Measurements of Mexico City nanoparticle size distributions: Observations of new particle formation and growth

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[1] Continuous measurements of the size distribution of atmospheric aerosol in the 3–48 nm diameter range were performed in the Mexico City metropolitan area. These measurements were made during the period 10–20 April 2003 at a ground-based, mountain pass site in the southeast corner of the Mexico City Federal District and during the period 2–11 May 2003 at the CENICA site located near the city center. The objectives of this work were to determine the frequency of new particle formation and to characterize the atmospheric chemical and meteorological conditions that lead to these events. Several new particle formation events were recorded during the study. Events observed in the mountain pass correlate with northerly winds and elevated levels of sulfur dioxide in the mid-morning while events observed in the city correlate with elevated concentrations of sulfur dioxide and low particulate matter mass concentrations in the afternoon hours. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. **Citation:** Dunn, M. J., J.-L. Jiménez, D. Baumgardner, T. Castro, P. H. McMurry, and J. N. Smith (2004), Measurements of Mexico City nanoparticle size distributions: Observations of new particle formation and growth, *Geophys. Res. Lett.*, *31*, L10102, doi:10.1029/2004GL019483.

1. Motivation

[2] Aerosol nucleation and subsequent particle growth in the nanometer diameter range has been observed in many parts of the world, including the remote troposphere [*Weber et al.*, 1999], the boreal forests of Finland [*Makela et al.*, 1997], the marine boundary layer [*O'Dowd et al.*, 1999], and Macquarie Island near Antarctica [*Weber et al.*, 1998]. Studies suggest that these processes play an important role in the nature and distribution of cloud condensation nuclei [*Adams and Seinfeld*, 2003]. Nucleation events have also been shown to be regular occurrences in many urban settings, including Atlanta [*Woo et al.*, 2001], Birmingham, UK [*Alam et al.*, 2003], St. Louis [*Shi et al.*, 2002], and Pittsburgh [*Stainer et al.*, 2002]. The high density of human populations in these cities, combined with a growing body of evidence suggesting atmospheric nanoparticles may be a significant health threat [*Oberdorster et al.*, 1995], makes continued investigation of urban nucleation of utmost importance.

[3] The urban region encompassing Mexico City, with a population estimated at 18.1 million in 2000, is the second-largest urban agglomeration in the world [*United Nations*, 2002]. This fact, together with an estimated 3.4 million automobiles and a unique geography combining high altitude (2240 m) with a surrounding ring of tall mountains has made the Valley of Mexico one of the most polluted regions in the world. In spite of this, there have been no reported measurements of the size distributions of atmospheric nanoparticles [*Raga et al.*, 2001], which cover the diameter range from 3 to 50 nm. The most comparable measurements to date were performed in 1997 at a mountain site in the southwest corner of the basin. In that study of particles as small as 10 nm, sulfate was found to be one of the most abundant chemical species in the particles, and increases in concentration of 10–100 nm diameter aerosol showed negative correlation with tracers of city air [*Baumgardner et al.*, 2000].

[4] The scarcity of information on the distribution and dynamics of new particle formation in Mexico City has motivated the current study. Here we report particle size

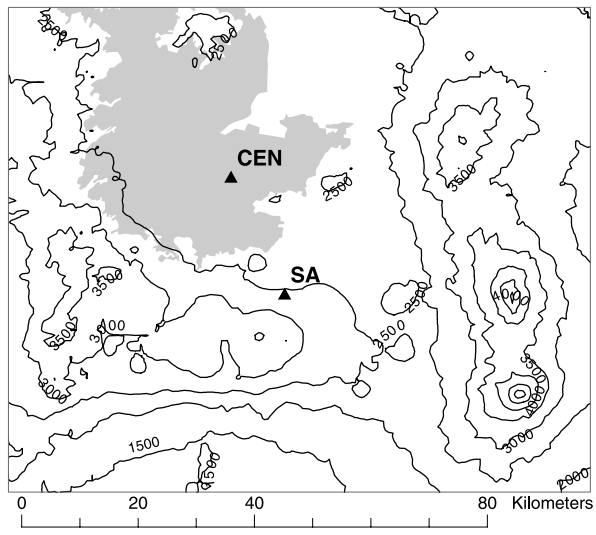

Figure 1. Topographical map of the Valley of Mexico showing Santa Ana (SA) and CENICA (CEN) sampling sites. The gray region shows the Mexico City limits.

