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Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry – Part II: overview of the results at the CENICA supersite and comparison to previous studies

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Abstract

An Aerodyne Aerosol Mass Spectrometer (AMS) was deployed at the CENICA Supersite during the Mexico City Metropolitan Area field study from 31 March–4 May 2003. The AMS provides real time information on mass concentration and composition of the non-refractory species in particulate matter less than 1 μm (NR-PM_1) with high time and size-resolution. Measurements of Black Carbon (BC) using an aethalometer, and estimated soil concentrations from Proton-Induced X-Ray Emission (PIXE) analysis of impactor substrates are also presented and combined with the AMS in order to include refractory material and estimate the total $PM_{2.5}$ mass concentration at CENICA during this campaign. In Mexico City, the organic fraction of the estimated $PM_{2.5}$ at CENICA represents 54.6% of the mass, with the rest consisting of inorganic compounds (mainly ammonium nitrate and sulfate/ammonium salts), BC, and soil. Inorganic compounds represent 27.5% of $PM_{2.5}$; BC mass concentration is about 11%; while soil represents about 6.9%. The NR species and BC have diurnal cycles that can be qualitatively interpreted as the interplay of direct emissions, photochemical production in the atmosphere followed by condensation and gas-to-particle partitioning, boundary layer dynamics, and/or advection. Bi- and trimodal size distributions are observed for the AMS species, with a small combustion (likely traffic) organic particle mode and an accumulation mode that contains mainly organic and secondary inorganic compounds. The AMS and BC mass concentrations, size distributions, and diurnal cycles are found to be qualitatively similar to those from most previous field measurements in Mexico City.

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1. Introduction

1.1. Particulate pollution in Mexico City

The Mexico City Metropolitan Area (MCMA) is one of the most populated cities in the world with 18 million people according to the 2000 census (INEGI, 2001). The MCMA is an elevated basin at about 2240 meters above sea level, surrounded by mountains on the south, west and east. At this altitude, there is 23% less oxygen available than at sea level, which causes combustion to be less efficient (Molina and Molina, 2002). More than three million vehicles and more than five thousand industries emit more than 28 metric tons day^{-1} of particulate matter smaller than 10 μm (PM_{10}), including 17 tons day^{-1} of particulate matter smaller than 2.5 μm ($PM_{2.5}$), and 2400 tons day^{-1} of potential particle precursors such as SO_2, NO_x and organic compounds (see Table 1) (SMADF, 2002).

Because of the altitude and the subtropical latitude of the Mexico City basin, it receives intense solar radiation, which promotes the efficient formation of photochemical pollutants. According to official reports, during 2001 and 2002, the ozone concentration exceeded the health-based standard (110 ppb for 1 h avg.) 70% of the days (SMADF, 2003). During the same years, the PM_{10} 24 h standard (150 μg m^{-3}) was exceeded one of every 12 days. In addition, the annual arithmetic mean PM_{10} standard (50 μg m^{-3}) was also exceeded. Currently, there is no Mexican Standard for $PM_{2.5}$. Negative health effects due to air pollution in Mexico city have been reported (Calderon-Garciduenas et al., 2003), including specific effects associated with fine particles (Gold et al., 1999; Osornio-Vargas et al., 2003).

In addition to the visibility and health effects that air pollution in the Mexico City Valley causes on a local scale, pollution emitted in Mexico City can have effects on regional and global scales. Barth and Church (1999) studied the fate of the SO_2 emitted in Mexico City with a global model. According to these authors, most of the sulfur emitted in the city travels westward and northward, but small concentrations can be found as

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far northeast as the Mediterranean basin. According to these authors the average atmospheric lifetime of the sulfur emitted from Mexico City is 5.5 days, which is larger than the average lifetime of sulfur emitted in the rest of the world (3.9 days).

1.2. Brief review of previous Mexico City PM studies

There are several published studies on particulate pollution in the MCMA. However, most of these studies lack highly time and size resolved data, or the compositional data needed to investigate the chemical and physical processes that lead to the pollution episodes (Raga et al., 2001). Furthermore, most of the previous studies focused on PM_{10}, which is not considered as important for human health effects as $PM_{2.5}$ (Dockery et al., 1993; Pope et al., 2002).

The most complete published study on MCMA PM chemical properties was the campaign "Investigación sobre Materia Particulada y Deterioro Atmosférico – Aerosol and Visibility Evaluation Research" (IMADA-AVER), carried out in March 1997. During this campaign, the chemical properties of $PM_{2.5}$ and PM_{10} were measured and their temporal and spatial variations were reported over averaging periods of 6 or 24 h at six core sites and at 25 satellite sites in and around Mexico City (Chow et al., 2002; Vega et al., 2002). According to Chow et al., in average over all sites, the largest $PM_{2.5}$ components in Mexico City were carbonaceous aerosols (~50% of mass), followed by inorganic aerosols (sulfate, nitrate and ammonium, 30%) and geological material (15%). Geological material was the largest component of PM_{10} with 50% of mass followed by ~32% from carbonaceous aerosols and 17% from secondary inorganic aerosols. Sulfate and nitrate were present as ammonium sulfate and ammonium nitrate. According to these authors, morning samples had the highest PM_{10} and $PM_{2.5}$ mass, secondary inorganics and black carbon concentrations, probably due to a shallow surface inversion and emissions from rush-hour traffic. Chow et al. focused on reporting the measured aerosol concentrations and composition, with little analysis of the relationship of the particles with gases or meteorological parameters.

Moya et al. (2003) reported 24-h averages for the size-resolved inorganic fraction

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of the aerosol in the MCMA, collected using a Micro-Orifice Uniform Deposit Impactor (MOUDI) in the main campus of the National University (UNAM), located in the south of Mexico City, from December 2000 to October 2001. These authors found that sulfate and ammonium were the dominant PM inorganic species during the year sampled. The more predominant mode was at 0.32 μm aerodynamic diameter. This peak of concentration was shifted to a larger mode (0.56 μm) during the rainy season. During the dry season (fall and winter), sulfate was mostly neutralized by ammonia. In contrast, during the rainy season (late April and June), particles were found to be generally acidic, due to significantly higher sulfate concentrations in all aerosol size ranges. This observation was attributed to moderate-high volcanic emissions (particularly, SO_2) from the neighboring Popocatepetl volcano, as well as high relative humidity that favors rapid oxidation of SO_2. No gas-phase or meteorological measurements were carried out during this campaign.

Most recently, Moya et al. (2004) measured the size-differentiated inorganic composition of atmospheric aerosol particles with MOUDIs along with gas-phase precursors (NH_3 and HNO_3) with an open-path Fourier Transform Infrared (FTIR) spectrometer near downtown Mexico City (La Merced) during 10 days in January-February 2003. Two particle modes were found: the accumulation mode in the size range 0.18–0.32 μm aerodynamic diameter; and the coarse mode over 1 μm. Chloride and sodium were the dominant ions over all of the study. However, sodium was combined with other anions, besides chloride, such as sulfate. The significant presence of sodium and the unexpectedly high concentrations of crustals were attributed to the potential influence of the dry salt-lake of Texcoco. Ammonium in the accumulation mode was inversely correlated with the gas-phase precursors (NH_3 and HNO_3). The authors suggest that this is caused by gas-to-particle conversion particularly during the late morning sampling periods.

This paper presents size and chemically speciated particulate matter measurements obtained with an Aerosol Mass Spectrometer during the MCMA-2003 campaign. The MCMA-2003 campaign was an intensive 5-week campaign that took place in the spring

of 2003 (31 March–4 May), with the goal of investigating the atmospheric chemistry of the MCMA, with particular focus on emission characterization and quantification, gas-phase photochemistry and secondary PM formation. A focal point of the campaign was a highly instrumented "Supersite" located at the "Centro Nacional de Investigación y Capacitación Ambiental" (CENICA), in the south east of Mexico City (see Fig. 1). Part I of this series of papers described the operation of the AMS at the CENICA site and presents intercomparisons between the AMS measurements and those obtained with other collocated particulate instruments (Salcedo et al., 2005). In this paper, we describe the aerosol size, chemical composition, and mass concentration time trends observed in CENICA. In order to account for the refractory aerosol material we include in the analysis measurements of Black Carbon (BC) with an aethalometer and an estimation of the aerosol soil component from Proton-Induced X-Ray Emission (PIXE) analysis of impactor substrates. We compare these results with those published in previous studies of Mexico City aerosol and with data from the recently deployed city-wide $PM_{2.5}$ monitoring network.

