

Internally mixed soot, sulfates, and organic matter in aerosol particles from Mexico City

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Received: 7 April 2008 – Published in Atmos. Chem. Phys. Discuss.: 22 May 2008

Revised: 1 September 2008 – Accepted: 26 September 2008 – Published: 13 November 2008

Abstract. Soot particles, which are aggregated carbonaceous spherules with graphitic structures, are major aerosol constituents that result from burning of fossil fuel, biofuel, and biomass. Their properties commonly change through reaction with other particles or gases, resulting in complex internal mixtures. Using a transmission electron microscope (TEM) for both imaging and chemical analysis, we measured ~8000 particles (25 samples) with aerodynamic diameters from 0.05 to 0.3 μm that were collected in March 2006 from aircraft over Mexico City (MC) and adjacent areas. Most particles are coated, consist of aggregates, or both. For example, almost all analyzed particles contain S and 70% also contain K, suggesting coagulation and condensation of sulfates and particles derived from biomass and biofuel burning. In the MC plumes, over half of all particles contained soot coated by organic matter and sulfates. The median value of the soot volume fraction in such coated particles is about 15%. In contrast to the assumptions used in many climate models, the soot particles did not become compact even when coated. Moreover, about 80% by volume of the particles consisting of organic matter with sulfate also contained soot, indicating the important role of soot in the formation of secondary aerosol particles. Coatings on soot particles can amplify their light absorption, and coagulation with sulfates changes their hygroscopic properties, resulting in shorter lifetimes. Through changes in their optical and hygroscopic properties, internally mixed soot particles have a greater effect on the regional climate of MC than uncoated soot particles.

1 Introduction

Aerosol particles have important influences on Earth's radiative and hydrological balance (Ramanathan et al., 2001), human health (Dockery et al., 1993), and visibility. Knowledge of their contribution to radiative forcing is inadequate (IPCC, 2007). Our study focuses on soot (black carbon) particles that are coated with or attached to organic matter (OM) and sulfate (hereafter we refer to such mixtures as internally mixed particles) collected during the MILAGRO (Megacity Initiative: Local and Global Research Observations) campaign in and near Mexico City (MC) and their implications for global climate. Many developing megacities, such as MC, are located in tropical areas. Their importance will increase through growing economic activity and populations. Many details of the aerosol particles emitted from tropical megacities are not well known, although they have important effects on the troposphere and people living in it.

Soot particles, which are aggregated carbonaceous spherules a few tens of nanometers in diameter and with graphitic structures, are emitted through incomplete combustion of fossil fuel, biofuel, and biomass carbon together with OM. The latter is amorphous carbonaceous material that, in our samples, mainly formed through condensation and coagulation. Soot particles produce a net warming effect in the atmosphere through absorption of sunlight (Chung and Seinfeld, 2002, 2005; Jacobson, 2001; Haywood et al., 1997; Myhre et al., 1998; Penner et al., 1998; Bond and Bergstrom, 2006). Internally mixed soot particles are estimated to be the second most significant component of global warming after CO_2 in terms of direct radiative forcing (Jacobson, 2001; Ramanathan and Carmichael, 2008).

Here we focus on particles of soot, OM, and sulfate, with emphasis on internally mixed particles. Climate models assume that aerosol particles are single phases (external



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mixtures), mixtures of different materials (internal mixtures), or both (Jacobson, 2001; Chung and Seinfeld, 2002, 2005; Bond et al., 2006; Bond and Bergstrom, 2006; Takemura et al., 2005; Stier et al., 2007). The external mixing assumption is unrealistic for many atmospheric situations as many, and perhaps most, aerosol particles are internally mixed (e.g., Murphy et al., 2006; Pósfai et al., 1999). Internal mixtures are a better assumption, assuming that appropriate morphological and mixing properties are applied in the models.

Current climate models either assume that soot is concentrically encapsulated by another material (core-shell model) or that a single effective refractive index for the entire mixed particle can be used (Bond et al., 2006). In the latter case, the effective refractive indices are calculated for the mixed materials using various mixing rules (Bond and Bergstrom, 2006; Bond et al., 2006; Stier et al., 2007; Bohren and Huffman, 1983). These calculations need volume ratios of the components of mixed materials in individual particles to determine their optical properties, although these values are commonly not well known but can be determined by using transmission electron microscopy. Also, mixtures of different materials affect hygroscopic properties, i.e., hydrophilic coatings make soot particles hygroscopic. Therefore, a detailed analysis of internally mixed particles is appropriate.

A transmission electron microscope (TEM) is a powerful instrument for determining the morphologies, sizes, and compositions of individual aerosol particles (Abel et al., 2003; Buseck and Pósfai, 1999; Buseck and Schwartz, 2003; Niemi et al., 2006; Johnson et al., 2005; Utsunomiya et al., 2004). Soot is a common constituent of such mixtures, and the TEM can be used to recognize it based on its distinctive morphological features. Moreover, several TEM studies have shown that OM with sulfate coatings on soot particles are widespread (e.g., Chen et al., 2006; Kojima et al., 2005; Pósfai et al., 1999; Li et al., 2003; Okada et al., 2005; Johnson et al., 2005). The single-particle soot photometer (Schwarz et al., 2008) is also good for detecting soot, but because it destroys the particles, one cannot see details of coatings, intergrowths, and aggregations.