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Table 1. Summary of Particle Formation Events and Background Conditions at Santa Ana

date	description	hours	num. conc. 3–10 nm (cm^{-3})	num. conc. 10–50 nm (cm^{-3})	solar irradiance (langley)	$[SO_2]$ (ppb)	$[NO_x]$ (ppb)	PM 1.0 ($\mu g \cdot m^{-3}$)	wind direction (deg)
12 April	before	5–9	1.41E + 03	2.37E + 03	0.08	1.6	14.5	5.3	164
	during	9–13	1.22E + 05	5.33E + 04	1.10	12.9	13.1	5.3	28
19 April	before	5–9	1.11E + 03	1.90E + 03	0.09	1.9	11.4	4.9	180
	during	9–13	1.18E + 05	8.02E + 04	1.14	13.9	13.7	6.1	346
20 April	no event	5–9	7.69E + 02	1.39E + 03	0.10	2.2	7.0	6.3	188
	no event	9–13	5.89E + 03	2.86E + 03	1.15	3.2	14.3	8.6	23

All entries are averages over indicated time span.

distributions in the 3–48 nm diameter size range measured continuously in a mountain pass southeast of Mexico City and in the center of the city during the spring, 2003. These measurements were performed concurrent with the Mexico City Metropolitan Area 2003 campaign (MCMA-2003).

2. Method

[5] Figure 1 shows a map of the Valley of Mexico highlighting locations of the sampling sites of this study. Aerosol size distributions were continuously measured during the period 10–20 April 2003, at a ground-based site in the northeastern corner of Santa Ana Tlacotenco (19.1772°N, 98.99°W, hereafter referred to as Santa Ana). This small, rural town lies near the southeastern border of the Mexico City Federal District and on the western rim of a mountain pass that channels the southern outflow of air from the city. Then, during the period 2–11 May 2003, measurements were made inside Mexico City, at the Centro Nacional de Investigación y Capacitación Ambiental (CENICA) roof-top laboratory on the campus of Universidad Autónoma Metropolitana (UAM) in the Iztapalapa delegation (19.358°N, 99.073°W; hereafter referred to as CENICA).

[6] Particle size distributions were measured using a scanning mobility particle sizer (SMPS) system assembled at the University of Minnesota and consisting of a nanoparticle differential mobility analyzer (NDMA, model 3085 TSI, Inc.) [*Chen et al.*, 1998] and an ultrafine condensation particle counter (UCPC, model 3025A TSI, Inc.) [*Stolzenburg and McMurry*, 1991]. Size distributions were acquired in 2.5-minute intervals using control and analysis software written in Labview (National Instruments, Inc., version 6.0i), and were corrected by the calculated aerosol losses through the inlet under laminar flow conditions.

[7] PM_{10} and $PM_{1.0}$ were obtained at Santa Ana with an optical particle counter (Lasair II, Particle Measuring Systems). Collaborators at CENICA and the Massachusetts Institute of Technology provided 15-minute averaged meteorological, particulate matter and trace gas data recorded at both research sites for joint analysis with nanoparticle size distributions. Meteorological data include temperature, wind direction and speed, relative humidity and solar radiation. Gas phase and particulate measurements include CO, O_3, SO_2, NO_x (NO_2 & NO), PM_{10}, and $PM_{2.5}$ (the latter at CENICA only).

3. Results and Discussion

[8] An archive of the continuous record of nanoparticle size distributions, meteorological parameters, and trace gas and aerosol concentrations for all sampling days in this study is available (in color) in the electronic data supplement archive[1].

3.1. Santa Ana

[9] Table 1 characterizes new particle formation events from Santa Ana with concentrations of particles above and below 10 nm in diameter, as well as and meteorological and trace gas data before and during these events and typical values for a non-event day (20 April). The 10 nm diameter cutoff was chosen to differentiate nucleated particles from primary particles of combustion sources, which are generally larger than 10 nm in diameter [*Kittelson*, 1998]. During new particle formation at Santa Ana, concentra-