2. Experimental

The Aerosol Mass Spectrometer (AMS) reports mass concentrations, size distributions, and mass spectra of non-refractory species in submicron particles (NR-PM_1). The AMS has been described in detail previously (Jayne et al., 2000; Jimenez et al., 2003) and a summary of the operation conditions and calibrations of the instrument used during the MCMA-2003 is included in the companion paper (Salcedo et al., 2005). Detection limits during this campaign were 0.01, 0.09, 0.11, 0.41 and 0.04 μg m^{-3} for nitrate, sulfate, ammonium, organics and chloride respectively for a 10 min averaging time. The uncertainty in NR-PM_1 due to the uncertainties in bounce-related particle collection efficiency is about −30% to +10%.

The black carbon (BC) content of fine aerosols in the 0.1 to 2.0 micron size (PM_2) range was measured using a seven-channel aethalometer (RTAA-1000, Magee Scien-

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tific, Berkeley, CA), which is also described in the companion paper.

Aerosol samples were collected continuously with a DRUM impactor onto Teflon strips in three size ranges: 1.15–2.5 μm, 0.34–1.15 μm, and 0.07–0.34 μm. PIXE analysis was carried out immediately following the campaign to determine concentrations of elements Na to Pb. Soil mass concentrations were estimated using the method of Malm et al. (1994). Concentrations are given in 6-h averages. Details of the sampling and analysis procedures are given elsewhere (Johnson et al., 2005a[1]).

CENICA is located in the campus of the Universidad Autónoma Metropolitana-Itzapalapa (UAM-I), approximately 10 km southeast of the city center, and within a medium income residential and commercial area. The main sources of pollutants are traffic and some small industries. The supersite was located inside a hut built on the roof of a 12 m tall building. Local Standard Time in Mexico City normally corresponds to Central Standard Time (CST) or Coordinated Universal Time (UTC) minus 6 h. On 6 April 2003 at 2:00 a.m. the Daylight Savings Time period started in Mexico; after that, local time corresponded to Central Daylight Saving Time (CDT) or UTC minus 5 h. All data in this paper is reported in Local Time, i.e. CST before 6 April and CDT after 6 April. All the mass concentrations presented in this paper for all instruments are at ambient temperature and pressure conditions (local pressure is approximately 76 kPa).

3. Results and discussion

3.1. Aerosol mass concentration and composition

The average mass concentrations of AMS + BC + soil during the entire measurement period are presented in Fig. 2 and Table 2. In Part I of this series, we showed that AMS + BC + soil was a good approximation to $PM_{2.5}$ mass concentration in Mexico City (Salcedo et al., 2005). In general, these concentrations and compositions are

[1] Johnson, K. S. et al.: Composition and Sourcing of Aerosol in the Mexico City Metropolitan Area with PIXE/PESA/STIM and Multivariate Analysis, in preparation, 2005a.

consistent with results in Mexico City from other campaigns (see Sect. 3.4). Organic species represent the main component of estimated $PM_{2.5}$ with 55% of the total mass concentration. Inorganic species represent about 27.5%, with sulfate and nitrate being the most abundant components with ~10% each of the total mass. Ammonium and chloride contribute to the average mass with 6.5% and 1%, respectively. The BC PM_2 mass concentration is 11% of the $PM_{2.5}$ mass, while $PM_{2.5}$ soil represents 7%.

Compared with AMS measurements in other cities, the average total NR-PM_1 mass concentration in the MCMA (30.9 μg m^{-3}) is much larger than the average concentrations measured in Pittsburgh in September 2002 and New York City in July 2001 with an AMS: 14.8 μg m^{-3} (Zhang et al., 2005) and 8.84 μg m^{-3} (Drewnick et al., 2004) respectively. Also, the PM composition is very different. While the largest component of NR-PM_1 in the MCMA is by far the organic matter, in Pittsburgh and New York City the major component is sulfate with 47% and 45% of the total mass, respectively. Organic matter accounts for 30% of the mass in both cities. Nitrate represents only 6% and 9% of the total mass in Pittsburgh and New York, respectively, which is slightly lower than its fraction in Mexico City. 17% of the NR-PM_1 in Pittsburgh and 16% in New York City is Ammonium, which is larger than in Mexico due to the much larger sulfate fraction in those two cities.

3.2. Time variations and diurnal cycles of the aerosol species

Figure 3a–c shows the time series of the speciated mass concentration of NR-PM_1 from 3 April to 5 May 2003, measured at CENICA with the AMS. The "Total" concentration is defined as the sum of all the AMS-measured NR species (nitrate, sulfate, ammonium, chloride and organics). We also show the time series of BC and soil in panels (d) and (e) of the figure. Finally, in panel (f), we show the fractional species mass contribution for the estimated $PM_{2.5}$.

The organic species show a clear diurnal cycle, as does black carbon. The ammonium concentration follows the nitrate and sulfate concentrations in time, which suggests that these three species exist mainly in the forms of NH_4NO_3, and sulfate-

ammonium salts (ammonium sulfate, bisulfate, and/or letovicite; Schlenker et al., 2004). To support this statement, we verified that the amount of ammonium present in the particles roughly corresponds to the amount necessary to completely neutralize the nitrate and sulfate during most of the campaign. This is to be expected since the atmosphere of Mexico City is characterized by high NH_3 concentrations (C. Kolb, Aerodyne Research, personal communication). The only exceptions are a few periods with high concentrations of sulfate when there is only enough ammonium to form NH_4HSO_4 instead of $(NH_4)_2SO_4$. During those periods when there was not enough ammonium to neutralize the nitrate and sulfate present, we cannot rule out the presence of organic nitrates. However, because most of these periods also corresponded to high concentration of sulfate (i.e. 8–12 April), it seems more probable that the aerosol was acidic. Chloride is generally present at very low concentrations, but some very large spikes (up to 26.3 μg m^{-3}) are observed throughout the campaign. Finally the soil concentration is remarkably constant during the campaign.

Since vehicle traffic is one of the main sources of particles and particle precursors in the MCMA (SMADF, 2002), it is expected that traffic patterns have an important effect in the observed particle concentrations. Time periods which are expected to have different traffic patterns are identified in Fig. 3. In Mexico City, weekends are expected to have different traffic patterns from weekdays partially due to the "Hoy no circula" (HNC, "Not driving today") program which limits a fraction of the cars from driving on one day depending on the last digit of the car's license plate. The driving restriction applies to cars older than 10 years and/or to those that do not comply with the emission standards. The HNC program is enforced on weekdays but not on weekends. During MCMA-2003 a traffic count that was obtained on one of the main avenues connecting the south of the city to downtown (Avenida Insurgentes Sur), showed that there is a small reduction in traffic on Saturday with respect to weekdays; on Sunday the reduction in traffic is more noticeable (~25%). These average traffic counts did not show any significant reductions during school vacation week (16 to 25 April), but during Holy weekend (19 to 21 April), which is one of the most popular vacation periods in the

MCMA, a considerable traffic reduction was observed (~30%). Average concentrations of AMS + BC + soil increase ~20% during Saturdays and decrease ~20% during Sundays. The average AMS + BC + soil concentration during Friday and Saturday of the holy weekend were among the lowest in the campaign (PM concentrations were 45% lower than average concentration on regular Fridays and Saturdays), as expected from a significant reduction in vehicle emissions of primary particles and secondary precursors.