Our goal is to characterize the chemical and physical properties of internally mixed soot particles in order to understand their optical properties and coating processes at the individual-particle scale. Using the samples collected from the MC plumes, we also aim to characterize the particles that were emitted from heavily polluted areas, where contributions of aerosol emissions to the regional and global environments are becoming increasingly important.

2 Materials and methods

2.1 Mexico City atmospheric research projects

The MILAGRO campaign was conducted in Mexico (Fig. 1) during March 2006 (Molina et al., 2008). The goal was to

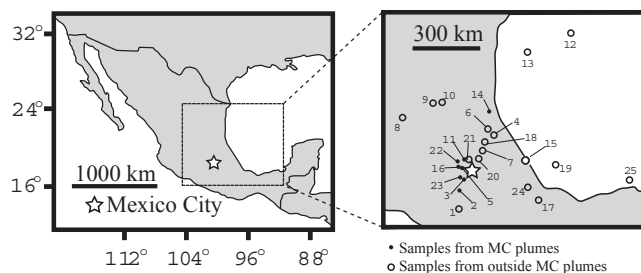


Fig. 1. Map showing sampling area. Sample numbers are shown in the right panel.

understand the evolution of trace gases and particles from anthropogenic emissions in and around MC as an example of a tropical megacity. Detailed meteorological conditions during the campaign are discussed in de Foy et al. (2008) and Fast et al. (2007). The prior MCMA-2003 (Mexico City Metropolitan Area field campaign 2003) also revealed important insights into the meteorology, primary pollutant emissions, ambient secondary pollutant precursor concentrations, photochemical oxidant production, and secondary aerosol particle formation in MC (Molina et al., 2007).

2.2 Sampling

Samples were collected using 3-stage impactor samplers (MPS-3, California Measurements, Inc.). Units were placed in both the NCAR/NSF C130 and the U.S. Forest Service Twin Otter (Yokelson et al., 2007) aircraft. Both contained isokinetic particle inlets with cutoff diameters of a few μm (Jonsson et al., 1995). The 50% cut-off aerodynamic diameters of the samplers are 2.0, 0.3, and 0.05 μm . In this study, we used the smallest impactor stage (0.05 to 0.3 μm). Particles smaller than 50 nm, which include individual or small clusters of soot spherules and freshly emitted sulfates and OM, can have large number concentrations, especially during particle-formation events (Smith et al., 2008). However, such small particles generally coagulate rapidly after emission (Seinfeld and Pandis, 2006; Jacobson et al., 2005), and the mass and number fractions of soot particles smaller than 50 nm are small (Salcedo et al., 2006; Saathoff et al., 2003). Thus, our underestimate of the number of small particles has minor effects on conclusions based on total volume of particles in the air. Sampling times were mostly between 4 and 6 min, although they ranged from 3 to 17 min (Table 1) depending on the particle concentrations.

Scanning electron microscope stubs, each having one TEM grid attached, were placed in each stage of the samplers. Lacy carbon grids were used for TEM sample collections. Such grids, which have “spider net” carbon substrates, are designed to be used for chemical analyses and high-resolution imaging (e.g., Figs. 2 and 3). The substrate causes minimal overlap with samples and yields clear images

