

## ***Interactive comment on “Water uptake is independent of the inferred composition of secondary aerosols derived from multiple biogenic VOCs” by M. R. Alfarra et al.***

**M. R. Alfarra et al.**

rami.alfarra@manchester.ac.uk

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We are grateful to both reviewers for their insightful and generally supportive comments on this work. Each reviewer provides a few comments and technical corrections, which we are taking into full consideration when producing the revised version of manuscript. Responses to these comments are now provided.

Reviewer # 1

The study by Alfarra et al. presents measurements of the water uptake properties of chamber-generated biogenic SOA particles. The paper is well written and structured

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and I recommend its publication in ACP after the following few comments and suggestions for correction and improvement have been addressed.

We thank the reviewer for this assessment of our manuscript and for the conditional acceptance for publication in ACP. In the following section we address all corrections and suggestions made by the reviewer.

Specific comments:

Comment: Figure 1, Table 1: I would recommend writing the used substance directly in the individual panels of Fig. 1 and not (only) in the caption as well as mentioning the experiment number in the caption. This would make it much easier to compare the figure with Table 1.

Response: We agree with the reviewer comment and have implemented the suggested changes in the revised manuscript.

Comment: Is it Exp. 10 that you show in panel e? It looks like that from the half-life time but it is not the experiment with the lowest initial mixing ratio of  $\beta$ -caryophyllene. Can you explain why there is such a difference in the chemical half-life for Exp. 9 and 10 although the initial precursor mixing ratio is quite the same?

Response: Yes, the reviewer is correct that the trace in panel e is for Experiment 10. The exact reason for the difference in the chemical half-life between experiment 9 and 10 is not clear. The initial VOC/NO<sub>x</sub> ratios for both experiments were not identical and changed from 1.4 to 1.8. This could influence the gas phase chemistry to some extent, but may not necessarily explain the full difference. As already stated in the manuscript, the chemical half-life is an empirical representation of the inverse of the total loss rate of the parent hydrocarbon under the specified experimental conditions. This parameter accounts for losses via reaction with oxidants (e.g. ozone, hydroxyl radical), any potential photolysis and physical losses to the chamber walls. Variations in any of these conditions could have also contributed to the observed difference between

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the two experiments.

Comment: Temporal profile of hygroscopicity ( $\kappa_{\text{HTDMA}}$ , Sect. 3.3): In Sect. 3.3.1 to 3.3.6 you discuss the temporal trends of  $\kappa_{\text{HTDMA}}$  after start of photooxidation but you do not show these interesting results in a figure. On the other hand for  $\kappa_{\text{CCN}}$ , you show Fig. 6a, although no temporal trend could be observed. Therefore I would recommend adding a figure plotting  $\kappa_{\text{HTDMA}}$  versus photooxidation time.

Response: According to the reviewer's recommendations, we have included a new figure showing the temporal trends of  $\kappa_{\text{HTDMA}}$  in the supplementary material of the revised manuscript.

Comment: Can you explain/speculate why there is no similar temporal evolution for  $\kappa_{\text{CCN}}$  as for  $\kappa_{\text{HTDMA}}$ ? I would have expected similar trends.

Response: This could be controlled by factors influencing kappa differently at sub- and super-saturation. For example, any concentration dependant property would have a different behaviour in the high concentration solution at sub-saturation as compared to the much dilute solution at activation. Another potential reason could be the presence of compound with deliquescence RH higher than the RH inside the HTDMA. Additionally, kinetic effects related to particle phase determining the uptake of water at sub- and super-saturated regimes might be potentially responsible.

The observed different temporal evolution of  $\kappa_{\text{CCN}}$  and  $\kappa_{\text{HTDMA}}$  has been previously reported in the literature, both directly and indirectly. Jurányi et al. (2009) investigated the dependence of the CCN activity on precursor concentration for  $\alpha$ -pinene SOA, and while they established a relationship between precursor concentration and  $\kappa_{\text{HTDMA}}$  (as shown by Duplissy et al. (2008)), a similar trend was not observed for the  $\kappa_{\text{CCN}}$  within their experimental uncertainty. Additionally, no variation of CCN activity as a function of chemical aging was detected. Several other studies have not been able to determine a trend between  $\kappa_{\text{CCN}}$  of SOA particles and their O/C ratio (Massoli et al., 2010; Lambe et al., 2011, Frosch et al., 2011).