While traffic patterns may explain some of the trends in organic aerosol loading, they do not explain features such as the high aerosol concentrations on 9–11 April. In this case, meteorology must also be taken into account to understand the observed dynamics of particle concentrations and properties. A review of the meteorology in Mexico City during the MCMA-2003 campaign is presented by de Foy et al. (2005), who discuss the fact that synoptic weather patterns, regional land-sea breezes, and local thermally driven flows influenced by the mountains combine to produce very complex meteorological patterns. According to de Foy et al. (2005), 9 to 11 April corresponded to "Cold Surge" days which were influenced by the arrival of a cold air mass that caused reduced vertical mixing in the morning and a lower boundary layer height throughout the day, which favored the accumulation of pollutants. Despite the cloudiness on 9 April, intense photochemical activity (evidenced by uniform O_3 levels over most of the eastern part of the Mexico City valley) combined with reduced dilution lead to the highest NR-PM_1 concentrations observed during MCMA-2003. On 10 April, a large SO_2 plume covered the northern half of the city, with maximum concentrations of 277 ppb; this might explain the large concentrations of sulfate observed in the NR-PM_1. 11 April, which also had the highest CO concentrations during the campaign, presented one of the strongest surface inversions.

Figure 3a shows a clear increase in aerosol fraction during the second half of the campaign. One possible reason for this is the impact of extensive biomass burning in Southern Mexico which steadily increased from mid-April according to satellite fire counts (Christine Wiedinmyer, NCAR, personal communication). The plumes from

these fires appear to have been transported to the vicinity of Mexico City during this period according to satellite data, an issue which is being further investigated (Steven Massie, NCAR, personal communication).

The average diurnal cycles of all the species are shown in Fig. 4, panels (a)–(g); panel (h) shows the diurnal cycle of the fractional composition of $PM_{2.5}$ (approximated as AMS + BC + soil) composition. Panels (a) and (h) show that nitrate has a very sharp diurnal pattern with a maximum at midday. We attribute this behavior to nitric acid being formed photochemically during the day from the reaction of NO_2 and OH; the acid reacts with ammonia to form ammonium nitrate on preexisting particles. Thus, ammonium has a diurnal cycle that is very similar to that of nitrate. However, the ammonium concentrations at other times than midday are not as low as the nitrate concentrations. This is because at these times a significant fraction of the particulate ammonium is in the form of sulfate-ammonium salts. The diurnal pattern of sulfate does not have changes as large as that of nitrate, remaining around 2–3 μg m^{-3} most of the time. The highest concentrations of chloride occur during the morning, with very low concentration most of the day. Black carbon is primarily emitted by combustion sources and, as it is expected, its diurnal cycle has a peak early in the morning during the rush hour. At midday, the concentration of BC decreases again because the boundary layer rises causing a dilution of the accumulated BC that is much faster than the rate of emission at that time. Organics have a diurnal pattern that appears to be a combination of traffic sources in the morning and photochemistry during sunlit hours, with perhaps some regional contributions.

3.3. Size distribution of NR-PM_1

The image plots of the NR-PM_1 species concentrations at the CENICA Supersite as a function of time and size are shown in Fig. 5, and highlight the dominance of the accumulation mode and the diurnal cycles observed for most species. The average size distributions for the whole campaign are shown in Fig. 6 (note the different axis scales in which the inorganic and organic distributions are plotted in Fig. 6a). Figure 6b shows

all the size distributions scaled to the same maximum in order to compare their relative shapes. Figure 6c shows the percent concentration of each species as a function of particle size. The organic size distribution is much broader than those of the other species. The size distributions of the inorganic species clearly show an accumulation mode and they also present a shoulder at smaller sizes, indicative of a second mode. Chloride shows an intermediate size distribution between those of organics and the other inorganics.

In order to determine the mode diameters and widths of the size distributions shown in Fig. 6, they were fitted to log-normal modes of the form:

$$\frac{\mathrm{d}M}{\mathrm{d}\log d_{va}} = \sum_i \frac{M_i}{(2\pi)^{1/2}\log\sigma_i} \exp\left[-\frac{(\log d_{va} - \log d_{va,i})^2}{2\log^2\sigma_i}\right] \quad (1)$$

where M_i, $d_{va,i}$, and σ_i are the mass concentration, mean diameter, and geometric standard deviation of the ith lognormal mode, and log is the base 10 logarithm (Seinfeld and Pandis, 1998). For organics, three log-normal modes were required to obtain a good fit. For nitrate, sulfate and ammonium, we used the sum of two modes; and for chloride only one lognormal mode was required. The results of the fits are presented in Fig. 7, Fig. 8 and Table 3.

Studies in many urban areas have reported a multimodal size distribution for organics similar to that reported here, including Boston (Jimenez et al., 2003), Manchester and Edinburgh, UK (Allan et al., 2003), New York City (Drewnick et al., 2004), Vancouver, Canada (Alfarra et al., 2004; Boudries et al., 2004; Mozurkewich et al., 2004), Pittsburgh (Cabada et al., 2004; Stanier et al., 2004; Zhang et al., 2004, 2005), and Tokyo (Takegawa et al., 2005). There is strong evidence from these studies as well as from laboratory studies (DeCarlo et al., 2004; Slowik et al., 2004) and direct sampling of traffic emissions (Canagaratna et al., 2004) that combustion/traffic emissions are the main source of the small organic particles. Condensation of secondary organics (SOA) onto pre-existing ultrafine particles has also been observed in an urban area (Zhang et al., 2004), but this process seems to make a smaller contribution to the ultrafine parti-

cle composition on average. In Mexico City, the smaller modes of the organic aerosol appear dominated by traffic emissions since they show a good correlation with CO and BC; although there are indications of condensation of SOA in this mode in some cases (Dzepina et al., 2005[2]).

The accumulation mode (400–800 nm) organic aerosol is found in all urban areas as well as rural and remote sites and typically contains internally mixed organics and inorganics (Lee et al., 2002; Alfarra et al., 2004; Topping et al., 2004). In most locations the accumulation mode dominates, and many times it is the only mode present (especially at remote sites). In Mexico City, a large fraction of the organic accumulation mode consisted of oxygenated organic compounds (Dzepina et al., 2005[2]). Zhang et al. (2004, 2005) reported similar observations in Pittsburgh.

The high aerosol surface area present at most times in the MCMA provides a large sink for low-volatility species, and thus hinders new particle formation by homogeneous nucleation of gas phase inorganic species such as sulfuric acid, water, and ammonia. However, new particle formation events were observed inside the city during this study when the aerosol surface area was low (Dunn et al., 2004), and sulfate modes at small sizes indicating of growth of new particles were also observed in many occasions (see Fig. 5). Hence, the bi- and tri-modal size distributions observed in Mexico City appear to be a combination of direct particle emission by traffic, nucleation and growth of new particles, condensation/coagulation growth of the small particles in the city, and some influence of the aged regional aerosol. The relative roles of traffic and nucleation in the ultrafine particle population will be explored in a future publication.

The fact that ammonium, nitrate and sulfate have approximately the same size distribution supports the conclusion that these three species are present mostly as NH_4NO_3 and sulfate/ammonium salts. Electron microscope studies of particles collected during MCMA-2003, found that ambient soot particles were generally internally mixed with sulfate (Johnson et al., 2005b), while fresh soot particles in vehicle exhaust were not. However, the different size distributions of the organic and inorganic fractions (except

[2]Dzepina, K. et al.: The Organic Aerosol during MCMA-2003, in preparation, 2005.

for chloride) suggest that these two groups of species are not always internally mixed. The small organic particles emitted by combustion can grow due to condensation of secondary organic and inorganic compounds (such as nitrate, sulfate, or chloride), by cloud processing, by slower and thus more regional processes (such as gas-phase sulfate production), and also by coagulation. The main sources of SO_2 are located north of the city, at least 20 km away from the CENICA site. Since SO_2 to sulfate gas-to-particle conversion (via gas-phase oxidation) is a slow process, it is expected to occur on larger spatial and vertical scales, where the small traffic mode is not as prevalent. In addition, SO_2 to SO_4^{2-} conversion in clouds tends to produce larger particle sizes in the "droplet" mode (Seinfeld and Pandis, 1998). In the case of nitrate, the highest concentrations of this particulate component occur at midday, by which time the early morning small organic particles may have partially grown by condensation and been diluted by the rise of the boundary layer. This might explain why nitrate, sulfate and ammonium occur mainly in the accumulation mode.