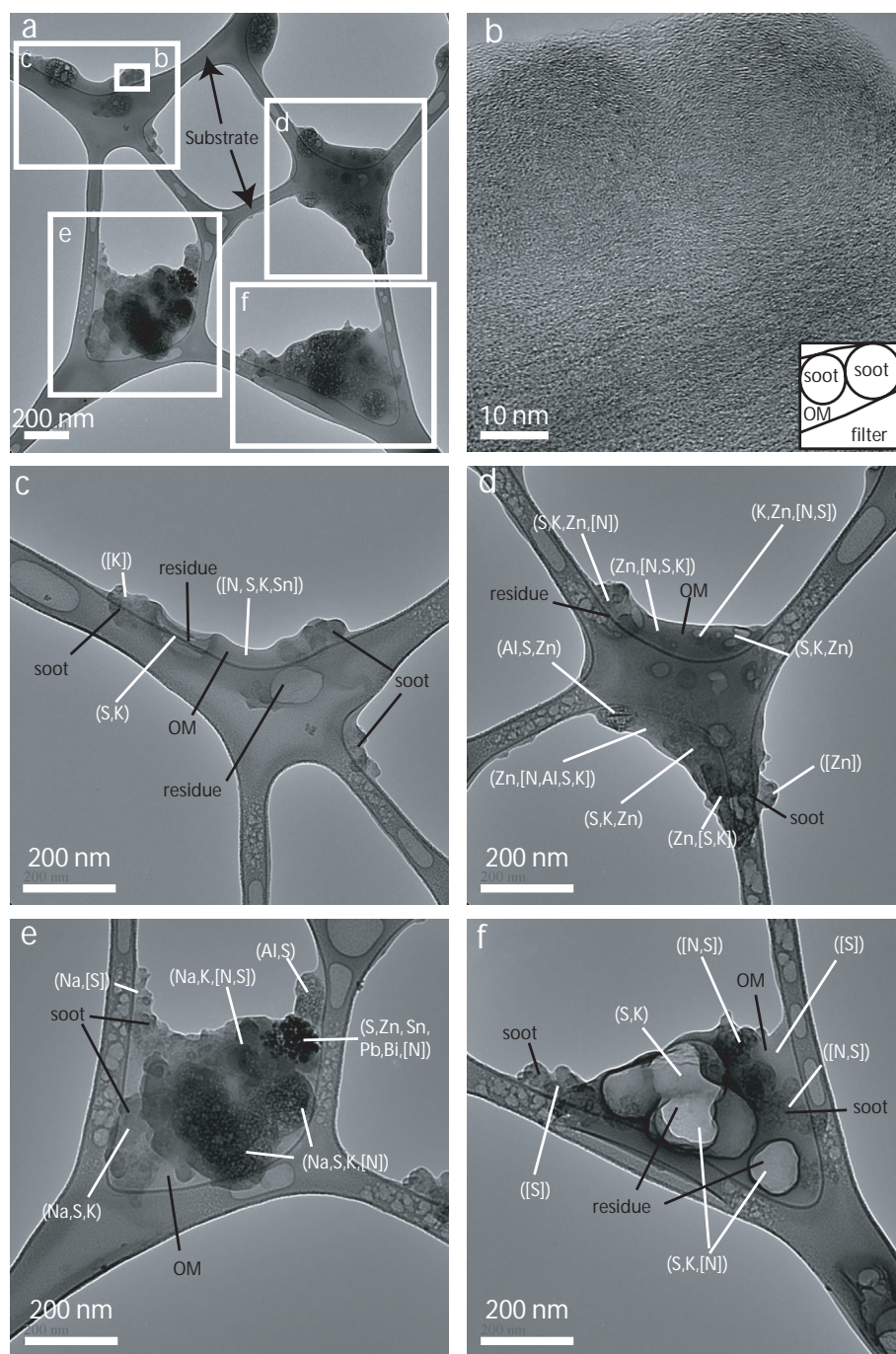


Fig. 2. Morphologies and compositions of internally mixed particles. Particles were deposited on lacy carbon filters. This sample was collected from MC (Sample #3 in Table 1). EDS analyses typically indicate minor to trace amounts of the elements in the other phases. **(a)** Low-magnification image of particles c to f. **(b)** High-resolution image of soot particles, OM, and filter. The lower-right illustration shows a sketch of the image. Soot particles have curved graphitic layers. OM and the filter, both of which consist of amorphous carbon, have disordered structures. **(c–f)** Typical images of internally mixed particles; their compositions were obtained using EDS and are given in parentheses, with the results shown in white. Elements in square brackets are in concentrations <1 wt%. C, O, and Si occur in all particles and are not shown in the figure. Soot, OM, and residue, which are indicated using black lines, were identified from their morphological properties.

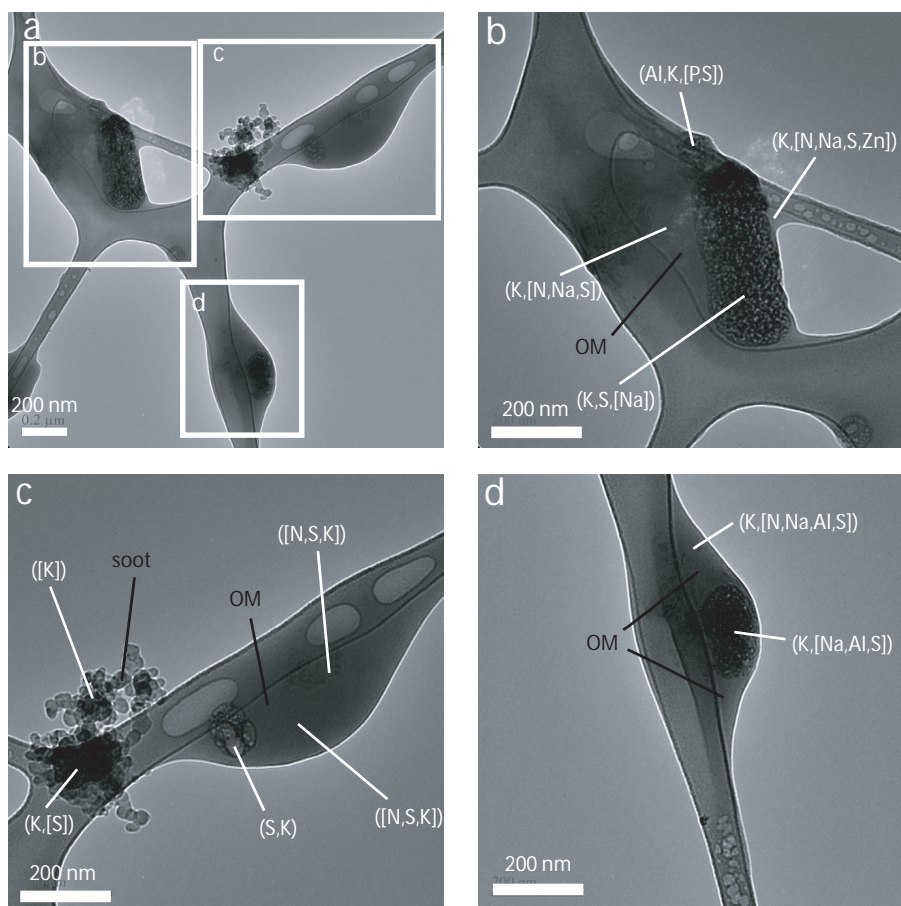


Fig. 3. Morphologies and compositions of externally mixed OM-S and soot particles. Experimental conditions are the same as those in Fig. 2.

where the particles extend over holes in the substrates (Pósfai et al., 2003).

