

Interactive comment on “The sensitivity of Secondary Organic Aerosol component partitioning to the predictions of component properties: part 2; determination of particle hygroscopicity and its dependence on “apparent” volatility” by D. O. Topping et al.

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Response to referee *1

The authors would like to thank the referee for their helpful comments and questions, which we have addressed below:

*1. The impact of the manuscript would be more significant if the authors were to more

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closely examine the consequences of their claims for previous laboratory and field studies of hygroscopicity. The limit of discussion by the authors is on page 9030 when they state: “However, discrepancies in measurements of SOA particle hygroscopicity with multiple instruments have been reported in chamber experiments that could be attributable to effects such as those described here (Good et al., 2010; Duplissy et al., 2009), as has failure to achieve closure under nitrate rich conditions attributed to HTDMA evaporation of semi-volatiles”. Specifically, I think it is important that the authors expand on the phrase “that could be attributable to effects such as those described here”. Based on their description of the effect, it may be important to classify techniques according to how likely the equilibrium partitioning is to be maintained throughout the experiment. For example, measurements using a HTDMA approach might be expected to be susceptible to repartitioning to a different degree to EDB measurements. In the latter, the partitioning into a gas phase of continually flushed wet/dry nitrogen will be irreversible whereas measurements made using the former approach may, to some extent, allow the repartitioning to be reversible. In this case, the reported GFs could, presumably, just include an inherent correction factor for the greater partitioning by mass into the condensed phase at higher RH.

Response: Within the HTDMA system, there are a number of potential artefacts. As a particle is deflected across the gas flow streamlines in a DMA, it potentially moves from higher concentrations of semi-volatile vapours in the sample air into lower concentrations in the sheath air, shrinking as it is being sized. This can occur in the first DMA where it is sized dry. In the second DMA where it is sized wet, the sample flow will already have been stripped of semi-volatile vapours, so shrinkage may occur throughout the trajectory through the instrument. In the drier before DMA 1, there is the potential for shrinkage as a result both of the intentional evaporation of water and the unintentional stripping of other semi-volatile vapours. In the humidification section, shrinkage by evaporation of semi-volatile components will be accompanied by hygroscopic growth. The net effect on growth factor will depend on the shrinkage prior to initial sizing and that prior to final sizing, in turn depending on the time spent in each

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section and whether the volatile material has time to evaporate in each section. We will include this discussion within the paper for clarity.

'Would this still not mean that using the reported low GFs is a satisfactory first order treatment if the complexity of dealing explicitly with the gas-condensed phase partitioning is to be avoided?'

Response: As we state within the manuscript, there is currently no way of assessing if the behaviour of aerosols within current instruments used to measure hygroscopicity in the sub-saturated humid regime is truly representative of behaviour within the atmosphere. This is further complicated by the inability to reconcile aerosol hygroscopicity in both sub and saturated humid conditions. In addition to the effects described above in the HTDMA instrument, there will likely be a different amount of evaporation in the DMA-CCNc instrumentation used to derive cloud activation potential. There is no a priori reason that the timescales for equilibration or the saturation ratios of all components in the atmosphere are the same as those in instruments used to measure particle hygroscopicity. It is possible that hygroscopic growth and cloud activation in the atmosphere fortuitously proceed in a manner analogous to those same processes within the instruments designed to measure them: Also, the validation of simplified representations of aerosol behaviour using complex theoretical tools should not be avoided due to sheer complexity surrounding the latter. This approach is fraught with difficulty since it is readily possible to obtain the right answer for the wrong reason. For example, fortuitous reconciliation of sub- and supersaturated water uptake may be found in some environments under some conditions, but a simple representation based on such reconciliation may fail spectacularly under different conditions.

'By surveying some past measurements, can the authors be more specific about the evidence that already exists in the literature that their claims are important?'

Response. The results from this study raise the question why larger growth factors are not observed due to semi-volatile re-partitioning and does this effect occur in the atmo-

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sphere and under what conditions. It is difficult to judge this based on past measurements alone. Designing experiments to test this effect would also require measurement of gas phase concentrations within the instrument. Direct evidence that semi-volatile re-partitioning can take place is provided by use of the TDMA to derive pure component vapour pressures from measurement of the shrinkage of particles of known composition (Bilde et al 2003).

'As a follow up, it is not immediately clear how the increased partitioning to the condensed phase at high RH can lead to GF that should be larger than previously reported. If the partitioning of the organic into the condensed phase follows the partitioning of water, leading to a larger mass of organic in the condensed phase at high RH, should the real GF actually not be smaller than the reported one? '

Response: If the dry size at zero %RH is recorded and only water is allowed to re-equilibrate between the gas and condensed phase as RH is increased, this will lead to smaller growth factor than that which would occur if increased partitioning of all semi-volatiles occurred at higher RH because in the latter the total mass, and therefore radius, is larger.

'2. The authors mention that they are neglecting the effects of kinetically limited mass transfer and condensed phase chemistry in this study. They are also presumably neglecting the possibility that the SOA may contain residual water on drying etc. ?'

Response. This is correct. It would be difficult to prescribe an accurate estimate of accommodation coefficients for each compound. The referee has raised another important point here as the physical state of the aerosol on drying can alter the predicted and measure growth factor. In previous work we have briefly discussed this with regards to oxalic acid, which seems to form a stable di-hydrate on drying within the HTDMA (Topping et al 2005). Other studies have focused on re-structuring effects of proteinaceous material on drying (Mikhailov 2004). Beyond these relatively simple mixtures, recent work suggests that the physical state for a complex mixture of atmospherically

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representative organics could be a sub-cooled liquid or glassy substance (Zobrist et al 2008). Despite these effects, the impact of semi-volatile re-partitioning at different conditions would still alter the predicted the growth factor compared to the currently upheld idealized model as the sub-cooled liquid is the required reference state within models.

3. The authors make the following statement on page 9030 “If these predicted sensitivities are reasonable, it appears evident that semi-volatile organic components present in secondary aerosol in the atmosphere or smog chambers do not equilibrate in instruments designed to expose them to varying humidity.” Does it really “appear evident”?

Response: We believe it does. If the predicted sensitivities presented in this study are likely to occur, then the fact that much smaller growth factors are observed within measurements of aerosol hygroscopicity suggests that full equilibration of all semi-volatiles has not taken place, which would otherwise lead to growth factors in some cases close to those for common inorganic salts.

‘4. Figure 1: This is largely a helpful figure, but the distinction between the light green and dark green volumes on the right side of Figure (b) is not made. I presume the light green represents the equivalent volume fraction that partitions into the gas phase on drying.’

Response: This is correct and has been appropriately referenced in the figure caption.

‘5. Figure 4: Line 3 of caption, ‘on’ should be ‘no’, presuming I understand the figure correctly. i.e. the sentence should read ‘. . .simulations assuming no re-equilibration. . .’

Response: This is correct and the text has been changed accordingly.

References: Bilde, M., Svenningsson, B., Monster, J. and Rosenorn, T.: Even – Odd Alternation of Evaporation Rates and Vapor Pressures of C3-C9 Dicarboxylic Acid Aerosols, *Environ. Sci. Technol.*, 37, 1371–1378, 2003. E. Mikhailov, S. Vlasenko,

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