other cations/anions were included, it seems unlikely that this could explain the qualitatively different cation-to-anion correlations for the months of April and June. Fig. 7b shows that for these 2 months, the cation-to-anion ratio is substantially below unity with a significantly positive anion intercept, which is strongly indicative of the presence of  $\text{H}^+$ , and thereby of the acidic nature of the particles sampled (Kerminen et al., 2001). Given the significance of these

findings, a detailed discussion is presented in the next section.

### 3.3. Total ammonium/total sulfate molar ratio

In this section, we examine the electroneutrality of the April and June data based on the concentrations of ions that were measured. The electroneutrality balance is defined as follows:

$$\sum v_a n_a - v_c n_c = 0, \quad (1)$$

where  $v$  is the ion charge and  $n$  is the number of moles. Subscripts a and c denote anions and cations, respectively. Substituting in Eq. (1) the anions and cations measured in this study:

$$\frac{[\text{SO}_4^{2-}]}{96} + \frac{[\text{NO}_3^-]}{62} = \frac{[\text{NH}_4^+]}{18} + \frac{[\text{K}^+]}{39}. \quad (2)$$

Eq. (2) is valid assuming non-acidic conditions, i.e., the amount of ammonia and potassium is enough to fully neutralize the sulfate and nitrate present in the environment and there is no other form of sulfate present (such as bisulfate and/or letovicite). In practice, during April and June ammonium and sulfate were the dominant ionic species. To evaluate if the cases under study are ammonia-rich (non-acidic environment) or ammonia-poor (acidic environment), one needs to evaluate the total ammonium/total sulfate (TA/TS) molar ratio. According to theory (Seinfeld and Pandis, 1998) if the TA/TS molar ratio is  $< 2$ , then the regime is defined as ammonia-poor environment. On the contrary, if the TA/TS molar ratio is  $> 2$ , then the regime is defined as ammonia-rich environment. Specifically, if the TA/TS molar ratio is:

- (1) less or equal to 0.5, the aerosol particles exist primarily as  $\text{H}_2\text{SO}_4$  solutions;
- (2) between 0.5–1.25,  $\text{NH}_4\text{HSO}_4(\text{s})$  (or an  $\text{NH}_4^+$  and  $\text{HSO}_4^-$  solution) is the dominant component of the system;
- (3) between 1.25–1.5,  $\text{NH}_4\text{HSO}_4(\text{s})$  and  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  (letovicite), or a solution with the corresponding ions, coexist in the system;
- (4) equal to 1.5, the aerosol phase consists exclusively of letovicite (or a solution with the corresponding ions);
- (5) equal to 2, all the ammonia is fully neutralized with the sulfate present, and therefore, the predominant component in the system is  $(\text{NH}_4)_2\text{SO}_4(\text{s})$  or a solution with the corresponding ions.

For the TA/TS molar ratio analysis, we are assuming that the amount of sulfuric acid in the gas phase is negligible. This is a reasonable assumption, as sulfuric acid possesses an extremely low vapor pressure. During our study, gas-phase concentrations of  $\text{NH}_3$  were not