We acquired 30 samples from the C130 during 10 research flights and 182 samples from the Twin Otter during 12 research flights. Some samples are primarily from the MC plumes and others from biomass burning. In this study we focus on the samples from the MC urban plumes and adjacent areas near MC (Fig. 1).

Samples were collected from a wide range of locations and weather conditions. We classified the samples as from either within the MC plume (MC sample, 8 samples) or outside of it (17 samples) using the HYSPLIT back-trajectory model of Draxler and Rolph (2003). Except for #14, which was collected in a MC plume that was transported by a strong southwesterly wind toward the coastal Mexico-Texas border (Fast et al., 2007; Molina et al., 2008), all MC samples are from within 80 km of the city center (Table 1).

The ventilation of the MC basin is commonly rapid (de Foy et al., 2006, 2008; Molina et al., 2008). Residence time of the air in the basin is mostly less than 12 h, with little carryover from day to day. Recirculation of air back into

the basin is unusual. Thus, as most MC samples were collected around 2 p.m. local time (Table 1), most particles were within eight hours or less from emission. On the other hand, it is likely that samples from outside MC plumes are older than the MC samples, as most do not have definite sources within 1- to 2-day back-trajectories.

2.3 TEM analysis

We used a Tecnai F20 TEM for imaging and electron energy-loss spectroscopy (EELS) analyses and a CM 200 TEM (both from the FEI Corp.) for energy-dispersive X-ray spectrometer (EDS) analyses. Both TEMs were operated at an accelerating voltage of 200 kV.

The EDS analyses were used to measure compositions of particles ranging from nanometers to micrometers in diameter. By using expanded electron beams that included entire particles ($\sim 1 \mu\text{m}$), averaged compositions of individual particles were determined. We measured all particles in a certain area of a TEM image (~ 2000 to $5000 \times$ magnification) for the analyses. Each area had between 20 and 60 particles. We chose one or two areas from each of 12 samples

Table 1. Samples analyzed in this study.

Sample#	Aircraft ^a	Latitude	Longitude	Altitude (km)	Distance from MC ^b (km)	Start time (Local Time)	Sampling time (second)	Sampling date (2006/)	Location ^c	Analyses ^d
1	C130	18.00	260.82	3.2	166	12:27:00	266	03/08	outside	S
2	C130	18.81	260.79	3.0	79	14:33:52	257	03/08	MC	S
3	C130	19.23	260.97	4.1	30	15:17:26	277	03/08	MC	S&E
4	C130	21.00	262.27	2.4	216	10:35:25	267	03/10	outside	S
5	C130	19.71	260.86	3.7	28	14:44:45	332	03/10	MC	S&E
6	C130	21.30	261.87	3.0	220	13:34:12	995	03/12	outside	S
7	C130	20.41	261.84	3.5	136	17:30:01	242	03/12	outside	S
8	C130	21.50	258.34	2.8	367	11:29:16	284	03/16	outside	S&E
9	C130	22.20	259.75	4.1	327	10:50:02	346	03/18	outside	S
10	C130	22.20	259.90	3.5	321	12:32:43	250	03/18	outside	S
11	C130	20.00	260.97	3.8	55	14:54:37	255	03/18	MC	S&E
12	C130	24.97	265.34	4.8	768	14:44:34	248	03/19	outside	S&E
13	C130	24.25	263.57	3.2	594	17:13:37	246	03/19	outside	S&E
14	C130	21.90	262.01	4.0	286	18:29:34	247	03/19	MC	S&E
15	C130	20.08	263.53	4.2	286	11:38:48	251	03/22	outside	S
16	C130	19.73	260.73	4.1	40	14:48:55	250	03/22	MC	S
17	C130	18.53	264.01	4.8	348	16:30:04	356	03/23	outside	S
18	C130	20.64	261.84	4.1	155	5:33:08	309	03/28	outside	S
19	C130	19.85	264.67	4.9	405	6:30:07	310	03/28	outside	S
20	C130	20.01	261.60	3.7	86	11:32:23	348	03/29	outside	S&E
21	C130	20.00	261.11	3.5	57	12:55:29	256	03/29	outside	S&E
22	C130	19.50	260.71	3.7	32	13:38:52	249	03/29	MC	S
23	TO	19.32	260.82	4.1	28	15:43:33	180	03/17	MC	E
24	TO	19.06	263.55	1.5	284	16:58:00	300	03/28	outside	E
25	TO	19.17	267.82	3.7	751	16:31:00	420	03/29	outside	E

^a TO = Twin Otter. ^b 19.5° N and 99° W are used for the center of MC.

^c Outside indicates samples collected from outside of the MC plume. MC indicates samples collected from the MC plume.

^d S indicates samples used for size measurements (Fig. 5) and number fraction analysis (Fig. 6), and E indicates samples used for EDS analysis. Samples marked S&E were used for both types of analyses.

and analyzed 379 particles in total (Table 1). Thirty-second collection times were used.

2.4 Soot particles, organic matter (OM), and sulfates

Soot particles from MC typically consist of aggregated carbonaceous spherules ranging in diameter from 20 to 100 nm, with median value about 44 nm. They contain poorly ordered, curved graphitic layers separated by ~0.36 nm (Fig. 2b) and display a sharp π^* peak in EELS analyses. Soot particles can be recognized by their graphitic structure in TEM images even where they are internally mixed with OM, which is typically amorphous. The structural difference causes contrast in TEM images. However, if the grains are too thick (~1 μ m), it can be difficult to identify the soot particles. Therefore, although such thick grains are not common in our samples, our values for the number and volume of internally mixed soot particles could be underestimates. Soot particles in MC are mainly from vehicles, but some come from biomass burning (Moffet et al., 2008; Jiang et al., 2005), residential combustion of wood (biofuel burning), and aircraft (Bond et al., 2004; Mexico National Emissions Inventory 1999, 2006).

