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Atmospheric
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Discussions

Interactive comment on “Hygroscopicity of secondary organic aerosols formed by oxidation of cycloalkenes, monoterpenes, sesquiterpenes, and related compounds” *by* V. Varutbangkul et al.

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We would like to thank the reviewers for their valuable comments and suggestions to improve the manuscript. Below is our point-by-point reply to reviewer #3’s concerns or suggestions (which appear in italics).

Reviewer #3:

p. 1126, first paragraph: It is stated that “SOA coatings on inorganic aerosol are found to allow water uptake at lower RHs than the pure inorganic portion alone...” This is followed by the statement that “In fact, field measurements have shown that there is a substantial decrease in RH dependence of light scattering with increasing organic *mass fraction." The first sentence refers to water uptake as a function of RH, while the second refers to water uptake as a function of organic mass fraction. The paragraph needs to be constructed more carefully.*

We respectfully disagree with the reviewer that the two sentences refer to different effects. The first statement suggests that with the presence of organic compounds, water uptake can continue to occur at lower RH, a region where many pure inorganics do not take up water (due to efflorescence). Thus, with organics present in the particle, the dependence of growth factor on RH is not as steep as with a pure inorganic particle. The field results corroborate this concept when the light scattering (a proxy measurement for hygroscopic growth) is found to depend less on RH with increasing organic fractions.

Figure 4: There tends to be some repetition between the text and figure captions. For example, for Figure 4, the caption could simply state what it is plotted and omit the description of what is happening that is also given on p. 1133.

We had purposefully allowed for some minor repetitions between the text and some figure captions in order to aid readers who may be quickly glancing through the paper to capture the main points of the figures. We request to leave the figure captions as they currently appear.

p. 1142, line 4: clarify what is meant by "the corresponding DMA volume distributions AT THE RISING EDGE." How do the collection and transmission efficiencies compare for the Cal Tech AMS and DMA in this size range?

In determining the effective density of the SOA, the DMA volume distribution and the AMS mass distribution are compared to each other. They are "matched" together using the left (rising) edge of each distribution, that is, the portion that includes particle diameters less than the mode diameters in the volume and mass distributions. The transmission efficiency in the DMA is taken into account in the inversion routine by calculating the size-dependent diffusion loss to tubing walls, but the transmission is still very nearly unity. For the AMS, the transmission efficiency is also 100% in the range of 100-500 nm aerodynamic diameter (Jayne et al., 2000). Therefore, there should not be any transmission efficiency issues in comparing the two measurements in this range. This is one reason for choosing the rising edge (smaller diameter) rather than the falling edge of the volume/mass distribution to do the density estimation as the falling edge generally falls at D_{va} above 500 nm.

p. 1143, last paragraph: Provide reference(s) for the statement that the volume weighting approach to describe water uptake of an organic-inorganic mixture works with relatively dilute solutions.

References now provided (Choi and Chan, 2002; Prenni et al., 2003; Wise et al., 2003)

p. 1143, last paragraph: Given the very low mass fractions of AS (< 4% at 300 nm) how large is the effect of not taking into account thermodynamic interactions between the AS and the organics? Given the uncertainty of this discussion (the low mass fractions of inorganics and the treatment of the system only with volume-weighting mixing of components) it is overstepping to say that the water uptake of the inorganic portion is being enhanced or suppressed. p. 1146: The result that the discrepancy between the GForg is a result of non-ideal interactions in the mixture is based on ruling out other causes rather than an investigation of how significant this effect is for a mass fraction of inorganics of less than 4%.

Upon further consideration, we agree with the reviewer that non-ideal organic/inorganic interaction in the solution is unlikely in our system. As a first-order test, we estimated the molality of the solution in the particle with high organic fraction, and low inorganic/water content, assuming that the contribution of organics to the solute is limited by its solubility. Using pinonic acid as a model compound for particle-phase oxidation products, the calculated molality is on the order of 0.02 molal, with insignificant contribution from $(NH_4)_2SO_4$ due to its minute fraction. While the molality could potentially be an order of magnitude or so higher depending on the organic composition

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and solubility, it is likely not large enough to be in the regime where organic/inorganic interactions could become significant (5-6 molal). Therefore, we have removed from the manuscript the suggestion of this effect to explain our discrepancies in GF_{org}.

p. 1143 and throughout: Assessing small differences between growth factors (0.04) at different particle sizes or composition requires that the uncertainty in the growth factor measurements is well defined. It is stated in the methods section that the HTDMA is found to be able to reproduce the hygroscopic growth curve to within 1.5% of theoretical values. This accuracy appears to apply to a different set up than that at Cal Tech. What is the accuracy of the instrumentation used in these experiments? p. 1144, line 2: where does the uncertainty of +/- 0.01 come from? Is that based on an uncertainty analysis with the instrumentation used here?

As stated in our reply to reviewer 2: the uncertainty was estimated from a pure $(NH_4)_2SO_4$ run, which yielded a growth curve that agrees with published model calculations to within 1.5%, with the actual percentage being 1.35% (0.02 off in *GF* compared to theoretical value of 1.484 at 80% RH). We had multiplied this “percent uncertainty” to the nominal organic *GF* of 1.07 (at 80% RH) to arrive at the reported uncertainty value of about $\pm$0.01. Upon reviewing the calculation, we realize that this number should have been rounded upward to $\pm$0.02. And in fact, the discrepancy of 0.02 between the measured and theoretical $(NH_4)_2SO_4$ *GF* probably should have been used as the absolute uncertainty. We would therefore like to modify the reported uncertainty to $\pm$0.02. The change has been made in the manuscript and text added to explain the origin of the number.

p. 1144, line 13: Presumably the particles are internally mixed so it is not clear how the AMS would be overestimating the organic fraction of the larger particles. If particles are lost due to bounce or lens transmission, it would apply to all components and not just the organics.

The statement was merely posed as a hypothetical one rather than to suggest that the

AMS overestimation of the organic fraction the likely cause of the high ΔGF_c. We only intended to point out the “direction” of the experimental bias that would be consistent with the observation of positive ΔGF_c. The reviewer is correct, however, to suggest that loss due to bounce or transmission would probably apply to all components of the aerosol.

References

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