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Technical corrections:

P. 10707, L. 5: “: : : Frosch et al. (2011): : :”

This error has been corrected in the revised manuscript.

P. 10715, L. 12: “It has to be noted: : :”

This error has been corrected in the revised manuscript.

P. 10727, L. 11-12: “: : : to generate particles: : :”

This error has been corrected in the revised manuscript.

P.10744, table caption: write “kappa” as a Greek letter

This error has been corrected in the revised manuscript.

P. 10747, Fig. 1: Please label the y-axes for every panel (not only for the middle ones) or alternatively write in the caption that the mixing ratio of the precursor and the primary oxidation product are shown on the left and right axes, respectively. Also, you should additionally label the x-axis of panel e.

The reviewer's suggestions have been implemented in the revised manuscript.

Reviewer 2:

Alfarra et al. present measurements of hygroscopic growth and CCN activity for biogenic SOA generated inside a smog chamber. Results are presented in terms of the hygroscopicity parameter kappa. Kappa for sub- and supersaturated conditions are compared and kappa values are correlated with the fragment f44 and averaged carbon oxidation state (OSc). Sub and supersaturated kappa values are shown to agree within measurement uncertainty for all except one experiment. Temporal evolution shows strong correlation between f44 and kappa for individual systems. No overall relationship between f44, OSc and kappa could be determined. The manuscript contains new SOA data for precursors that heretofore have not been considered in the literature.

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All experimental methods are well established and adequately described. Overall the manuscript is suitable for publication if the authors are able to address my concerns.

We thank the reviewer for this assessment of our manuscript and for the conditional acceptance for publication in ACP. In the following section we address all comments raised by the reviewer.

Major comments:

Comment: The authors tackle a heretofore only partially solved problem: to establish relationships between sub- and supersaturated kappa as well as f44, OSc and kappa. My main concern with the analysis is that the authors do not attempt to fully explore the issue. A moderately large number of studies has looked into these relationships using O:C ratios and similar proxies (e.g. f44) as well as the issue of sub/supersaturated closure. These bodies of literature have been largely ignored in the discussion of the results.

Response: We accept the reviewer comment relating to the omission of some recent literature and have expanded the discussion in several places of the revised manuscript to include some of the key published work in the areas highlighted by the reviewer. However, a full exploration of the discrepancies between sub- and supersaturated kappa is still not accessible, as we will discuss in the revised manuscript. The discussion, whilst expanded, still leaves unresolved challenges which we argue cannot yet be addressed.

Comment: Further, the discussion seems to omit our more mechanistic understanding of the factors that contribute to the observed kappa. While oxidation state is clearly important, it is only so inasmuch as it controls solubility, surface tension, molecular weight, density, and particle phase. I believe that this is the main reason why nice trends were observed for single compounds, but overall there appears to be no systematic relationship between OSc and kappa. In individual ageing experiments, fewer of these properties vary. For example molecular weight/density changes less during

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again when compared to switching between precursors of vastly different molecular weight. The dependence of growth factors on precursor MW was noted by Varutbangkul et al. (2006) and is expected from theory.

Response: We agree with the reviewer comment. In fact, this was broadly the message we tried to get across, but obviously needed to expand our discussion to clarify the message. We have modified the relevant section of discussion in the revised manuscript to address the reviewer comment.

Comment: The absence of a gap between sub- and supersaturated regimes is remarkable and in contradiction to some of the authors' previous studies. No satisfactory discussion is provided why this gap was seen previously for  $\alpha$ -pinene (by multiple studies) but not in this study. This is a significant result that shouldn't be passed over.