OM commonly coats the surfaces of soot, sulfates, and mineral dust in our samples (Figs. 2, 3, and 4). In MC, about half the organic carbon comes from motor vehicles, and from 5 to 26% of organic carbon is from biomass burning (Stone et al., 2008). Except for tar balls, which are spherical (Pósfai et al., 2004; Hand et al., 2005), OM lacks a distinctive morphology. OM particles are less sensitive to the electron beam than sulfates, although they shrink slightly after strong radiation.

The sulfates readily decompose when exposed to an electron beam. Many are coated with OM and, when decomposing, they leave a carbonaceous residue (Fig. 2c, d, f) (Pósfai et al., 2003). We used Ca-coated TEM grids to detect H₂SO₄ and (NH₄)₂SO₄ using the same method as Kojima et al. (2006), Yamato and Ono (1989), and Yamato and Tanaka (1994). Most droplets did not react with the Ca coatings, which we interpret as indicating our sulfates had been neutralized by ammonium. Such neutralization is consistent with the results of DeCarlo et al. (2007) and Moya et al. (2003). The S that forms the sulfate comes from regional sources such as petrochemical and power plants, volcanic emissions (Grutter et al., 2008; Johnson et al., 2006; de Foy et al.,

2007; DeCarlo et al., 2008), and gasoline and diesel fuel, both of which contain >300 ppm of S in Mexico (Molina and Molina, 2002).

2.5 Particle classification

For purposes of this study, we classified particles into categories based on their morphological features described above: 1) internally mixed soot particles (soot with coatings of OM, sulfates, or both; hereafter, we will refer to mixtures of OM and sulfate as OM-S); 2) soot particles without coatings (externally mixed soot); 3) OM-S without soot; 4) tar balls; and 5) others. Category 1 includes soot particles that were attached to or partly coated by OM-S (soot size > OM-S size), which constitute ~20% of this category, and particles that have both soot and mineral or metal particles with OM-S coatings. If no coatings were recognized in the TEM images, the soot particles were included in category 2. Tar balls (category 4) are amorphous, spherical, carbonaceous particles. They are easy to recognize because they are not normally mixed with other materials and are relatively transparent in TEM images (Pósfai et al., 2004). All other particles were classified as category 5 and are mostly mineral dust and metal particles, all of which are crystalline and resist decomposition in the electron beam.

2.6 Particle selection

For particle measurements, we selected a single grid square ($125 \times 125 \mu\text{m}$) from a TEM grid of each sample, using the same method as Kojima et al. (2004). Between 100 and 300 TEM images were recorded for each sample. All particles with diameters greater than 50 nm in those TEM images, typically between 300 and 600 particles per sample, were sized and categorized. A total of more than 7700 particles from 22 samples were used for size measurements and particle categorization (Table 1). The procedure produces uncertainties of less than 10% relative in the pie chart (Fig. 6).

2.7 Particle size measurements

Averaged particle radii were determined by fitting ellipses to the particle outlines and taking the geometric mean of the semi-minor and semi-major axes (Pósfai et al., 2003; Mogo et al., 2005). If more than two soot-particle aggregates occur in an internal mixture, only the larger one was measured. The rationale was that these larger soot particles have the greatest effect on the particle optical properties.

Many particles containing OM-S were apparently liquid or at least relatively viscous when collected. In these instances, they spread when on the grid (Figs. 2 and 3). Assuming OM-S particles without soot (category 3) were spherical in the atmosphere, our measurements of those collected on TEM grids possibly overestimate their sizes by about 10%. We used lacy-carbon support films to minimize the effect. In some cases, they may have decreased in size because of loss

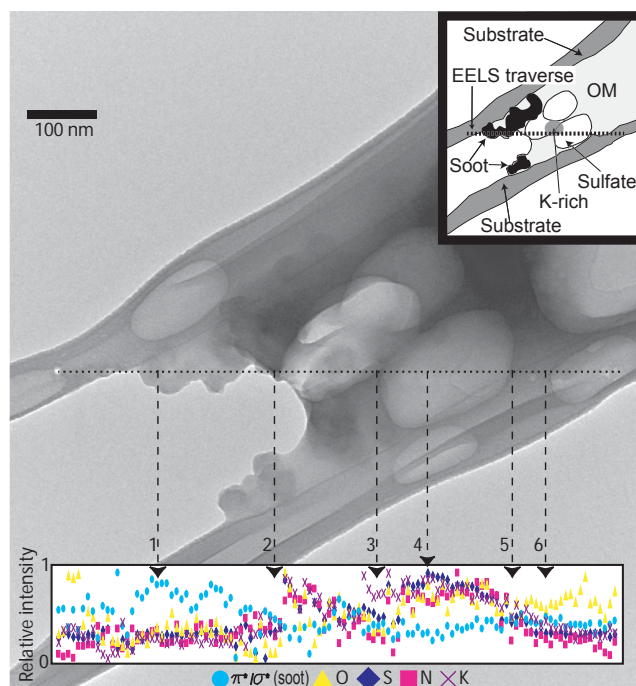


Fig. 4. Plot of composition vs. position in the internally mixed particle from the MC pollution plume (Sample #3). The sketch in the upper right shows the various species. Points 1 – soot, 2 – OM, 3 – K-rich particle, 4 – sulfate decomposition residue, 5 – OM, 6 – lacy-carbon filter. A total of 114 points were analyzed by using EELS at 10 nm intervals. The π^* and σ^* intensities were obtained by using the same method as Katrinak et al. (1992). We used intensities at 184.5, 294.5/ σ^* , and 402.5 eV in the EELS spectra for determining the relative abundances of S, K, and N, respectively. For O, total counts ranging from 531.5 to 536.5 eV were used. Exponential background extractions were applied.

