

Interactive comment on “Trends in particle phase liquid water during the Southern Oxidant and Aerosol Study” by T. K. V. Nguyen et al.

Anonymous Referee #2

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The manuscript describes measurements of aerosol water content using semi-volatile differential mobility analysis (SVDMA) during the Southern Oxidant and Aerosol Study (SOAS). This is an important topic and is appropriate for ACP. The manuscript, however, is under-developed and needs significant improvement prior to publication. One of the major omissions is a comparison with chemical composition data, without which the conclusions drawn by the authors appear to be mostly speculative. There are also issues related to data processing and interpretation that need to be addressed.

C2455

1 Main comments

I doubt that SVDMA can reliably measure semi-volatile material. The authors are correct in their assessment that SVDMA measures *only* "some" of semi-volatile material. A few seconds that air spends in the instrument is hardly enough to equilibrate the sampled particles at the fairly low ambient concentrations that were observed during the SOAS. The residence time will allow only a small fraction of semi-volatile material to evaporate. It is, thus, not surprising that very little semi-volatile material was observed in the instrument. A larger problem is that the fraction of evaporated material depends on the aerosol loading (condensational sink). This means that the evaporated fraction will change as the aerosol concentration changes. One can use a numerical model to derive the actual semi-volatile fraction, but this approach is still quite problematic as it requires accounting for wall effects and de-convoluting hygroscopicity of the semi-volatile and non-volatile material that are not known a priori. SVDMA, thus, does not provide a reliable measure of semi-volatiles, but only a measure of aerosol water content that is biased high by (hopefully) a small amount. Thus, I would suggest removing "semi-volatile" from the name of the method.

There is a potential bias in the data processing that involves fitting bi-modal lognormal distributions to size distribution data. I understand that this procedure reduces noise in individual size distributions, but I do not see the need for this when working with such a large dataset. Ambient aerosol distributions can and often do deviate from a lognormal shape. Further, even if a dry aerosol is lognormal, the distribution shape could be distorted upon growth due to differences in chemical composition at different particle sizes and the Kelvin effect. Using mean sizes for each mode and total volume concentrations (corrected for arcing artifacts, if needed) instead of fitted parameters should provide the necessary information without (potentially) biasing the results.

The instrument characterization is not entirely convincing, since it is based on particle count inter-comparison, while the measurements were concerned with a mass-based

C2456

property (aerosol water concentration). Number concentration is mostly determined by small particles, while volume concentration – by larger ones. If particle losses are size-dependent, which they often are, a number concentration comparison will not accurately represent inter-comparability of volume concentration measurements.

There is an error in Eq. 7. V_{dry} should be $V_{dry-humidified}$. I assume that the correct formula was used to interpret the data and that this is just a typo.

Calculation of aerosol water content used in this paper implicitly assumes that there is no particle-bound water at "dry" conditions. This is questionable. The presented measurements show that the ambient aerosol was in the meta-stable state. There is, thus, a good chance that the aerosol can retain some water even at "dry" conditions. The equations need to be edited to account for this possibility and its implications for the calculated κ values, etc., should be discussed.

The authors use diurnal variation of water content and the associated κ values to justify their conclusion that chemical composition changes on time scales of a few hours. While this could be true, the argument and data presented in the paper are not sufficient to prove it. κ is a measure of aerosol hygroscopicity, but not a strict one. For a single component aerosol it is equal to the ratio of the molecular weight of solute to that of water and multiplied by the maximum number of ions the solute can produce upon dissociation (the van't Hoff factor). As the authors admit, κ changes with relative humidity (due to higher solute concentrations at low RH values, the degree of dissociation, or solute activity, changes). Since RH changes during the day, κ values will change too. Thus, observing diurnal variability of κ does not provide enough information on aerosol chemical composition. This variation needs to be analyzed in the context of the RH dependence of κ .

The observed κ values need to be compared to chemical composition data to check whether the observed values can be explained by changes in aerosol chemical composition and whether these values are realistic. For example, are the estimated κ values

C2457

for the organic fraction realistic? Or, if one assumes κ for organics, does it lead to the organic mass fraction or the WSOC mass fraction that have been measured during the SOAS?

2 General and Minor Comments

p.7471, l.13-14. The direct aerosol effect is also affected by hygroscopic growth.

p.7473, l. 22. The temperature stability needs to be quantified.

p.7473, l. 22. What is the model number of PermaPure humidifier?

p.7477, l. 24-25. Since the flow has changed on 3 July, has the instrument performance been characterized for this flow?

p.7478, l. 6-8. I agree that losses at small sizes most likely do not affect measurements of *total* volume concentration, but they are important for the measured parameters of the smallest of the two modes. There is a significant fraction of particles below 50 nm even in dV/dLogD (see Fig.3), which could introduce errors in the measured GMD and lognormal fit parameters.

p.7481, l. 1-11. The discussion of fit performance is very confusing. It refers to Fig.3, but discusses "the medians of the differences between measured values" (number count or mean diameter? what is "the data distribution"?).

p 7484 A discussion of the effect of particle state (solid vs. liquid) on evaporation rate is out of place in this paper for two reasons: (1) as discussed above, the instrument cannot provide a reliable measure of semi-volatile material, (2) the physical state of aerosol will not, most probably, affect the instrument performance, because under cooling the supersaturated material will condense mostly on the walls of the instrument, while under re-heating the particles should melt to the original liquid state.

C2458

p.7485, l. 21-22 and Table 2. I find it surprising that the aerosol surface shrinks when it is humidified. Is it an artifact of fitting lognormal distributions?

p.7486, l. 27-28. This sentence is a non sequitur. Water volume is an extensive parameter, which is proportional to aerosol dry volume. If aerosol dry volume does not correlate with RH, the correlation between water content and RH will be disturbed.

p.7487 and Figure 7. Which of the calculated volume growth factors (based on the volume or size) is shown? Since k changes with RH, how valid is the inference that if kappa changes during the day then it necessarily means that chemical composition is changing too?

p.7489, line 27. This could be also due to the larger mode being more processed, i.e., more oxidized, not necessarily via aqueous pathways.

p.7491, line 2. Remove "that"

p.7492, line 7-9. There is nothing in this manuscript that can support this statement. The residence time used in the instrument and the aerosol concentrations during the SOAS are such that one cannot make any conclusions about kinetics or reversibility of partitioning based on the measured data.

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