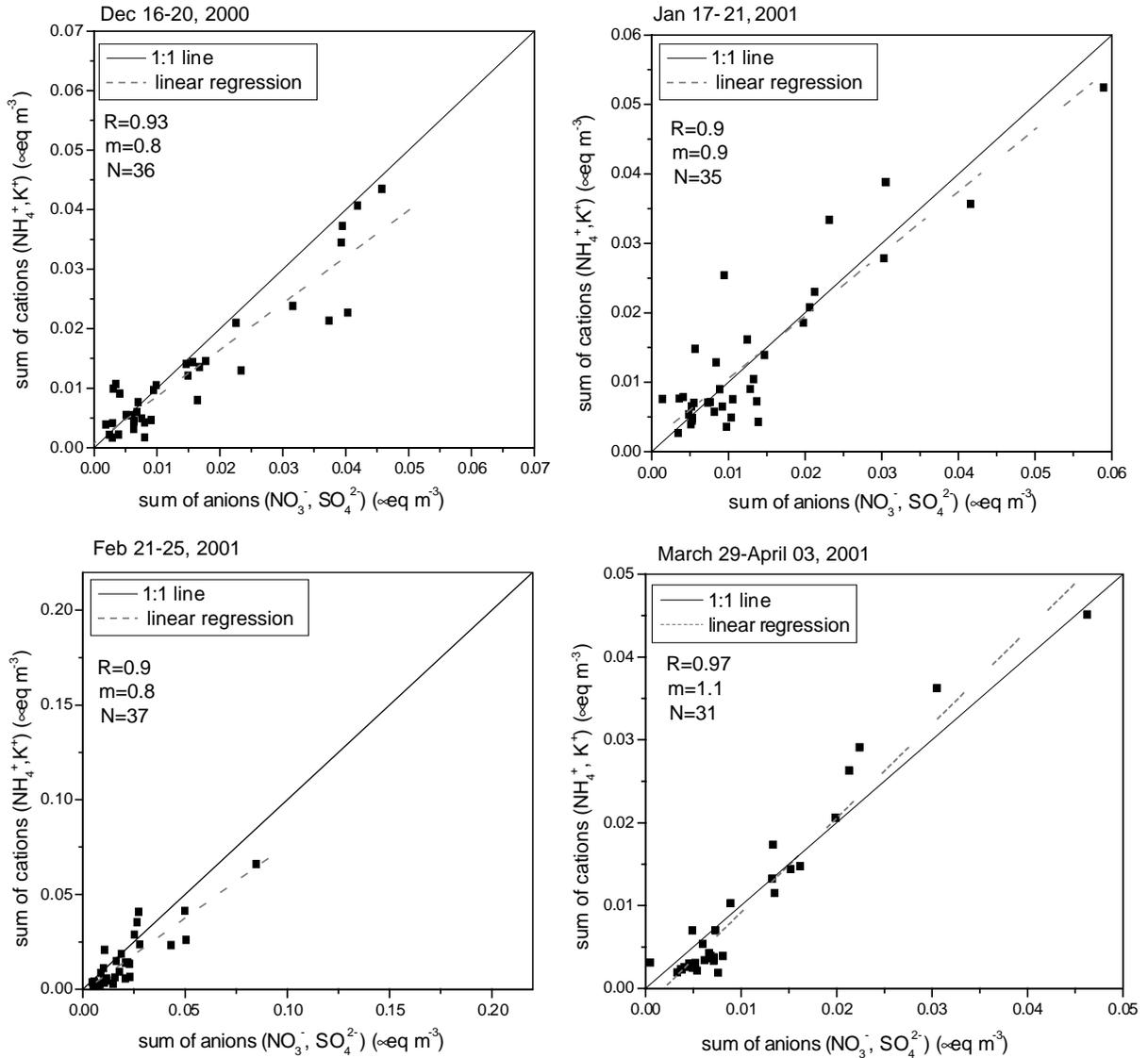


Fig. 5. Ion balances for all individual impactor stages achieved during December 2000, and January, February and March 2001 at the CU site. Units are in micro-equivalents per cubic meter ( $\mu\text{eq m}^{-3}$ ).

measured and we did not consider  $\text{NH}_3(\text{g})$  in the total ammonia concentrations. Therefore, we are assuming that all ammonia, if it exists, is converted to particulate-phase ammonium. It is important to note that the ammonium/sulfate molar ratio analysis is applied considering an idealized  $\text{NH}_3\text{-HNO}_3\text{-H}_2\text{SO}_4\text{-water}$  system. Measurements of water-soluble organic compounds such as organic acids and crustal species such as calcium and magnesium are needed in order to establish more fully the acid/base characteristics of size-resolved aerosols in this mega-city. However, for the analysis of the April and June cases, not considering water-soluble  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (accumulation mode) might have a

little effect in the findings reported here as previous studies in Mexico City (Chow et al., 2002) reported not significant concentrations of these species in the fine mode. Regarding water-soluble organic compounds, although these species are considered important constituents in the fine mode (Temesi et al., 2001) their inclusion might have a little effect in the findings reported here. Most of the organic compounds are weak acids (Saxena and Hildemann, 1996), and in any case they would not neutralize the excess of sulfate observed in the aforementioned cases.

Fig. 8(a and b) shows the ammonium/sulfate molar ratio analysis for the smaller ( $\sim 0.32 \mu\text{m}$ , aerodynamic