of volatile fractions. Vacuum condition causes ~20% shrinkage for ammonium sulfate particles (Pósfai et al., 1998). We used the same procedure for all samples, and therefore the comparison among our samples is internally consistent.

3 Results

3.1 Nature of aerosol particles

We found that many MC particles are internally mixed. This observation is consistent with the results from single-particle mass spectrometer measurements (Moffet et al., 2008) and scanning and transmission electron microscopy (Doran et al., 2008; Johnson et al., 2005), all of which were used to analyze MC samples.

Images of many MC particles show the intimate mixtures of constituent phases. Typical images and compositions of both internally and externally mixed particles are shown in Figs. 2 and 3, respectively.

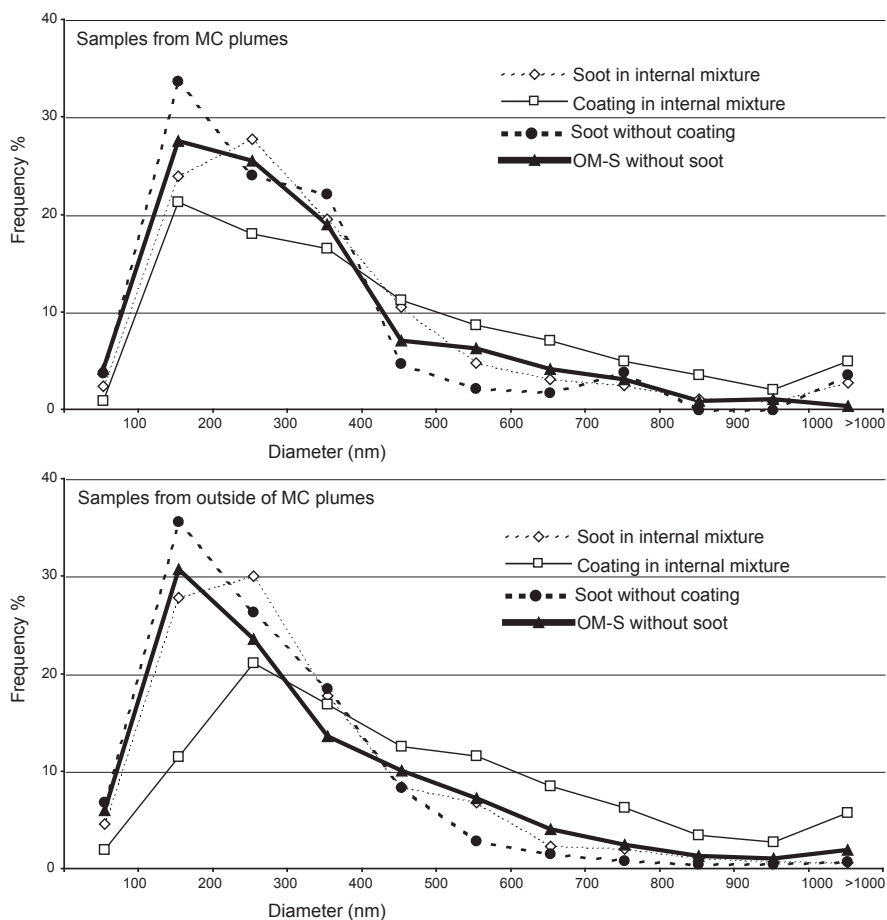


Fig. 5. Distributions of particle diameters. Total numbers of internally mixed particles, soot without coatings, and OM-S without soot are 1312, 176, and 789, respectively, and those of the samples from outside MC are 1492, 378, and 2989, respectively.

EDS measurements show that S occurs in more than 90% of all analyzed particles, and more than 70% of these also contain K. Since most such S-bearing particles were sensitive to the electron beam, we interpreted them as sulfates (possibly mixtures of K_2SO_4 , $(NH_4)_2SO_4$, and NH_4HSO_4) (Pósfai et al., 1995; Kojima et al., 2004). Si occurs in 75% of the particles, although discrete mineral grains were not evident. Small peaks in the EDS spectra showed one or more of V, Cr, Mn, Ni, Zn, Sn, Pb, and Bi in 50% of the particles. Other studies also reported metals in MC aerosol particles (e.g., Moffet et al., 2008; Chow et al., 2002; Johnson et al., 2006; Querol et al., 2008).

In order to explore details of the sorts of particles typical of the MC plume, we show a set of EELS analyses across a traverse of one such composite particle (Fig. 4). A plot of S, O, N, and K composition vs. position shows a sulfate decomposition residue (e.g., Point 4 in Fig. 4). The high π^*/σ^* ratios at, e.g., point 1, confirm the identity of soot. The low π^*/σ^* ratios at points 2 and 5 and the lack of a well-defined shape are consistent with the identity of OM.