The Non-refractory (NR) chloride size distribution peaks at the same diameter as the larger mode of the organic size distribution, which is 100 nm smaller than the accumulation mode of the rest of the inorganic species. Moreover, the highest mass concentrations of NR chloride occur in the early morning. The AMS ion balance, especially during chloride plumes (Salcedo et al., 2005[3]), and the non-refractory character of the chloride measured by the AMS support that the chemical form of chloride is predominantly ammonium chloride (NH_4Cl). NH_4Cl is a semivolatile solid with a partial pressure product of $P_{NH3} \times P_{HCl} \sim 8.0 \times 10^{-17}$ atm at 25°C (Clegg et al., 1998). For comparison, the partial pressure product of NH_4NO_3 is $P_{NH3} \times P_{HNO3} \sim 4.4 \times 10^{-17}$ atm at 25°C; i.e. NH_4Cl is more volatile than NH_4NO_3. These facts suggest that ammonium chloride in Mexico City preferentially condenses in the early morning due to the favorable conditions of lower temperature and higher relative humidity, as it has been suggested before (SanMartini, 2004). Since the organic traffic-emitted particles that

[3]Salcedo, D. et al.: The Inorganic Aerosol during MCMA-2003, in preparation, 2005.

dominate the aerosol at that time have not yet grown by condensation of nitrate and sulfate, the partitioning of ammonium chloride onto fresher traffic emissions may explain the smaller average size for this species than for the rest of the inorganic species.

3.4. Comparison with other studies

In order to provide a framework for the findings from this data set, we compare our results to previous aerosol measurements in Mexico City. Since the different measurements presented here have been carried out at different locations and seasons, and using different techniques, we do not expect that the results be identical. Instead, the comparison intends to explore the variability of the Mexico City aerosol.

During the IMADA-AVER campaign, from 23 February to 22 March 1997, $PM_{2.5}$ was measured at different sites in and around Mexico City (Chow et al., 2002). One of the sites was situated at Cerro de la Estrella (CES), located approximately 2.5 km southwest from the CENICA site. Four 6-h $PM_{2.5}$ samples (00:00–06:00, 06:00–12:00, 12:00–18:00 and 18:00–24:00 h MST, 1 h behind CST) were taken daily at the CES site. The samples were analyzed for water-soluble sulfate, ammonium, nitrate, sodium and potassium; for organic and elemental carbon (OC/EC); and for 38 elements.

Figure 9 compares the speciated diurnal cycles of species concentrations for $PM_{2.5}$ measured at CES during IMADA-AVER, and NR-PM_1 measured with the AMS at CENICA during the MCMA-2003 campaign. Aethalometer BC during MCMA-2003 and EC during IMADA-AVER are also compared. All data is plotted vs. local time. The IMADA-AVER nitrate is the "Total particulate nitrate" in Table 3 of Chow et al. (2002); organic mass is calculated from the organic carbon in the same table, multiplied by 1.6 in order to estimate the particulate organic mass (Turpin and Lim, 2001). The sulfate concentrations were slightly higher during IMADA-AVER. Nitrate was higher during MCMA-2003, which may be partially due to the lower sulfate concentrations and thus reduced competition for gas-phase NH_3 during this campaign. Ammonium and organics levels were similar between the two campaigns, although organics show an earlier maximum during MCMA-2003 than during IMADA-AVER. The diurnal profile of sulfate

was also different during both campaigns. On the other hand, diurnal profiles of nitrate, ammonium, and BC/EC were very similar.

Figure 10 compares the diurnal cycles of AMS + BC + soil during MCMA-2003, $PM_{2.5}$ mass concentration during IMADA-AVER ("Mass-all days" row in Table 3 of Chow et al., 2002) and average $PM_{2.5}$ mass concentration from April 2004 at CES, reported by the Air Quality Monitoring Network in Mexico City (RAMA, http://www.sma.df.gob.mx/simat/paginabases.htm). The $PM_{2.5}$ monitoring network started its operation in 2004, hence there is no 1997 or 2003 data reported to compare with IMADA-AVER or MCMA-2003. All measurements show a similar pattern, with a significant background concentration at all times and a peak in the middle of the day. Since the AMS + BC + soil data compare well to collocated $PM_{2.5}$ DustTrak and TEOM during MCMA-2003 (Salcedo et al., 2005), the difference between AMS + BC + soil in 2003 and the RAMA data in 2004 indicates the range of year-to-year variability at this site, likely driven by differences in meteorology and emissions.

In order to summarize the comparisons between the various studies of the speciated concentrations of the ambient aerosol in Mexico City, Fig. 11 compares the mass concentrations of several $PM_{2.5}$ components that have been reported in the literature. Soil concentration for the IMADA-AVER campaign was calculated using the method described by Malm et al. (1994) and the mass concentrations of Al, Si, Ca, Fe, and Ti reported by Chow et al. (2002). Mass concentrations of species reported by Moya et al. (2003) and Moya et al. (2004) were calculated adding the mass concentration of the MOUDI stages 1–4 (with 50% cutoffs at 0.18, 0.32, 0.56, 1.0 μm in d_a). The two studies that have reported organic concentrations report them to be the dominant group of species. Although there are some variations across the datasets, the different studies show a consistent picture of the $PM_{2.5}$ composition in Mexico City. The main exception is the high chloride concentration reported by Moya et al. (2004) and attributed to the influence of the Texcoco dry lake, compared to very low concentrations during IMADA-AVER and MCMA-2003.

The average mass concentration of BC measured during the MCMA-2003

(3.4 μg m^{-3}) is lower than the EC concentration reported by Chow et al. (2002) in CES during IMADA-AVER (4.65 μg m^{-3}), which was determined by the IMPROVE thermal/optical reflectance method. Baumgardner et al. (2002) reported concentrations of BC in the main campus of UNAM, between 27 February and 4 March 2000, measured with a particle soot aerosol photometer, an instrument that uses the same measurement principles as the aethalometer used here. Baumgardner et al. (2002) reported BC concentrations in the range of 1 and 25 μg m^{-3} (10 min averaging time), which is similar to the range in Figure 3d. Care must be taken when comparing black carbon concentrations measured with different instruments, specially if they are performed in different times and places, because it has been shown that measurements of BC using an aethalometer can be up to about a factor of three different than simultaneous measurements of elemental carbon (EC) using a thermal-optical method, depending on the physical and chemical characteristics of light absorbing species in the particles (Jeong et al., 2004).

In April, 2001, Moya et al. (2003) measured the size distributions of the inorganic aerosol components using a MOUDI impactor at the Campus of UNAM, in the south of Mexico City, about 11 km West of the CENICA site. Their results are compared with the AMS size distributions during MCMA-2003 in Fig. 12. The size distributions of Moya et al. have been converted to vacuum aerodynamic diameter using the size-dependent densities from the MCMA-2003 AMS data (Salcedo et al., 2005). Moya et al. report a peak of concentration at a larger particle size than the median diameter measured with the AMS during MCMA-2003 for nitrate, ammonium and sulfate. Also, the concentrations of nitrate and ammonium measured by Moya et al. are lower and sulfate is higher than in the present study. The aerosol appears to have been very acidic during the Moya et al. study, especially due to the much lower ammonium concentrations. The much larger acidity of the aerosol during the Moya et. al study suggests that the lower nitrate and ammonium mass concentrations are due to low gas phase NH_3 concentrations, which in turn prevented the condensation of nitric acid.

Comparisons with the Moya et al. (2004) size distribution data are not shown here

because they report sodium concentrations much larger than were observed during the MCMA-2003 campaign indicating that the conditions during both campaigns were very different.

4. Conclusions

The estimated $PM_{2.5}$ (NR-PM_1 + BC + soil) in the Mexico City Metropolitan Area during the MCMA-2003 campaign was composed of 55% organic compounds and 27% of inorganic compounds. The inorganics were mainly ammonium nitrate, sulfate/ammonium salts, and a small amount of ammonium chloride. The Black Carbon mass concentration was about 11% of the estimated $PM_{2.5}$, while soil represents ~7%. The NR-PM_1 species and BC have diurnal cycles that can be qualitatively interpreted as the interplay of (some or all of) direct emissions, photochemical production in the atmosphere followed by condensation; gas-to-particle partitioning, boundary layer dynamics, and horizontal advection. The aerosol presents monomodal, bimodal, and trimodal size distributions, which are consistent with small primary organic traffic particles that grow by condensation of organics and inorganics and by coagulation, and an accumulation mode that contains mainly of organic and secondary inorganic compounds. Comparison of the particle measurements during MCMA-2003 with those of previous studies show a broadly similar pattern of total and speciated concentrations. However some differences also exist, likely due to the variability in specific sources and meteorological conditions during different campaigns.