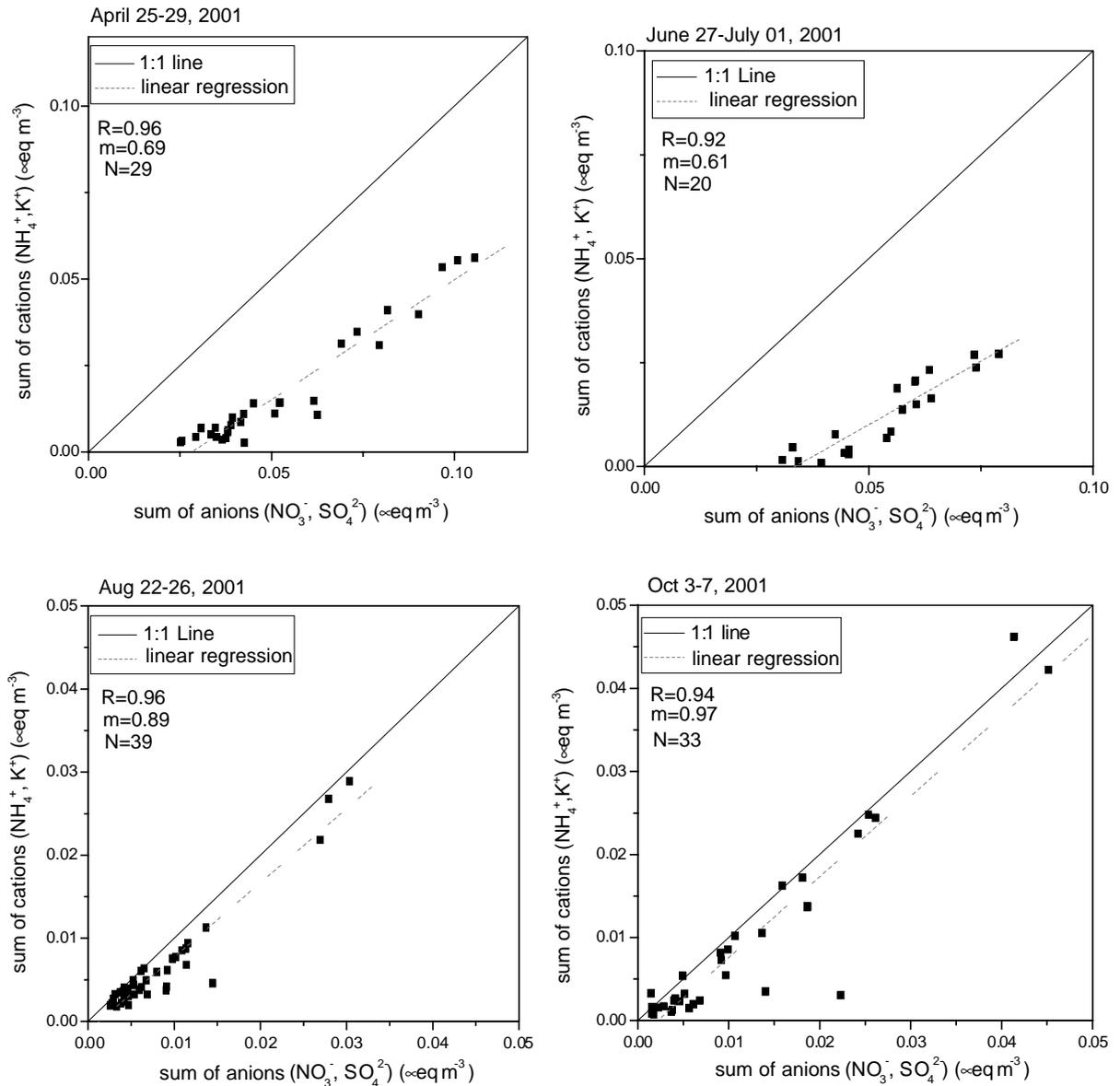


Fig. 6. Ion balances for all individual impactor stages achieved during April, June, August and October 2001 at the CU site. Units are in micro-equivalents per cubic meter ( $\mu\text{eq m}^{-3}$ ).

diameter) mode. Fig. 8a shows the analysis for all months sampled (except April and June). Fig. 8b shows the analysis for the April and June cases. Fig. 8c shows the ammonium/sulfate molar ratio analysis for the larger ( $\sim 0.56 \mu\text{m}$ , aerodynamic diameter) mode (April and June samples). For the first case (see Fig. 8a), a slope value  $\sim 2$ , which actually represents the TA/TS molar ratio, indicates that all the ammonia present neutralizes the sulfate, forming ammonium sulfate or an  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  solution in the system. This neutral characteristic of aerosols is in agreement with that

reported by Canagaratna et al. (2002) during a field study conducted at the PED site (see Fig. 1) in February 2002. In the case of April and June data ( $\sim 0.32 \mu\text{m}$ , aerodynamic diameter, see Fig. 8b), the slope value (1.17) is representative of all the points of the system and indicates that ammonium bisulfate is the dominant form of sulfate present (TA/TS molar ratio in the 0.5–1.5 range). However, one should note that the TA/TS ratio is in this 0.5–1.5 range only for 80% of the points. For the remaining 20% of the points, the TA/TS ratio is  $< 0.5$ , indicating that for these cases sulfuric acid is the