3.2 Sizes and aspect ratios of aerosol particles

The size distributions of MC samples are similar to those collected outside of MC (Fig. 5). However, the peak of the distribution for internally mixed OM-S coatings from the MC samples occurs for smaller particles than for those collected outside of MC. A possible explanation is that the MC samples include more young particles, which had less time for growth through coagulation. The median diameter of particles containing soot and OM-S coatings (thin solid line in Fig. 5) is about 290 nm and that of OM-S particles without soot (thick solid line in Fig. 5) is about 170 nm. i.e., coated particles tend to be larger.

The aspect ratio (long axis/short axis) is an indicator of compactness. Averaged aspect ratios (and standard deviations) are 2.2 (0.9), 2.1 (0.9), and 1.9 (0.8) for uncoated soot and that with coatings from MC and outside of MC, respectively. Those in our samples are not highly compacted but retain their chain-like structure.

3.3 Volumes and number fractions of aerosol particles

The volumes of particles are important for evaluating their optical properties and aging. Most particles have irregular shapes on TEM grids, but many were presumably liquid within the atmosphere. For simplification, we approximated their shapes as roughly elliptical when on the TEM grid. We used their measured semi-major and semi-minor axes to calculate their volumes. The volumes, V , of the soot particles within the internally mixed particles were determined using the relation $V=4/3 \times \pi \times a^3 \times N$, where a is the radius and N is the number of soot spherules in an aggregate particle. N was estimated from the statistical scaling law of fractal aggregates, $N=k_a \times (R_g/a)^{D_f}$, where k_a is the structural coefficient, R_g is the radius of gyration, and D_f is the fractal dimension (Adachi et al., 2007). We used the measured semi-major axes of soot particles for determination of R_g ($R_g = \text{semi-major axis}/1.5$) (Brasil et al., 2001; Köylü et al., 1995; Gwaze et al., 2006). For simplification, we divided the soot particles into their end values of either open or compact. For soot particles that have aspect ratios >2.0 (open clusters), we used $D_f=2.4$ and $k_a=0.7$ (Adachi et al., 2007). For the compacted soot particles (aspect ratios ≤ 2.0), we used $D_f=2.6$ and $k_a=2.1$ (Adachi et al., 2007; Liu and Mishchenko, 2005).

Approximately 80% and 50% by volume of the OM-S particles collected from MC and outside of MC, respectively, contained soot particles. The median value of soot volume fractions for internally mixed particles is 15% when the median value of $a=22$ nm is used and goes from 7 to 24% for our range of a values (from 10 to 50 nm) and for $D_f \pm 0.2$ from the D_f values shown above.

The number fractions of the major particle types also indicate that internally mixed particles dominated the MC samples (Fig. 6). Soot occurs in 62 and 35% of all particles in the samples from MC and outside MC, respectively, and more than 80% of the particles were coated by OM-S in both sample sets.

4 Discussion

4.1 OM-S coatings on soot particles

The proportion of particles containing internally mixed soot is higher than that reported by Okada et al. (2005) for Australia, Hara et al. (2003) for the Arctic, and Hasegawa and Ohta (2002) for Japan and Alaska, even though most of our MC samples were less aged. Since our MC samples were collected close to their sources, generally within less than eight hours after emission and yet were coated when collected, we conclude that the rate of coating was rapid, consistent with the results of Doran et al. (2007), Johnson et al. (2005), and Baumgardner et al. (2007). The rate is much faster than that used in climate models. For example, Cooke et al. (1999) suggested that an exponential lifetime of hy-

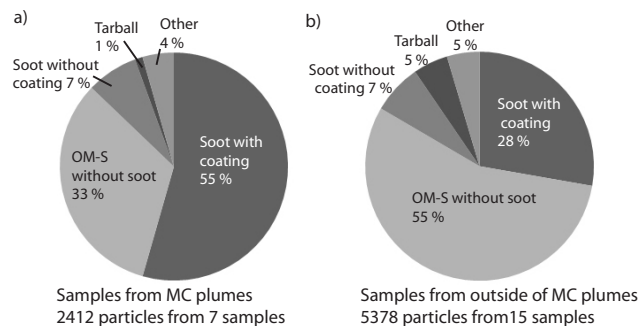


Fig. 6. Number fraction of particles.

drophobic soot is 1.15 days. Coated soot particles are removed by wet deposition and have shorter lifetimes, which reduce their radiative forcing (van Poppel et al., 2005).

The coated soot particles retained their chain-like structures as judged from TEM images and measured aspect ratios. A possible explanation is that rapidly deposited coatings covered the entire soot particle and fixed its structure before it became completely compacted.

Light absorption of soot is enhanced when it is coated by OM-S, which focuses sunlight on the soot and also enlarges the available absorption cross section (Fuller et al., 1999; Chýlek et al., 1995; Bond et al., 2006; Barnard et al., 2007). In our samples, the median coating fraction is 85% by volume in internally mixed particles. Mie calculations show that a spherical soot core surrounded by a concentric shell has its absorption enhanced by roughly 1.5 relative to one without a coating (Bond et al., 2006). However, such a configuration probably overestimates the light absorption of our soot particles that are not completely compacted because soot spherules located away from the center of the particle have reduced absorption (Fuller et al., 1999; Bond et al., 2006).

