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Atmospheric
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Interactive comment on "Aerosol mixing-state, hygroscopic growth and cloud activation efficiency during MIRAGE 2006" *by* S. Lance et al.

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This paper presents aerosol hygroscopicity growth and CCN activation spectra of submicron aerosol particles observed at T1 site outside of the Mexico City during MIRAGE 2006 study. During new particle formation (NPF) events, increased particle characteristic hygroscopicity (k*) and CCN activation fraction were observed, the increases were more significant for smaller particles. It was found that fresh traffic emissions resulted in large fraction of externally mixed particles in early morning, whereas at midday particles could be described as internally mixed.

The authors also report that the size dependence of κ* cannot be predicted using size-resolved AMS measurement alone. The discrepancy is attributed to the lack of information on mixing state and refractory material, which cannot be provided by AMS. Hygroscopicity derived composition measured by AMS (κAMS) was able to describe CCN concentration reasonably well, especially at highest CCN concentrations, partly because the highest CCN concentration was observed during the daytime when aerosol was more internally mixed and the organic fraction was relatively low. However, falling to account for aerosol mixing state often resulted in significant overestimation of CCN concentration during early morning rush hours. These findings are consistent with earlier studies. The topic is well suited for Atmospheric Chemistry and Physics. I'd like to compliment the authors on this interesting study. Following are my comments and suggestions.

We thank the reviewer for their careful and thoughtful critique of the paper. Responses to the issues raised are provided in italics.

Page 15712, line 1. After reading the section 3.4, I realized this is based on the comparison between CCN concentrations calculated using , E, σgnd the measured N. Therefore I'd suggest change the sentence to "gs able to describe CCN concentrations reasonably well, provided mixing state information is available, . . . "

Thank you for suggesting this clarification. We have added the requested change to the text.

Page 15712, line 3-5 (abstract). "is partly due to the fact. . . organic fraction is relatively low". The discussion on this point is missing from the main text. Please include relevant discussions in the manuscript.

While we do show in the paper that the aerosol is both more internally-mixed and with lower organic fraction during the daytime (Figures 2 and 5), we agree that this sentence could be more clearly stated. We deleted explicit reference to refractory material, given that direct measurements of refractory material are not reported here, and, that CCN predictions are more sensitive to the measured fraction of externally-mixed particles.

Page 15714, line 1- 12: When CCNC is operated at low supersaturations (i.e.

<$\sim$0.1%), the driving force for droplet growth is low. Therefore a reduced CCN flow is required such that particles could grow to sizes larger than the OPC detection threshold. This also ensures that interstitial aerosol particles under the low supersaturation could be distinguished from activated CCN (Roberts and Nenes 2005, Lance et al., 2006). The CCN counter was operated at a relatively high flow rate of 0.75. How did the high flow rate impact the measurements at lower supersaturations?

Since the CCN measurements were size-resolved, overestimation of activation ratios at low supersaturations from large unactivated haze particles is not problematic (Lance et al 2006). The activated fraction at the lowest supersaturations can be underestimated at high flow rates if droplets do not grow sufficiently to be detected by the OPC. However, particles with diameter less than 100nm and with atmospherically-relevant hygroscopicity are not CCN-active at the lowest supersaturation (~0.07%); any signal will likely be from the presence of multiply-charged particles.

Page 15715, line 5-7. Given the high RH, did RHs measured at different locations of the 2 DMA agree?

We measured RH at 4 points for each DMA column, at the inlet and the outlet of the sheath and aerosol flows. The average of the 4 measurements was monitored and controlled using PID controllers (one controller for each DMA). Standard deviation between these 4 measurements for DMA2 was 2.2% on average throughout the project.

Page 15715, line 12: I think the growth factor of NaCl at 90.8% RH is much larger than 1.3. Is this the value of k instead?

Indeed so! Thank you for noticing this typo.

Page 15716, Line 21: As described later, the function is influenced by both the chemical characteristics of the activated particles and the shape of DMA transfer function.

We have revised this sentence as follows: "... and can be used to derive the chemical characteristics of the activated particles."

Page 15719, line 9, "the fraction of particles with Sc<S is", is this fraction the normalized activated fraction for size selected particles (i.e., Ra*(s))? Please clarify.

Yes. We have revised this paragraph, as discussed below, in response to the comment that follows.

Page 15719, line 11, "The measured and simulated CCN concentrations..." Is the measured CCN concentration total CCN concentration or size resolved? This paragraph appears to be quite confusing. Please rewrite and clarify.

This paragraph describes the method for obtaining the CCN distribution as a function of particle size and supersaturation, nCCN(dp,s). We have rewritten this section to improve clarity.

Page 15720, line 13-14: Please rephrase this sentence. I assume that your method (Eqn. 11) does not include externally mixed non-CCN-active particles. However, the sentence appears to suggest that method reported by Su et al. (2010) does not include externally mixed non-CCN-active particles.

We apologize for the confusion. Indeed, Eq 11 does not include externally mixed non-CCN-active particles. The sentence is modified to reflect this.

Page 15721, line 9-10. These assumptions are not always appropriate, especially during early morning traffic hours. Please include some discussions on the appropriateness of these assumptions.

Indeed, this is a major result of the paper: i.e. the assumptions upon which calculation of k_AMS relies do not always apply (especially during the early morning rush hour). We make this conclusion after comparing k_AMS with k_CCNc and k_HTDMA measurements.