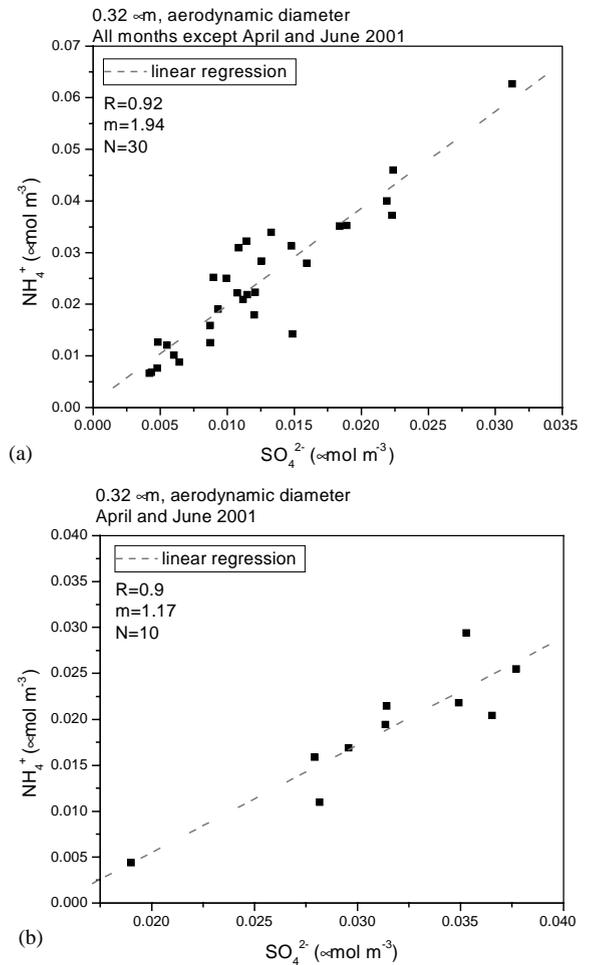
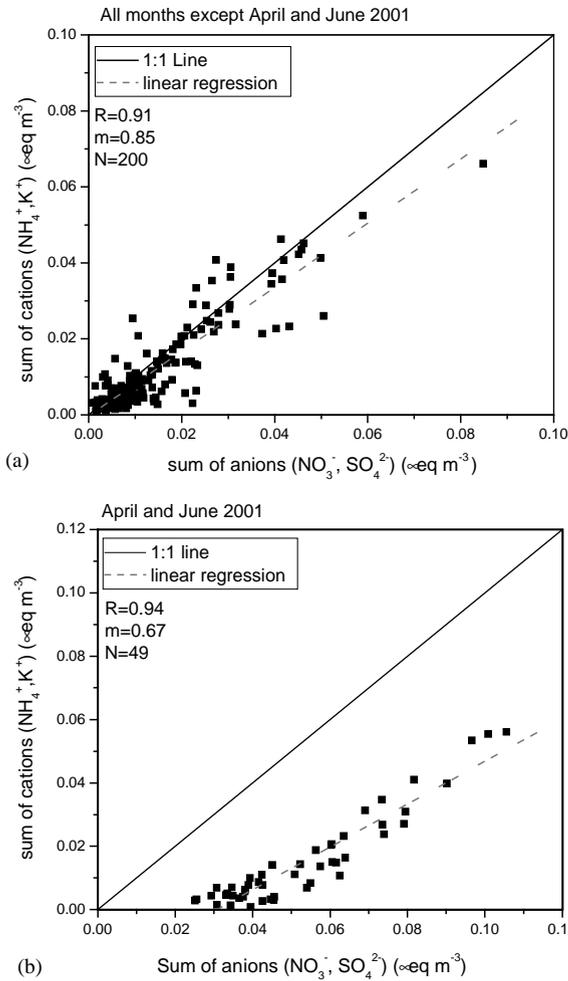


Fig. 7. (a) Ion balances for all individual impactor stages considering all months sampled (except April and June 2001). (b) Ion balances for all individual impactor stages considering only the months of April and June 2001. Units are in micro-equivalents per cubic meter ( $\mu\text{eq m}^{-3}$ ).

dominant form of sulfate present in the system. In the case of April and June data ( $\sim 0.56 \mu\text{m}$ , aerodynamic diameter, see Fig. 8c), the slope value (1.47) representative of all the points indicates ammonium bisulfate and letovicite co-exist (TA/TS molar ratio is in the 1.25–1.5 range). However, one should note that for 20% of the points the TA/TS ratio is  $< 0.5$ , indicating that for these cases sulfuric acid is the dominant form of sulfate present. Although not shown, for other size ranges (April and June) the ammonium/sulfate molar ratio analysis mostly corresponds to values less or equal to 0.5, indicating that aerosol particles might exist primarily as  $\text{H}_2\text{SO}_4$  solutions (very acidic particles). It is important to note that not considering the presence of crustal species (e.g., water-soluble calcium and magne-