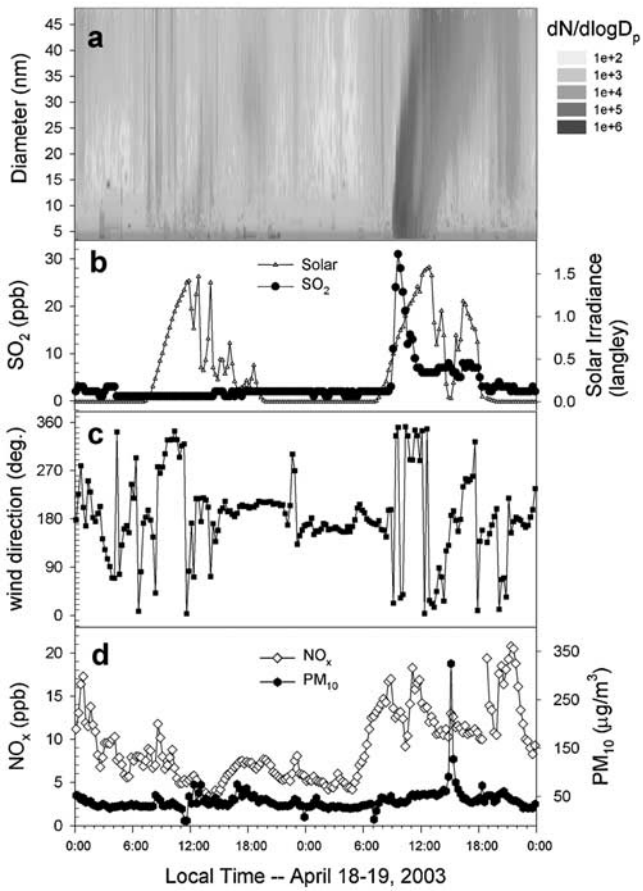

Figure 2. Measurements performed during the period 18–19 April 2003 at Santa Ana: (a) nanoparticle size distribution, (b) solar irradiance and SO_2 mixing ratio, (c) wind direction in degrees (N = 0, 360; E = 90), and (d) NO_x mixing ratio and PM_{10} mass concentration.

[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2004GL019483.

Table 2. Summary of Particle Formation Events and Background Conditions at CENICA

date	description	hours	num. conc. 3–10 nm (cm^{-3})	num. conc. 10–50 nm (cm^{-3})	UV solar irradiance ($mW \cdot m^{-2}$)	$[SO_2]$ (ppb)	$[NO_x]$ (ppb)	PM 2.5 ($\mu g \cdot m^{-3}$)	wind direction (deg)
3 May	before	10–13	1.32E + 03	1.17E + 04	–	14.8	49.7	85.0	352
	during	13–16	3.12E + 04	4.59E + 04	–	15.9	3.6	15.9	17
6 May	before	11–11:30	1.56E + 03	2.18E + 04	–	9.9	40.0	61.1	327
	during	14:45–15:15	3.84E + 04	8.01E + 04	–	24.5	5.0	7.9	25
11 May	before	11–13	7.13E + 04	4.91E + 04	461	15.8	25.6	53.6	358
	during	13–15	2.98E + 05	1.09E + 05	530	16.7	11.5	4.5	21
9 May	no event	11–13	3.30E + 03	1.32E + 04	484	3.4	6.8	22.9	6
	no event	13–15	4.17E + 03	1.65E + 04	483	4.3	9.1	3.0	6

All entries are averages over indicated time span.

tions of particles with diameter greater than 10 nm increased an order of magnitude, and concentrations of sub-10 nm diameter particles increased at least two orders of magnitude over concentrations just before the event or on a day without nucleation. Large increases in SO_2 concentrations and northerly winds also coincide with these events. These observed concentrations are comparable to the higher intensity events reported in Atlanta [*Woo et al.*, 2001].

[10] Figure 2a shows a 48-hour plot of the particle size distribution ($dN/d\log D_p$) vs. local time beginning on 18 April. The size distributions and gas phase concentrations for 18 April are typical of non-event days at Santa Ana while the 19 April distributions show new particle formation occurred near 09:00 that day. The sustained growth profile over several hours of steady wind direction indicates that new particle formation was a regional event, occurring simultaneously over a large air mass. The evolution of the distribution towards larger sizes is interpreted as particle growth by condensation and coagulation; from 09:00 to 15:00, the diameter of mean concentration progresses toward larger sizes at a linear rate of 4.7 nm hr^{-1}. Gas and meteorological measurements (Figures 2b–2d) for this period show that the detection of 3 nm particles at the start of this event coincided with a sudden change in wind direction from South to North and a peak of almost 30 ppb in ambient SO_2 levels. Nearly identical conditions were observed in Santa Ana on 12 April, with a corresponding growth rate of 4.4 nm hr^{-1}. In both events, no consistent correlations were seen between NO_x, CO, or PM_{10} concentrations and the onset of new particle formation. Because these events occurred during daylight hours while high levels of SO_2 were observed, these data strongly suggest that sulfuric acid, a product of the reaction of SO_2 and the OH radical in the presence of water vapor, assisted homogeneous nucleation [*Eisele and McMurry*, 1997]. The observed growth rates are within the range (0.5–9 nm hr^{-1}) reported for other urban sites and slightly higher than rates reported for non-coastal rural sites (2–4 nm hr^{-1}) [*Kulmala et al.*, 2004].

