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Atmospheric
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Interactive comment on "Internally mixed soot, sulfates, and organic matter in aerosol particles from Mexico City" *by* K. Adachi and P. R. Buseck

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Response to Reviewer #2

RC: reviewer's comments
AC: Author's comments

Referee #2

General comments:

This paper discusses observations of internally mixed soot, sulfates and organic

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matters in and around Mexico city, indicating single particles come from multiple sources; the organic coating can change the light absorption property of soot particles and the attachment of sulfate to soot particles makes them hydrophilic, these results contribute to the properties of Mexico city aerosols and are useful for model calculation. However, some results need more analysis and some concerns need to be addressed. The paper also includes a large amount of speculation about sources, lifetimes, and impacts, that is probably beyond the scope of its findings. Furthermore, much of the language is very casual and lacks clear definitions in the literature.

AC: We appreciate reviewer #2's comments. We revised this manuscript to make these points clear as the reviewer suggested.

Specific comments:

RC2-1: Page 3.

OM should be defined.

AC2-1: We defined it in the Introduction.

Revised: Introduction

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.

RC2-2: Page 3, line 13-22.

This discussion is a throwback to 10 years ago, before our field progressed to

the current clear consensus that atmospheric particles are not represented by either a "simple external mixture of pure components" or a "single internal mixture in all particles." A review of recent literature would show this, and the authors clearly need to incorporate those references here. Their argument here needs to account for the realities of multiple types of different internal mixtures using clear and precise language on this topic. The current discussion obfuscates the issue with vague and overly simplistic terminology that ignores 5 years of published, peer-reviewed progress by models and measurements (by groups that include their own). The continuing failure of models to reflect this complexity is not their lack of knowledge of its existence, but the limitations associated with computing power for large models.

AC2-2: We revised the introduction as the reviewer suggested.

Revised: Introduction

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 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,

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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.

RC2-3: Page 5, line 23.

for sample #14, the distance from MC of is 286 km, why is it considered an "MC" sample while the criteria is that "MC samples are from within 80 km of the city center"?

AC2-3: We classified our samples as MC samples if they were collected from MC plumes. We used the HYSPLIT back-trajectory model to identify them. As seen in Fig.6 in Molina et al. (2008), when we collected sample #14, the MC plume moved rapidly toward the northeast from Mexico City. Back-trajectory models also show the sample traveled from MC. We changed the related sentences to make it clear.

Revised: Section 2.2

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).

RC2-4: Page 6, line 26.

it says "OM commonly coats the surface of soot," Figure 5 shows soot with coating accounts for 55% of all particles studies; in the conclusion section, line 23,

“sulfate commonly attaches to OM and soot particles”: coating and attachment mean the components are not really mixed, are coating and attachment equivalent to internally mixed?

AC2-4: In this study, we use the term “internally mixed” when particles are coated by or attached to other aerosol particles. We followed the definition of Bond and Bergstrom, 2006, where *“The term internal mixture is used inconsistently. It can be used to describe any occurrence of multiple species in the same particles but it is an incomplete description of the mixing that may affect absorption”*. Thus, we also use “Coating” and “attachment” to describe their mixing states adequately. We added the definition.

Revised: Introduction

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.

RC2-5: Page 7, line 3.

the authors identifies tar balls, is “spherical shape” the only criteria of identifying tar balls? This may not be enough.

AC2-5: We added the definition.

Revised: Section 2.5

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).

RC2-6: Page 9, line 24-25.

“the peak of the distribution for internally mixed OM-S coatings from the MC samples is smaller than that from particles collected outside of MC”, what is the reason of this?

AC2-6: We added the possible explanation in the text.

Revised: Section 3.2

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 coagulation.

RC2-7: Page 9, Line 26.

“Where OM-S coats soot, the particle sizes are larger than those without soot.”, but from Figure 4 (upper panel), the particle sizes of “coating in internal mixture” is smaller than soot in internal mixture.

AC2-7: In figure 4 and the sentence, we compare the sizes of “coating in internal mixture” (solid thin line with square symbol) and OM-S without soot (solid thick line with triangle symbol). We revised the sentence to make it clear.

Revised: Section 3.2

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.

RC2-8: Page 10.