Secondary organic aerosol particles form through condensation of precursor gases on pre-existing particles such as soot, ammonium sulfate, and primary organic aerosol as well as through homogeneous nucleation (Seinfeld and Pankow, 2003). In our samples, we observed such secondary organic aerosol particles as the coatings on soot. Soot occurs in 62% of our OM-S particles, and 80% by volume of all OM-S particles contain soot. Additionally, OM-S particles that contain soot are larger than those that do not (Fig. 5). These results imply that soot particles are important nuclei for the development of secondary organic aerosol particles in MC.

4.2 Contributions from biomass and biofuel burning

Biomass and biofuel burning are major sources of aerosol particles in MC (Moffet et al., 2008; Stone et al., 2008; Yokelson et al., 2007). K is a key element for identifying such particles (Andreae, 1983; Li et al., 2003; Pósfai et al., 2003; Hudson et al., 2004; Murphy et al., 2006). In our samples, K occurs in more than 60% of the particles, most

of which are sulfates. Sulfate condensation on the biomass-burning particles probably occurred during transport, as was also observed in biomass-burning particles in southern Africa (Pósfai et al., 2003; Gaudichet et al., 1995; Andreae et al., 1998; Gao et al., 2003; Kreidenweis et al., 2001; Liu et al., 2000).

K concentrations are variable among particles (Figs. 2, 3, 4). Some were presumably produced by biomass burning outside of MC. Such burning occurred during the campaign in the central and southern parts of Mexico such as Yucatan and around MC (Yokelson et al., 2007; Fast et al., 2007). Locally, residential wood combustion (biofuel burning) is another source of K-bearing particles (Moffet et al., 2008; Mexico National Emissions Inventory 1999, 2006).

Tar balls are also an indicator of biomass and biofuel burning (Pósfai et al., 2004). Their number fractions were smaller than those in other areas that had large contributions of biomass and biofuel burning such as southern Africa, Hungary (Pósfai et al., 2004), and Yosemite National Park (Hand et al., 2005). The relatively low biomass- and biofuel-burning contributions to bulk samples are consistent with the study by Stone et al. (2008), although our findings suggest they make important contributions since they occur in many individual particles.

4.3 Sulfate implications

Sulfate particles are attached to OM, soot, or their mixtures, or are embedded in OM (Fig. 2). They are commonly smaller than 200 nm across. Although in areas such as the northern Atlantic Ocean (Pósfai et al., 1999) and southern Finland (Niemi et al., 2006), sulfates encapsulate entire soot particles, the dominant material in the MC samples is OM, and the sulfate as well as soot is either embedded within the OM or attached to its edges. The difference arises because the MC plume included large quantities of OM (Salcedo et al., 2006; Jiang et al., 2005; Zavala et al., 2006; Stone et al., 2008; Querol et al., 2008; Takahama et al., 2007; DeCarlo et al., 2008; Molina et al., 2007; Kleinman et al., 2008), which produced coatings on the soot prior to the development of the sulfate particles.

The attached sulfates hardly enhance the light absorption of soot (Mishchenko et al., 2004). On the other hand, sulfates can change the OM and soot particles from hydrophobic to hydrophilic and eventually make them efficient cloud condensation nuclei (CCN) (Lohmann et al., 2004; King et al., 2007). Meanwhile, those embedded in hydrophobic OM do not work well as CCN (Abbatt et al., 2005; King et al., 2007). Since we found some sulfates embedded in OM, their CCN properties will be overestimated if all are assumed to be on the surface. Although instruments such as single-particle mass spectrometers can rapidly determine particle compositions, the morphologies of individual particles, which are only obtained by using electron microscopy, are important for interpreting their contributions to climate, e.g., as CCN.

5 Conclusions

Over 50% of the aerosol particles that we sampled from the MC plume consist of internally mixed soot, OM, and sulfates. MC sulfate commonly contains K, suggesting contributions from biomass and biofuel burning. These findings indicate that individual particles typically contain materials from multiple sources. OM is a dominant material in the MC plume, and soot particles are common. As a result, OM rapidly coats most soot particles. Additionally, attached sulfate on OM and soot particles possibly changes them from hydrophobic to hydrophilic.

In a city where pollution is heavy and formation of secondary organics is rapid, as is the case in MC, assuming that soot particles are internally mixed is relatively reliable for modeling. Our results also imply that, depending on their nature, the coatings can have either negative or positive effects on the radiative forcing. They reduce soot lifetimes in the atmosphere through the changes in particle hygroscopicity and increased mass, which together result in both washout and dry deposition and, on the other hand, they amplify light absorption. Their complicated morphologies also suggest that coated soot particles will not enhance light absorption as efficiently as those assumed in many climate models. Since soot is the dominant primary particle in many urban areas, its properties, especially when coated, are important for accurate evaluation of its effects on local and regional climate. Moreover, soot occurs in more than 60% of all particles in the MC plumes, suggesting its central role in the formation of secondary aerosol particles.

Acknowledgements. The authors thank T. Karl, F. Flocke, and S. Madronich for their help with collection of the C130 samples and R. Yokelson, T. Christian, S. Urbanski, C. Wold, D. Toohey, M. Fisher, E. Thompson, G. Moore, J. Stright, A. Knobloch, and K. Bailey for their help with collection of Twin Otter samples. C. Wilson and J. Cagle helped greatly with the aircraft inlets. We are grateful to E. Freney, L. Garvie, and S. H. Chung for their discussions of this manuscript. We gratefully acknowledge the use of TEMs within the LeRoy Eyring Center for Solid State Science at Arizona State University. This study was supported by NSF grant ATM-0531926.

Edited by: S. Madronich

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