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Table 1. Daily emission rates of particles and potential particle precursors in the MCMA, which includes the Federal District and 18 municipalities in the State of Mexico (SMADF, 2002). SO_2 emissions are given in mass of SO_2 and NO_x is reported as mass of NO_2.

Pollutant	(metric ton/day)
PM_{10}	28
$PM_{2.5}$	17
SO_2	40
NO_x	530
Total Organic Compounds	1829
Volatile Organic Compounds	1177
Isoprene and Monoterpenes	31

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Table 2. Summary of the AMS, BC, and soil mass concentration data during the MCMA-2003 campaign. Averages are made over the complete time interval where data is available. The averaging time interval is different for NR-PM_1, BC and soil (see Fig. 3).

	Average ($\mu g\ m^{-3}$)	Std. Dev. ($\mu g\ m^{-3}$)	Minimum ($\mu g\ m^{-3}$)	Maximum ($\mu g\ m^{-3}$)
Nitrate	3.7	5.1	0.1	49.0
Sulfate	3.1	2.3	below DL	22.7
Ammonium	2.2	1.6	below DL	14.8
Chloride	0.3	0.7	below DL	26.3
Organics	21.6	14.8	1.3	106.5
Total NR-PM_1	30.9	19.0	1.7	125.0
Black Carbon	3.4	2.5	0.2	52.7
Soil	2.1	0.7	1.1	4.6

Table 3. Mass concentration (M_i), median diameter ($d_{va,i}$) and geometric standard deviation (σ_i) of the modes calculated by fitting log-normal functions to the AMS size distributions in Fig. 6. The modes are shown in Figs. 7 and 8. Note that M_i is negative for two modes for which σ_i<1, since log(σ_i) is also negative for those modes.

	M_0 (μg m^{-3})	$d_{va,0}$ (nm)	σ_0	M_1 (μg m^{-3})	$d_{va,1}$ (nm)	σ_1	M_2 (μg m^{-3})	$d_{va,2}$ (nm)	σ_2
Nitrate	3.4	437	1.8	0.17	142	1.3			
Sulfate	2.8	457	1.7	0.21	144	1.4			
Ammonium	2.0	435	1.8	0.08	132	1.3			
Organics	19.5	343	1.9	−1.13	125	0.8	−0.49	71	0.7
Chloride	0.3	345	1.8						

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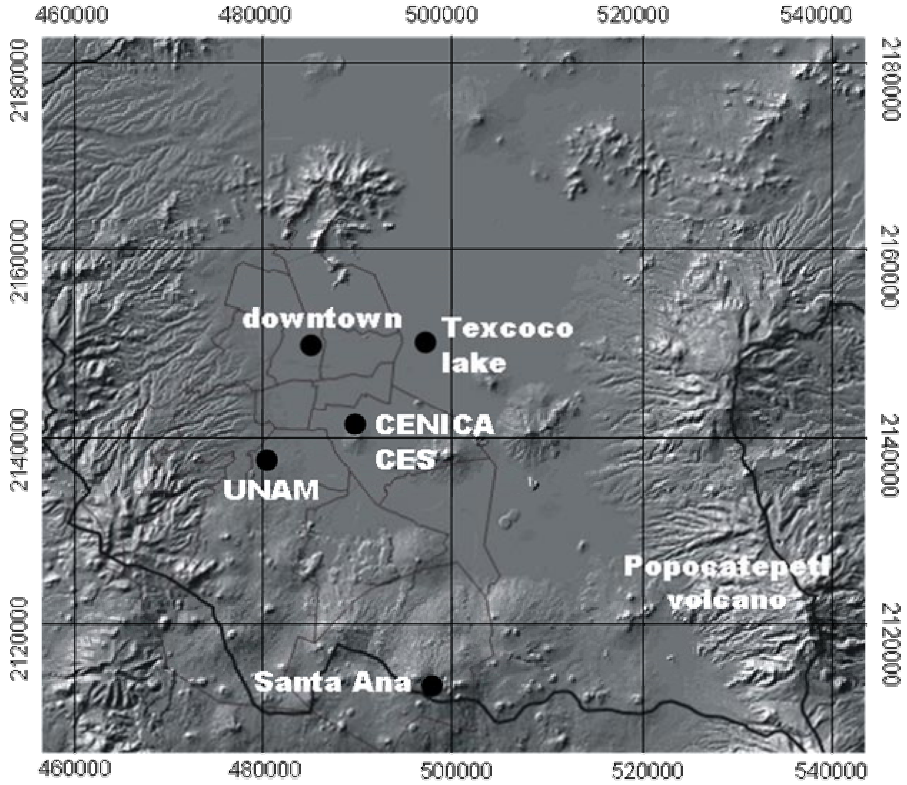

Fig. 1. Topographical map of the Mexico City Metropolitan Area and surrounding region. The dark line represents the limits of the basin. The grey line represents the division and limits of the Federal District. The map is referenced to the Universal Transverse Mercator system (UTM).

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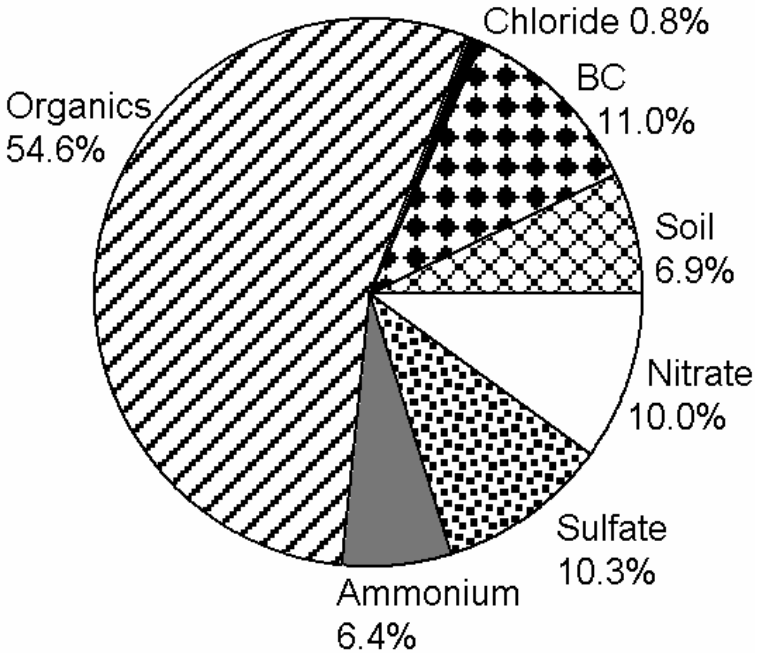

Fig. 2. Average mass composition of $PM_{2.5}$ (approximated as AMS + BC + soil) for the MCMA-2003 campaign. Average was made over all time periods where data from the three measurements were available.