“particles become more compact during aging,” is not appropriate, since the aspect ratios are very close, and the standard deviations are big.

AC2-8: We took out the sentences.

RC2-9: Also, the author mentioned the liquid particles spread on the grid, how much error does this cause in calculating particle diameter?

AC2-9: We added an estimate.

Revised: Section 2.7

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%.

RC2-10: Page 11, line 11.

“we conclude that the rate of coating was rapid”: the life time of the particles of diameter 300 nm can be as long as several days, so the particles collect are not necessarily fresh, this conclusion is not appropriate.

AC2-10: During the campaign, we specially collected samples younger than 1 day as MC samples. Although MC is surrounded by mountains, the basin is ventilated daily and has little day-to-day accumulation of pollutant (de Foy et al., 2006, 2008). Such rapid ventilation was confirmed during the campaign (de Foy et al., 2008). Thus, although it is possible that particles with about 300 nm diameter can remain suspended for several days in elsewhere, most of our particles were young. In the revised manuscript, we explained the air circulation in MC.

Revised: Section 2.2

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 hours, 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 pm local time (Table 1), most particles were within eight hours or less from emission.

RC2-11: Page 11, line 19-20.

“A possible explanation is...”, is this observed from TEM images?

AC2-11: Yes. We explained it in the text.

Revised: Section 4.1

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.

RC2-12: Page 11, line 21.

“Light absorption of soot is enhanced when it is coated by OM-S.” why is that? Should cite some references here.

AC2-12: We explained that and put citations after the sentence.

Revised: Section 4.1

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).

RC2-13: Page 12, line 12-13.

“K occurs in more than 60% of the particles, most of which are sulfates.” How is this conclusion reached? Is there other measurements? Since on Page 7, line 10-11, it says “our sulfates were neutralized by ammonium”.

AC2-13: We added the explanation. We believe that they are mixture of K_2SO_4 and

$(NH_4)_2SO_4$, both of which can crystallize together to form approximately homogeneous mixed crystals (e.g., Karan et al., 2003). Our results by using EELS and EDS and single-particle mass spectrometry during the campaign by Moffet et al. (2008) support the possibility that all K (as K^+), S (as HSO_4^-), and N (as NH_4^+) occur together in single particles.

Revised: Section 3.1

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).

RC2-14:Page 12.

it says “Biomass burning is one of the most important sources of aerosol particles in MC” (line 9) and “K occurs in more than 60% of the particles” (line 12), but as a result this study observed “relatively low biomass-burning contribution” (lines 25-26), and the tar ball fraction is small (Figure 5), do these statements contradict?

AC2-14: The sentence “K occurs in more than 60% of the particles” describes the biomass-burning contributions on an individual-particle scale. The sentence “relatively low biomass-burning contribution” describes their bulk composition, where their mass contributions are probably less than 30 % (Stone et al., 2008). We revised the sentences to make their relation clear.

Revised: Section 4.2

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.

RC2-15:

In some sections, the authors didn't clearly indicate their own new/original contribution, for example, on Page 13, "sulfate implications" section, there is no proof from the data from this study to confirm how sulfate coating changes the particle property; also on Page 14, line 1-7, these conclusions are not from the analysis of data of this study.

AC2-15: We revised section 4.3 and Conclusions.

Revised:

Section 4.3

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

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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.

Conclusion

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.

RC2-16:

“Moreover, soot occurs in more than 60% of all particles in the MC plumes, sug-

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gesting its important role in the formation of secondary aerosol particles." does this conclusion really follow?

AC2-16: We revised section 4.1 to support the statement.

Revised: Section 4.1

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.

Technical corrections:

RC2-17:

In the abstract, lines 1-7 can be put into introduction; lines 13-15, "Coatings on..." and lines 17-18, "Through changes...", these statements are only implications and are not direct from the data.

AC2-17: We revised the abstract but retained some introductive sentences and implications consistent with the instructions for "ACP-manuscript preparation" (*The abstract (150-300 words) should be intelligible to the general reader without reference to the text. After a brief introduction of the topic, the summary presents the key points of the article and provides future directions where research could focus on in the near future. Reference citations are not permitted in this section, and non-standard abbreviations should not be included.*)

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Revised: 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.

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