Response: We disagree with the reviewer comment regarding contradiction with some of our previous studies; the mean kappa values from the HTDMA is consistently lower than from the CCN counter for several of the experiments reported in Figure 7. Our previous work by Good et al., (2010) reported results from three different HTDMAs and found that the ability of the single parameter  $\kappa$  model to predict cloud activation behaviour of secondary organic aerosol particles produced by the chamber photo-oxidation of  $\alpha$ -pinene was dependent on the instrument used to measure sub-saturated hygroscopicity and the relative humidity used to provide the model input. However, agreement was observed for inorganic salt solution particles, which were measured by all instruments in agreement with theory. In that study, the reported  $\kappa$ HTDMA values were between 0.04 and 0.1 depending on the instrument used for measurements. In addition, differences in the sub-saturated hygroscopic growth were observed when different initial mixing ratios of  $\alpha$ -pinene were used. The reported  $\kappa$ CCN values for the same experiments were very close to 0.1 and did not seem to change with the initial mixing ratio of  $\alpha$ -pinene. The study concluded that the difference in HTDMA data from validated and extensively used instruments meant that it could not be stated with certainty the detail required to predict the CCN activity from sub-saturated hygroscopicity.

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The HTDMA used in our current study is different to those used in the Good et al., (2010) and the mean  $\kappa$ HTDMA values for  $\alpha$ -pinene SOA varied between 0.04 and 0.12 depending on the experimental conditions. We have already acknowledged in our discussion of Figure 7 in section 3.5 that it was a little surprising that the relatively large scatter in the data shown was not even larger given the condition encountered by SOA particles in the HTDMA and CCN instruments (details of the conditions are already included in the manuscript).

The more complex model ADDEM, incorporating surface effects, was used by Good et al., (2010) to assess the detail required to predict the cloud condensation nucleus (CCN) activity from the subsaturated water uptake. Results suggested that predictions of CCN activity made from two HTDMAs compared well with the experimental data when employing the full complexity approach used within ADDEM along with a surface tension parameterisation based on fulvic acid. However, predictions made from the third HTDMA compared well using either the ADDEM model and assuming the surface tension of water or the  $\kappa$  model.

In addition to Good et al., (2010), several other studies have compared sub- and super-saturated hygroscopic properties of  $\alpha$ -pinene SOA and reported variable findings. For example, both Duplissy et al. (2008) and Jurányi et al. (2009) reported that  $\kappa$ HTDMA and  $\kappa$ CCN could be reconciled within experimental uncertainties for SOA produced from photooxidation of  $\alpha$ -pinene (with initial precursor concentration of 10–270 ppb). In contrast, Prenni et al. (2007) observed discrepancies for SOA produced from ozonolysis of  $\alpha$ -pinene, although the initial precursor concentration was much greater (>400 ppb) than other studies. Massoli et al., (2010) found that  $\kappa$ HTDMA values for  $\alpha$ -pinene SOA were consistently lower than  $\kappa$ CCN. It has to be noted that the SOA particles investigated in the studies listed here were all generated using different experimental conditions, in terms of initial concentrations, oxidation regimes and oxidant levels.

This brief review of our own reported findings, as well as results reported in the liter-  
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ature confirm that our recent findings are not in contradiction with our previous work and that discrepancies between  $\kappa$ HTDMA and  $\kappa$ CCN values appear to be dependent of several factors including the HTDMA systems employed for measurements and the experimental conditions used.

Comment: The proposed allusion to semi-volatiles is speculative and needs to be backed up by data and a better worked out conceptual explanation. A revised manuscript needs to take these points into account.

Response: We disagree with the reviewer comment. The onus is clearly on the referee to refute that semi-volatile material will behave as we have stated, just as water does. It is well known, from numerous studies utilising thermal denuders, that chamber generated SOA particles contain substantial fraction of semi-volatile material (e.g. Stanier et al., 2007; Asa-Awuku et al., 2009; Kostenidou et al., 2009; Salo et al., 2011). In the manuscript, we have already discussed that in both HTDMA and CCNc instruments, the RH of the SOA sample is actively controlled but not the saturation ratio of any other semi-volatile component. It is assumed that the particles have equilibrated with the RH in the sub-saturated measurement in the HTDMA and supersaturated measurement in the CCNc. Since there is no active control of other semi-volatile components (i.e. SVOCs), these molecules are free to condense or evaporate towards their equilibrium concentrations in the measurement timescales of the instruments. Therefore, hygroscopic growth and cloud activation of SOA particles are likely to be substantially impacted by the tendency of these semi-volatile molecules towards co-equilibration during the drying prior to initial size selection and humidification in determining their sub-saturated growth or cloud activation potential. A smog chamber is typically an extensive continuous source of vapours of ranging volatility. Given the lack of active control of semi-volatile compound saturation ratios and the very different values likely to be experienced in the HTDMA and CCN, we argue that semi-volatiles should be considered as one of the factors that could be controlling kappa to an extent that has not yet been quantified.

