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Interactive comment on “Processing of soot in an urban environment: case study from the Mexico City Metropolitan Area” *by* K. S. Johnson et al.

K. S. Johnson et al.

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We would like to thank the two referees for their reviews and helpful comments. In the following we address their questions, and have revised our manuscript to incorporate the changes as outlined.

Referee #1

Pg. 5589, line 22 “What is the source of the polydimethylsiloxane contamination?"

– We observe PDMS in unused substrates. PDMS is commonly detected in TOF-SIMS studies because it "wets" surfaces very well and provides a strong secondary ion signal.

Pg. 5594, line 16 “Does the overlap confirm ammonium sulfate ... Can this technique distinguish between ammonium sulfate and ammonium bisulfate?”

– Overlap of ammonium and sulfate ions in TOF-SIMS analysis supports other evidence for ammonium sulfate including tracking of S/C, O/C, and N/C ratios from CC-SEM/EDX, particle damage in SEM and TEM analyses, and AMS data showing that aerosols were neutralized during most of the MCMA-2003 campaign (Salcedo et al., 2005). The referee is correct to highlight that these microscopy techniques cannot unequivocally distinguish ammonium sulfate from bisulfate. In this case, information from AMS provided additional support to suggest that S was largely in the form of ammonium sulfate.

Pg. 5595, line 8 “... could this be an artifact of the collection method?”

– We have added description of the TRAC collection method and storage of samples. The TRAC is designed to continuously advance the collection grid in order to minimize artifacts from particle impact. Sampling plates were sealed after particle collection before analysis.

“Also how frequent are particles similar to the ones shown in image (i) observed compared to particles similar to the ones shown in image (ii), Figure 8.”

– The bulk of this study was done with CCSEM/EDX analysis with less emphasis on TEM. Unfortunately we do not have enough statistics at this time to determine the ratio of particles of type (i) vs. type (ii). However, we felt that it was important to report that both were observed for possible implications on particle lifetime and radiative properties.

Follow-up comment on TEM analysis:

– The current lack of laboratory data and inherent complexity of field samples make it difficult to hypothesize on the mixing mechanisms involved. We observed sulfate inclusions on soot as well as sulfate surrounding the entire soot particle, which suggest that multiple soot/sulfate mixing mechanisms may occur. In order to compare Figures 8(i)

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and (ii) to Posfaí et al. (1999), it is necessary to consider differences in environment (urban vs. remote marine) including particle concentrations and relative amounts of soot and sulfate, as well as possible differences in running TEM analysis. In our experience, time after exposing the particle to the electron beam influences the extent of the sulfate damage, and appearance of the image. While it is possible that the intensity of the electron beam displaces soot within the sulfate particle, this is perhaps less problematic for the types of well-mixed particles featured in Figures 4-6 and Figure 8(i). Regarding our Figure 8(ii) suggesting a soot core, Posfaí et al. did find it more like for soot to be at the center rather than edge of a sulfate particle.

Pg. 5596, line 20 “This statement should be weakened, unless the authors an justify that coagulation occurred in the atmosphere and not on the collection grids”

– We have rephrased the statement to read “seem to provide evidence ...”

Referee #2

“There is very little information about the storage of samples from the moment of sampling to analysis unless on-line techniques were used. It would be informative to learn about the storage of such samples and their potential changes during storage”

– We have added description on TRAC collection and sample storage prior to analysis (see response to ref #1). Samples were analyzed immediately after the campaign to minimize the possibility for contamination and/or other artifacts. At this time it is not known to what extent the immediate or eventual loss of more-volatile particles would alter their physical nature upon sampling. Based on the degree of internal mixing observed, we would not expect loss of volatiles to have changed our observations or conclusions as stated.

“On page 5591, line 10, a distinction between sampled carbonaceous particles and soot is made Ě What were the criteria of distinction between the two types of particles?”

– We refer to both “soot” and “carbonaceous particles” to include the indirect evidence

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of organics from the apparent splashes around the particles. Since soot itself is of course carbonaceous, we have revised our statement to read "soot and other carbonaceous particles."

pp. 5592, lines 20 ff. "... Are the authors able to distinguish between H2SO4 adsorbed on primary emitted particles and H2SO4 that is deposited as an aerosol onto the soot particles during sampling? In other words, did the authors check for a sampling artifact in the presence of H2SO4 aerosols that is always emitted in much larger numbers compared to H2SO4 that is already adsorbed on soot?"

– The collection method employed by the TRAC minimizes sampling artifacts by continuously moving the grid during collection (see response to ref #1). We have not done a detailed study on the characteristics of H2SO4 aerosols in mobile emissions; indeed it would be difficult to do for such a variable sampling basis as Mexico City traffic.

Pg. 5596, line 5 ff. "Is the liquid coating of soot particles really from lubrication (engine) oil or could it be a partially oxygenated organic phase of low vapor pressure?"

– The limitation of microscopic analysis techniques to measure volatile and semi-volatile compounds makes it difficult to determine the chemical makeup of the splashes surrounding the freshly-emitted soot particles. Since particles were sampled from a diverse fleet of vehicles, with and without catalytic converters, it would be impractical to discuss oxygenated organics with any certainty. Compositional studies done on diesel particulate emissions (Sakurai et al., 2003) which found a signature of unburned lubricating oil appeared to provide the most logical explanation, although condensation of low vapor pressure organics should have been possible as well. We have added a comment to this effect in the revised manuscript.

Pg. 5598, line 8 ff "what kind of "meter" for the hygroscopic properties of soot are the authors thinking of?"

– The way in which processing of soot aerosols translates to increased hygroscopicity is an important question. We assume that as soot becomes more heavily mixed with sulfates (the more soluble components it contains), the more likely it is to be washed out. It is true that hygroscopic properties of the types of mixed particles shown here would not be easily quantified on a single particle basis, although we have found this approach useful for studying the hydration of oxidized soot particles (Zuberi et al., 2005). Bulk measurements may also be instructive.

References:

Pósfai, M., Anderson, J. R., and Buseck, P. R.: Soot and sulfate aerosol particles in the remote marine troposphere, J. Geophys. Res., 104, 21685-21693, 1999.

Sakurai, H., Park, K., McMurry, P. H., Zarling, D. D., Kittelson, D. B., and Ziemann, P. J.: Size-dependent mixing characteristics of volatile and nonvolatile components in diesel exhaust aerosols, Environ. Sci. Technol., 34, 5487-5495, 2003.

Salcedo, D., Dzepina, K., Onasch, T. B., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Gaffney, J., Marley, N., Johnson, K. S., Zuberi, B., Molina, L. T., Molina, M. J., and Jimenez, J. L.: 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, Atmos. Chem. Phys., 5, 4183-4221, 2005.

Zuberi, B., Johnson, K. S., Aleks, G. K., Molina, L. T., Molina, M. J., and Laskin, A.: Hydrophilic properties of aged soot, Geophys. Res. Lett., 32, L01807, doi:10.1029/2004GL021496, 2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5585, 2005.

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