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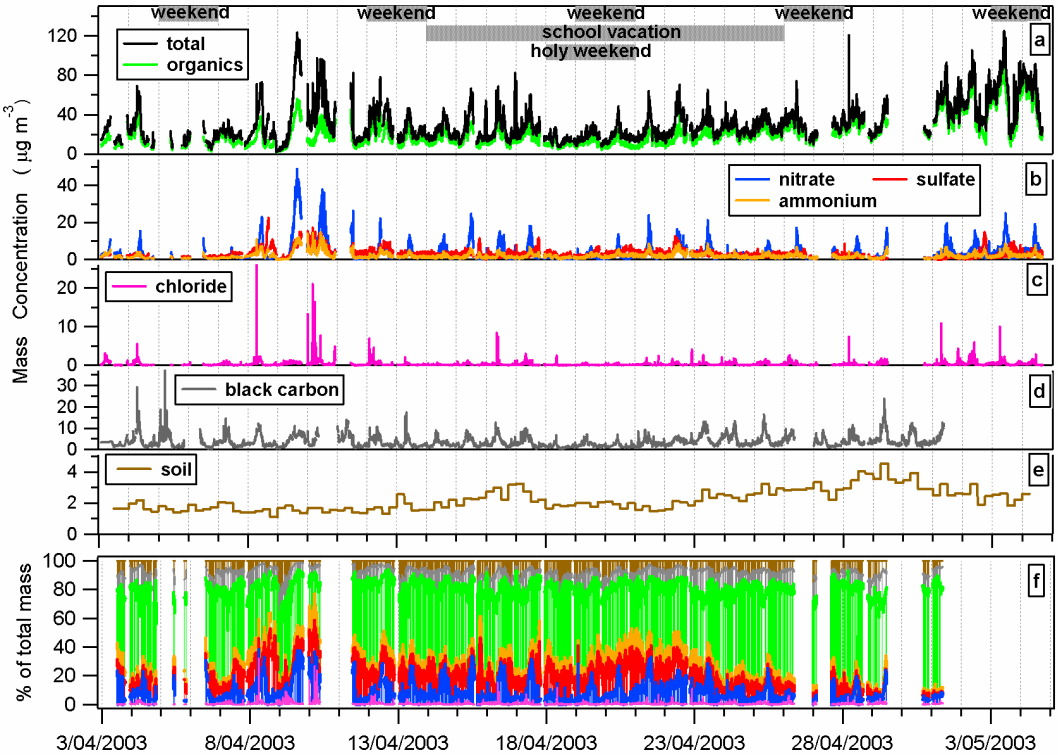

Fig. 3. Panels **(a)**–**(e)**. Time series of the mass concentration of the AMS NR-PM_1 species (Total = nitrate + sulfate + ammonium + chloride + organics), aethalometer BC, and estimated soil at the CENICA Supersite. Panel **(f)**: Time series of the percent mass composition of Total AMS + BC + soil.

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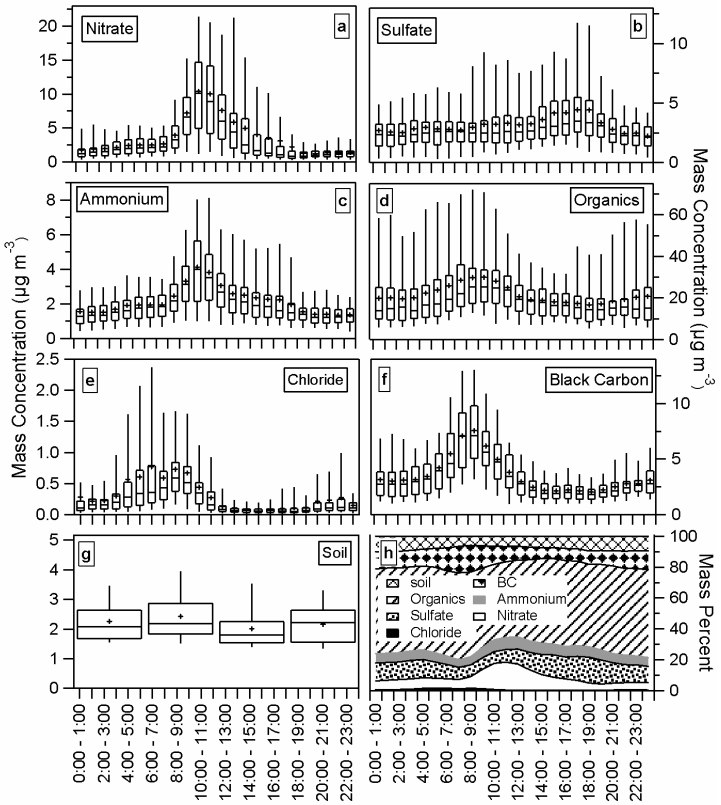

Fig. 4. Panels **(a)**–**(g)**: box-whisker plots of the diurnal cycles of the mass concentration of particulate species. Crosses represent the average mass concentration; horizontal lines represent the median; bottom and top of the boxes represent the 25 and 75% limits respectively; and the bottom and the top whiskers represent the 5 and 95% limits respectively. Averages are made over the complete time interval where data is available. Panel **(h)**: Diurnal cycle of the fractional mass concentration of various aerosol species to $PM_{2.5}$. Average was made over the time interval where AMS, BC, and soil data are available (see Fig. 3).

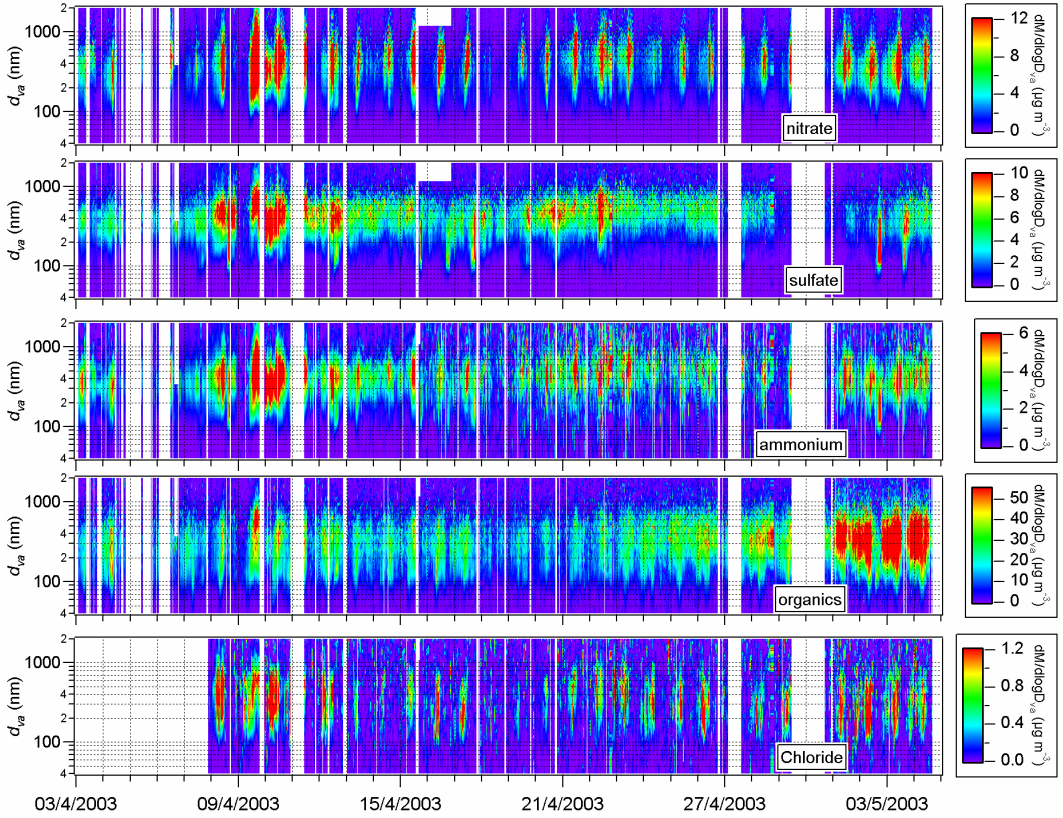

Fig. 5. Image plots of the mass concentration of the main NR-PM$_1$ species as a function of time and size for all of MCMA-2003.