Page 15721, Line 14-15. I understand that soot often has fractal geometry, but how does it contribute to measured increase in organic mass fraction at smaller particle sizes? Are you suggesting that particles with higher organic mass fraction were more fractal, such that their d was smaller? Please clarify.

The AMS measures the mass distribution of ensemble aerosol particles as a function of the particles' d_{va} (vacuum aerodynamic diameter) (DeCarlo et al 2004 and Slowik et al 2004). The d_{va} is a function of the particle's material density, volume equivalent diameter (d_{ve}) and shape factor (χ), as detailed in equation 6 of Slowik et al. (2004). Thus, nonspherical particles, such as fractal-like soot particles from incomplete combustion of diesel/gasoline engines, will have a smaller d_{va} than spherical particles, such as fractal-like soot particles coated with nonrefractory particulate material such as primary and secondary organic aerosol (POA and SOA) material and inorganic material such as sulfates and nitrates. As discussed in Figure 9 of Cross et al. (2009) and again in Figure 5 from Canagaratna et al. (2010), the organic aerosol particles in Mexico City at T0 and T1 during the 2006 study exhibited larger organic mass fractions at smaller particle sizes (d_{va}) due to soot particles from traffic emissions. These primary soot particles were dominated by HOA (hydrocarbon like organic aerosol) chemical signatures, in-line with these soot particles being coated with POA (primary organic aerosols) material. So, yes, due to traffic generated HOA-coated soot particles, the AMS size distributions (PTOFs') exhibited higher organic mass fractions at smaller particle sizes (40-150 nm d_{va}) than in the accumulation mode (near spherical) measurements ($\sim$300-600 nm d_{va}). This bias will affect the K_AMS calculated from the size-resolved AMS data, which were done assuming that all particles were spherical.

Page 15723, line 15. Based on Figure 2b, $f$org should be lower at 40 nm than that at 100 nm (f of activated CCN).

If kCCNc was equivalent to kAMS, then this would be true. Figure 2 does not show f_org measurements. Figure 5 shows that f_org is greater for 40nm particles than for 100 nm particles. This discrepancy between f_org (or kAMS) and kCCNc is the reason we produced Figure 8, and why we postulated that much of the organic mass was in the externally-mixed particles, and therefore the kAMS measurements were not always representative of the CCN-active population.

Page 15723, line 16. Please clarify what the "aerosol dilution" means.

Aerosol dilution refers to the amount of water present as the aerosol swells hygroscopically, and eventually becomes a cloud droplet. We have revised to clarify this.

Page 15723, line 25-26. =0.04 and 0.21 for 100 and 40 nm, respectively. Do AMS data show higher POA at 100 nm?

The AMS size-resolved data exhibit higher HOA (hydrocarbon-like organic aerosol, which is correlated with primary organic aerosol or POA, see e.g., Zhang et al., 2005) in the 40-100 nm d_p ($\sim$ 64 – 160 nm d_{va}) size range than for larger particle size ranges. The reasons for this are explained above in the response to the comment about Page 15721, Line 14-15. As discussed in the text, the results at 40 nm are less robust due to the smaller amounts of total ambient particle mass loadings and the transmission efficiency of the AMS at these small particle sizes.

Page 15726 and 15727. Among the main results of the paper are (1) externally mixed primary particles emitted during the morning rush hours rapid grew into larger particles that were internally mixed; and (2) mixing state information is important for describing CCN concentration during the morning rush hour, and calculated Nccn often significantly overestimates measured CCN concentration. In addition, the calculated CCN concentration agree well with the measured during daytime when aerosols are more internally mixed. I would suggest discuss these results in relation to earlier studies pointing in the same direction, especially those carried out in the Mexico City during the same field campaign:

Moffet, R. C., and Prather, K. A.: In-situ measurements of the mixig state and optical properties of soot with implications for radiative forcing estimates, Proc Natl Acad Sci USA, 106, 11872-11877, 2009.

Wang, J., Cubison, M. J., Aiken, A. C., Jimenez, J. L., and Collins, D. R.: The importance of aerosol mixing state and size-resolved composition on CCN concentration and the variation of the importance with atmospheric aging of aerosols, Atmos. Chem. Phys., 10, 7267-7283, 2010.

Thank you very much for the citations! We now include reference to these papers in these sections.

Page 15727, section 3.4. Does Figure 9 show the comparison of total CCN concentration (as a function of S) or size resolved CCN concentration (a function of S and Dp)? It appears that the comparison is for total CCN concentration. But I couldn't find any description on total CCN concentration measurements in the manuscript. In addition, if the comparison is for predicted and measured total CCN concentrations, then the data point would be colored by supersaturations instead of particle size. Please clarify and include more details on what quantities are compared in the figure.

nCCN is the distribution of CCN concentration over s and dp (and further clarified in the revised text). This is now clarified throughout the text.

Page 15727, section 3.4. I'd suggest include the comparison for CCN predicted using kAMS, E=1, σ=0. This represents the calculations when only AMS data are available, and particles are assumed as internally mixed.

The requested change would satisfy curiosity, but is not seen as a necessary result, since we have already shown that CCN concentrations are not highly sensitive to k. This is consistent with the conclusions from Wang et al (2010).

References

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Zhang, Q, Worsnop, DR, Canagaratna, MR & Jimenez, J-L 2005, "Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols." Atmospheric Chemistry and Physics Discussions, vol. 5, no. 5, pp. 8421–8471.

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