3.2. CENICA

[11] On average, the concentration of 10–48 nm diameter particles at CENICA was more than three times that observed at Santa Ana. Each morning large concentrations (ca. 10^5 cm^{-3}) of 15–25 nm diameter particles correlated with high levels of CO and NO_x. The likely source of these particles is road traffic emissions [*Kittelson*, 1998], and so, as mentioned previously, a diameter of 10 nm was chosen to differentiate these from those that nucleated in the atmosphere. Several new particle formation events were observed at CENICA in the presence of sulfuric acid. Table 2 summarizes these events, and includes data from a day without new particle formation (9 May) for reference. Compared to the Santa Ana events, the concentrations of 3–10 nm diameter particles during the 3 and 6 May events are much lower, yet the 11 May event corresponds to the largest concentration of nanoparticles observed at either location.

[12] Figure 3a shows the plot of the particle size distribution vs. local time for the 48-hour period beginning 10 May. High concentrations of larger particles correlating with spikes in NO_x can be seen the night

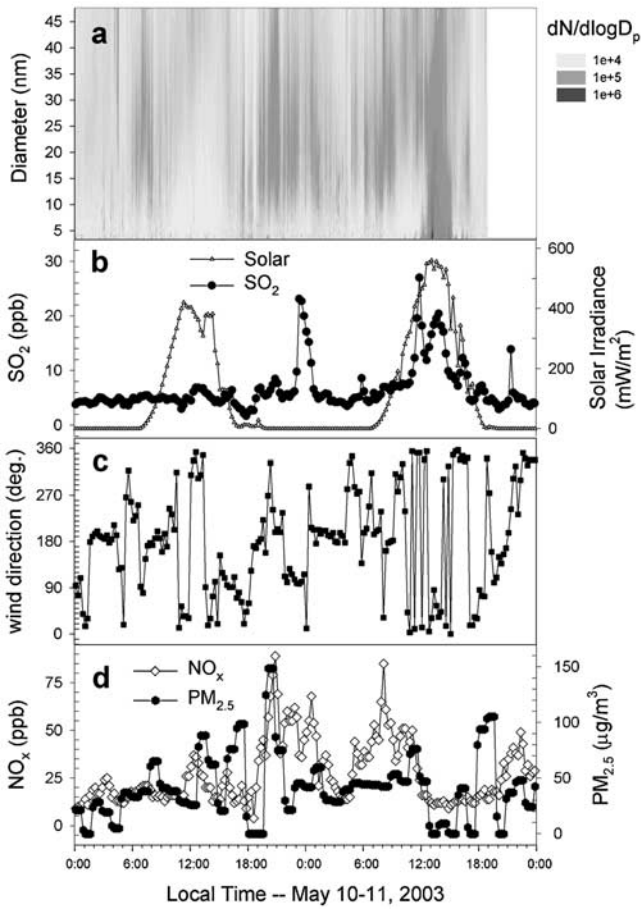

Figure 3. Measurements performed during the period 10–11 May 2003 at CENICA: (a) nanoparticle size distribution, (b) solar irradiance and SO_2 mixing ratio, (c) wind direction in degrees (N = 0, 360; E = 90), and (d) NO_x mixing ratio and $PM_{2.5}$ mass concentration.

of 10 May and the morning of 11 May, but at 13:00 that day, the time of maximum solar radiation, a burst of ca. 4×10^5 cm^{-3} 3–10 nm diameter particles was observed. Akin to new particle formation events at Santa Ana, ambient SO_2 rises to nearly 30 ppb during the event. According to the city's air pollution monitoring network (RAMA), elevated levels of SO_2 were observed citywide at this time and during the other two events on 3 and 6 May. However, the number of 3 nm diameter particles does not immediately increase at the onset of elevated SO_2 levels as they did at Santa Ana. Particulate matter, however, was at its minimum at the start of this event (Figure 3d) as with all new particle formation events observed at CENICA. We believe that this sudden decrease in condensational surface area allowed new particle formation to occur, although from the data available we are unable to explain the cause of the sudden decreases in $PM_{2.5}$. A notable difference seen in the CENICA events compared to those at Santa Ana is that the CENICA events span a large range of sizes and do not appear to undergo diametrical growth (see Figure 3a). In summary, three criteria consistently characterize new particle formation events within the city: the events occur during daylight hours, while SO_2 is elevated, and when particulate matter mass concentrations are at significantly lower values than their averages.

4. Summary

[13] The first reported measurements of nanoparticle size distributions at a rural site near Mexico City and within the city provide evidence that new particle formation regularly occurs during the springtime in this region. These observed events occurred only during daylight hours and when the ambient concentration of SO_2 was significantly greater than background levels, suggesting an important role for sulfuric acid in new particle formation. In the southern mountain pass, events also occurred when the wind direction began blowing from the North, and in the city, new particle formation also correlated with much lower concentrations of particulate matter, which may have lowered total aerosol surface area and therefore promoted nucleation and growth.

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