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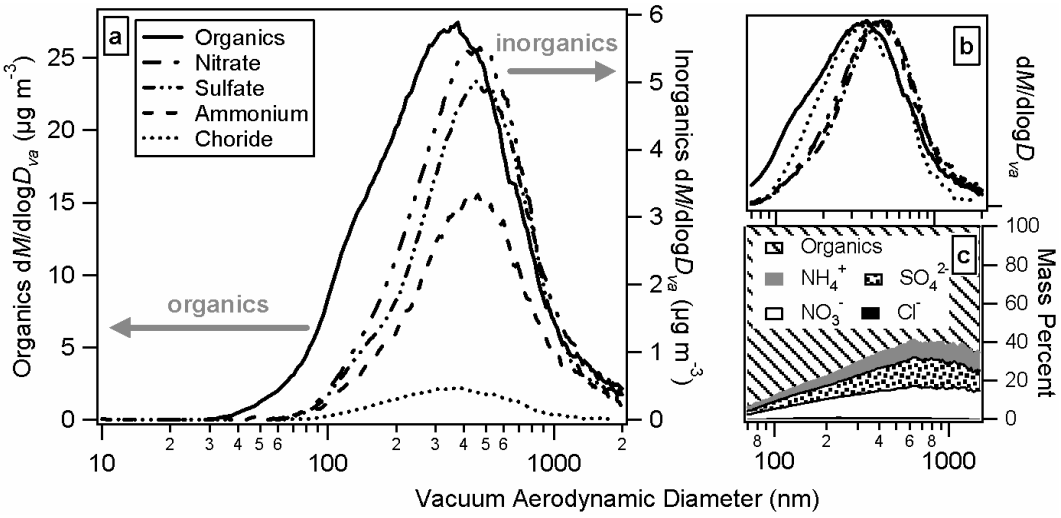

Fig. 6. Panel **(a)**: Average size distributions of NR-PM_1 species for the entire measuring period. Panel **(b)**: size distributions normalized to the same maximum so that their relative shapes can be appreciated. Panel **(c)**: percent concentration of the total NR-PM_1 mass as a function of particle size. Note the different axis scales in which the inorganic and organic distributions are plotted in panel (a).

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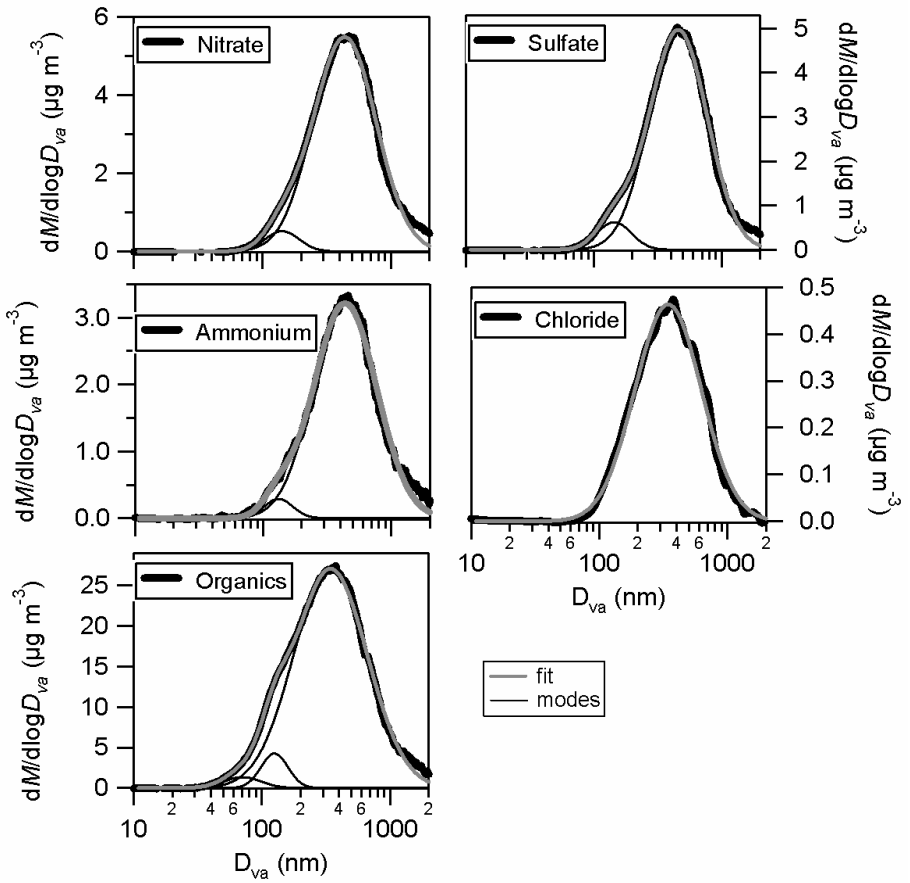

Fig. 7. Results of the multimode lognormal fits performed to the size distributions of the NR-PM_1 components. In each plot the lognormal modes resulting from the fit are shown. The sum of the modes is plotted in grey, while the data is plotted in thick black.

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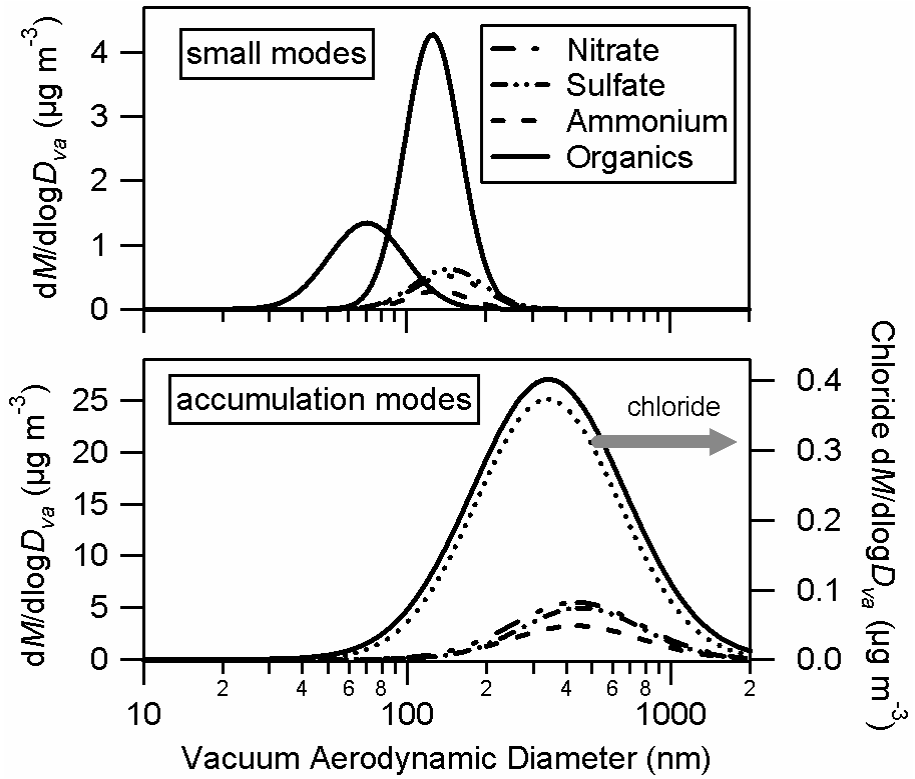

Fig. 8. "Small" and "accumulation" modes of the NR-PM_1 species as calculated from the multi-mode lognormal fits.

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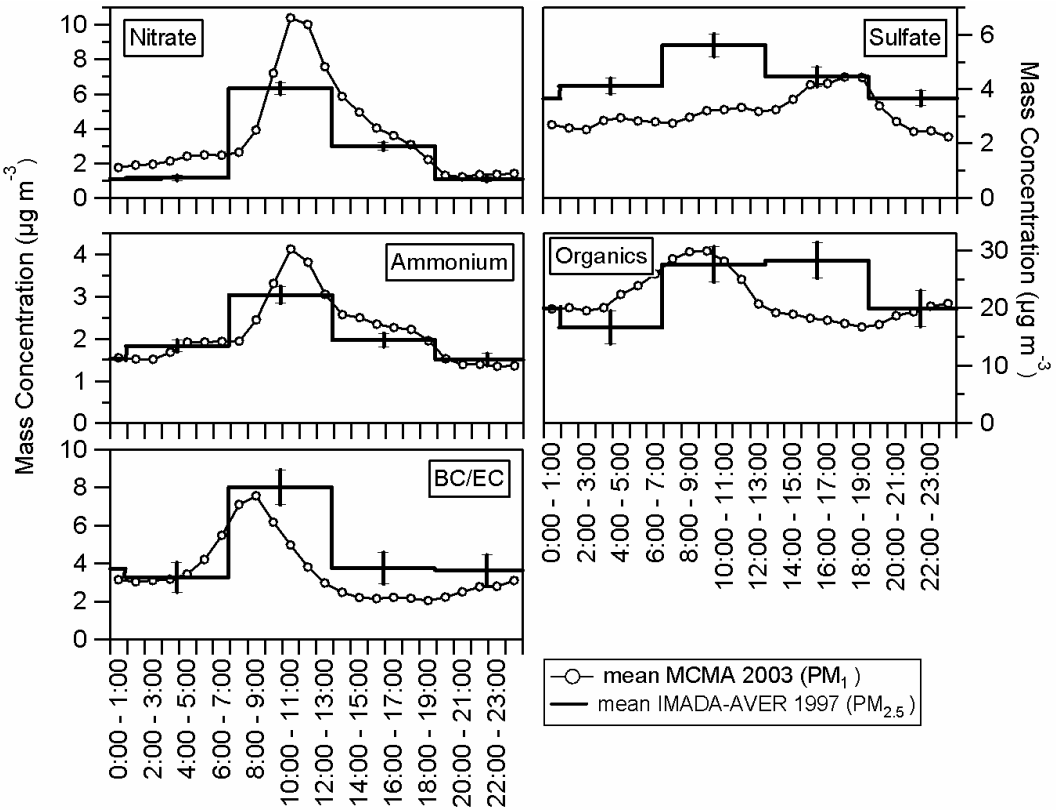