Fig. 8. (a) Ammonium/sulfate molar ratio at  $0.32 \mu\text{m}$ , aerodynamic diameter, considering all months sampled (except the April and June cases). (b) Ammonium/sulfate molar ratio at  $0.32 \mu\text{m}$ , aerodynamic diameter, for the April and June cases. (c) Ammonium/sulfate molar ratio at  $0.56 \mu\text{m}$ , aerodynamic diameter, for the April and June cases. Units are in micro-mole per cubic meter ( $\mu\text{mol m}^{-3}$ ).

sium) might have an effect on our findings of the acidity of particles in the coarse mode. On the other hand, not considering the presence of water-soluble organic compounds (e.g., organic acids) might have a little effect on our findings of the acidity of particles in the accumulation/coarse modes. If particles of this nature occurred, the particles would, in reality, be more acidic than those calculated in our analysis.

Summarizing, our findings indicate that during the dry season non-acidic nature particles are predominant (i.e., sulfate is mostly neutralized by ammonia) at the CU site. On the contrary, for late April and June (part of the rainy season), acidic particles are common (i.e., sulfate is not fully neutralized by ammonia). These acidic sulfate particles, observed in all aerosol size ranges (fine and coarse modes) at the CU site, appear to result from moderate–high SO<sub>2</sub> emissions from the neighboring volcano, Popocatepetl, as well as environmental conditions (particularly humidity) that favor rapid oxidation.

#### 4. Summary and conclusions

Measurements of size-segregated atmospheric aerosol particles collected at the CU site during December 2000–October 2001 have provided a wealth of information regarding the inorganic chemical composition of PM in Mexico City. Chemical analysis of these aerosols indicates that sulfate and ammonium, which were specifically correlated in the fine mode, were the dominant species of the size distributions during the year sampled. Our findings indicate that the more predominant mode was at  $0.32 \pm 0.1 \mu\text{m}$ , aerodynamic diameter. This peak of concentration was shifted to the droplet mode ( $\sim 0.56 \mu\text{m}$ , aerodynamic diameter) during late April, June and August (the rainy season). The smaller mode is the result of condensation of secondary aerosol components from the gas phase. The larger mode is the result of aqueous-phase reactions (Seinfeld and Pandis, 1998). Regarding the coarse mode, small peaks of concentration of nitrate and sulfate were observed in the 1.8–10  $\mu\text{m}$  size range. Size-differentiated coarse ammonium and sulfate concentrations measured during this study at the CU site compared well with “bulk” coarse (PM<sub>10</sub>–PM<sub>2.5</sub>) concentrations measured at the neighboring sampling site, PED (IMADA study). Size-differentiated coarse nitrate concentrations obtained at the CU site were also comparable with coarse (PM<sub>10</sub>–PM<sub>2.5</sub>) non-volatilized nitrate concentrations (IMADA). Important limitations of the present dataset are: (1) the lack of measurements of volatilized nitrate, which may introduce some errors in the size distributions for particulate nitrate; (2) the lack of measurements of crustal species such as calcium and magnesium in the coarse mode; (3) the lack of measurements of

water-soluble organic compounds such as organic acids in the fine/coarse modes. Based on our analysis, during the dry season (fall and winter seasons), the sulfate is mostly neutralized by ammonia. On the contrary, during the rainy season (late April and June), there were significantly high sulfate concentrations in all aerosol size ranges (two-, three-fold higher than that measured from the rest of the months). This is explained by moderate–high volcanic emissions (particularly, SO<sub>2</sub>) from the neighboring volcano, Popocatepetl, as well as ambient conditions that favored production of sulfate (humidity). The influence of volcanic emissions as well as conditions of high humidity on sulfate production in the southwest sector of the Mexico City basin has been observed previously (Raga et al., 1999). Based on our analysis of the ammonium/sulfate molar ratios for the cases April and June, H<sub>2</sub>SO<sub>4(aq)</sub>, ammonium bisulfate and letovicite (or a solution with the corresponding ions) were the predominant forms of sulfate present. These acidic particles (where the ammonia is not enough to fully neutralize the sulfate concentration) observed during part of the rainy season at the CU site could be of importance to possible health effects of inhaled particles (Spengler et al., 1990; Dockery et al., 1992), and should be further analyzed. Future work is being considered to fully characterize the inorganic and organic fractions of PM throughout the metropolitan area of Mexico City.

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