Fig. 9. Average diurnal profiles of $PM_{2.5}$ species measured during IMADA-AVER at CES in February–March 1997 (Chow et al., 2002) and during MCMA-2003. All data is plotted vs. local time. Soil diurnal cycles are not compared because Chow et al. (2002) only report 24-h average concentrations for particle metals.

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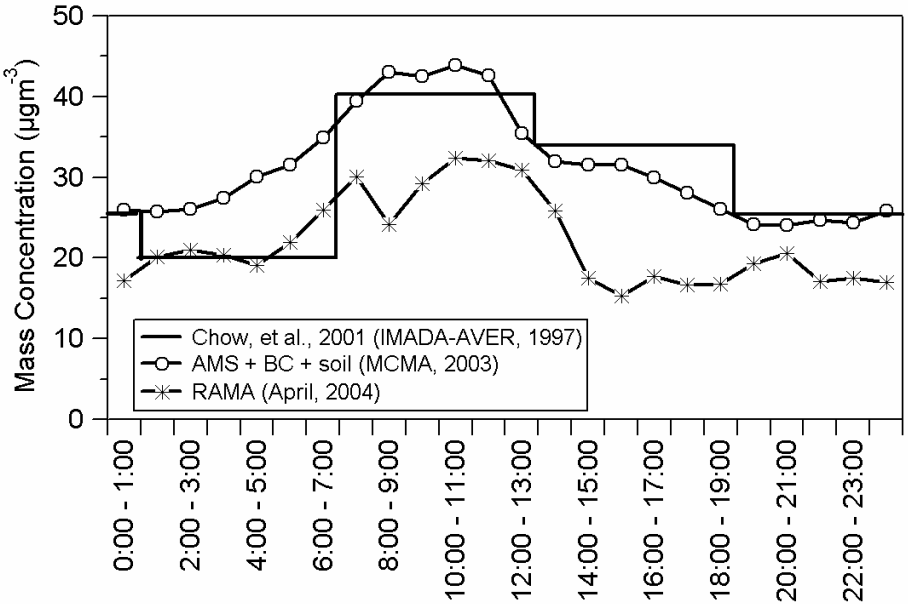

Fig. 10. Average diurnal cycle of $PM_{2.5}$ mass concentration reported by the City Air Quality Monitoring Network (RAMA) at CES in April 2004; by Chow et al. during IMADA-AVER at CES in February–March 1997 (Chow et al., 2002); and AMS + BC + soil at CENICA during MCMA-2003 in April 2003.

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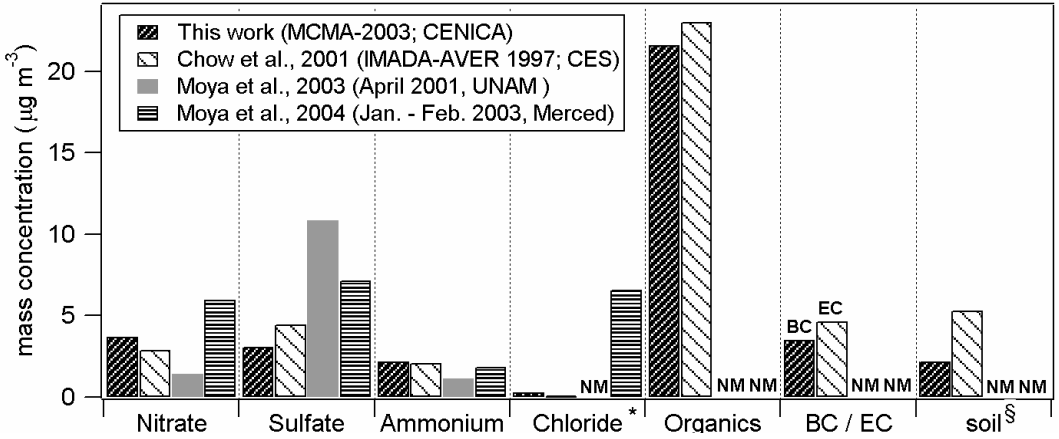

Fig. 11. Comparison of the average mass concentrations of some $PM_{2.5}$ species reported for Mexico City by the authors at CENICA during MCMA-2003 in April–May 2003; by Chow et al. during IMADA-AVER at CES in February–March 1997 (Chow et al., 2002); by Moya et al. (2003), at the main campus of UNAM in April 2001 (0.18–1.8 μm d_{va}); and by Moya et al. (2004) at Merced in January–February 2003 (0.18–1.8 μm d_{va}). NM = no measurement available.

* Chow et al. (2002), and Moya et al. (2004) report total chloride, while we are plotting non-refractory chloride. Refractory chloride during MCMA-2003 determined with PIXE was 0.05 μg m^{-3}.

§ Soil concentration during the IMADA-AVER campaign was calculated using the method described by Malm et al. (1994) and the metal concentrations reported by Chow et al. (2002).

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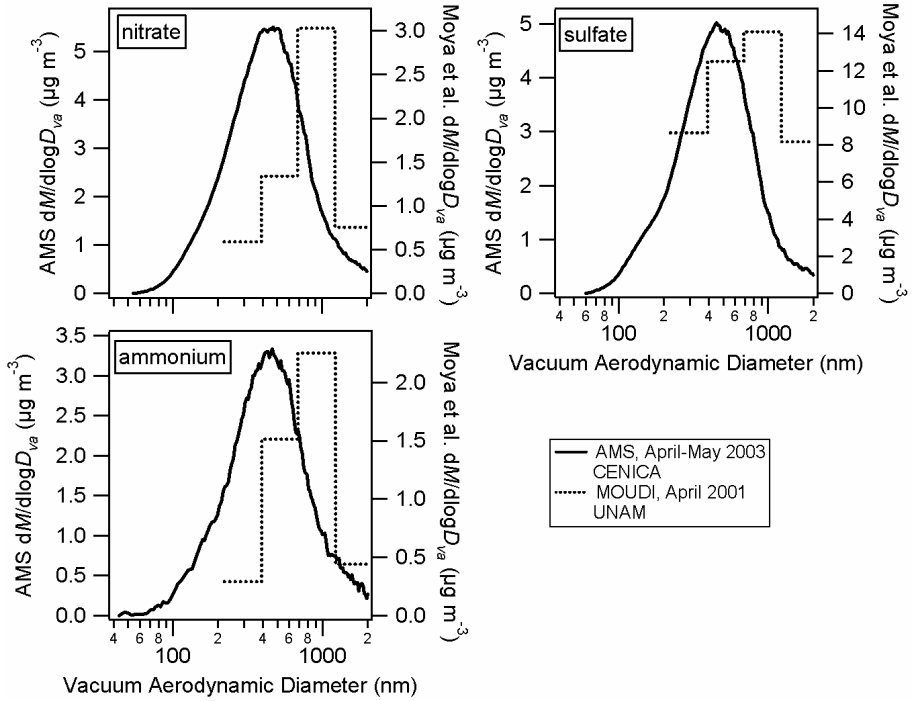

Fig. 12. Size distributions of the main inorganic components of the Mexico City aerosol measured with the AMS at CENICA during the MCMA-2003 in April–May 2003; and by Moya et al. (2003), measured with a MOUDI in the main campus of UNAM in April 2001. Note the different scales for both datasets.