Specific comments:

Comment: Pg 10712: A flow rate of 3 m<sup>3</sup> min<sup>-1</sup> seems very high for a 47 mm filter/filter holder. What was the initial volume of water for the filter extraction? What were the approximate total aerosol mass loadings on the filter?

Response: We have not encountered any problems with using this setup, which we have employed for over five years. The initial volume of water used for filter extraction was 5 ml. The approximate total aerosol mass loadings on the filter varied depending on precursor type and initial mixing ratio but ranged approximately between 80 and 1600 micrograms. The estimation was calculated using the mass concentration measured by a DMPS just before filters were collected and multiplied by the approximated sampled volume.

Comment: Pg 10715: "Assuming the latter is unimportant (Matsunaga and Ziemann, 2010), the chemical half-life can be used to infer and compare the reactivity of the parent hydrocarbons under the reported experimental conditions." I don't quite understand the sentence. Matsunaga and Ziemann demonstrate that wall-losses are important for lower volatility compounds. The authors should clarify if they believe that wall loss is not an issue in their experiment, or that they ignore the effect in their calculations even though it is known to be an issue and thus the estimate of half-life may be in error. In principle, the reaction rates with respect to attack by OH and O<sub>3</sub> are well known. Thus the observed half-life must be interpreted as uncertainty with respect to oxidant abundance in the chamber, wall-loss, and the formation of O<sub>3</sub> during the reaction. The section on the observed chemical half-life should be expanded to explicitly discuss these issues.

Response: We agree with the reviewer that our statement is confusing and needs to be clarified. With the exception of  $\beta$ -caryophyllene, the reported precursors have 10 carbon atoms and are expected, to a first approximation, to have comparable loss rates to the chamber walls. Thus the observed half-life could be used to infer the overall

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rate of gas phase oxidation of precursors. Given the larger molecular size and lower volatility of  $\beta$ -caryophyllene, its observed half-life is a combination of its loss due to gas phase oxidation and physical loss to the chamber walls (Matsunaga and Ziemann, 2010). We have clarified this point in the revised manuscript.

Comment: Please clarify why the peak particle number concentration should be related to precursor reactivity. One would expect that nucleation rates of new particles is tied to supersaturation (rate of generation of low volatility products) but nucleation is also tied to the presence of trace amounts of highly specific compounds unrelated to the reaction (e.g. amines) and probably very specific compounds that form in the reaction.

Response: We disagree with the reviewer. Whilst the nucleation rate may well be determined by unmeasured nucleation precursors such as amines and sulphuric acid (at likely below detectable levels), the rate of growth of such particles to sizes at which they can be measured is directly determined by the reactivity of the precursor to produce sufficiently low vapour pressure molecules to grow them. The onset of formation of detectable particles and their subsequent growth is clearly broadly related to the reactivity of the system provided the molecules are sufficiently oxidised and sufficiently large.

Comment: Pg. 10727/10728 OSc and f44 are different and incomplete measures of particle composition. I would not expect a general correspondence between those measures. The fact that the two don't agree doesn't necessarily mean that there is "an inconsistency in determining the degree of oxidation of particles between the employed online and offline analyses methods". It simply means that the fragment f44 is a highly idealized and abstract representation of the oxidation state. The failure to establish robust relationships between f44, OSc and kappa in this study seems to be due to lack of temporal resolution in OSc data, and the absence to consider other factors that control kappa (e.g. solubility, surface tension, and molecular weight). Correlations between f44 and OSc can only be expected to the extent that oxidation state determined the more fundamental properties that control the observed kappa. See for example Cappa

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et al. (2011) for discussion. Detailed cross-reference to previous studies that attempt similar correlations in terms of O:C and f44 is needed (e.g. Chang et al., 2009, Massoli et al., 2010, Cappa et al., 2011, Lambe et al., 2011, Tang et al., 2012). While some of these are cited, what is needed is perhaps a summary figure that overlays these results by making use of the observed tight correlation between O:C and f44.

Response: We agree in general with the reviewer comment with regard to f44 and OSc derived from online and offline analysis. In the revised manuscript, we have modified this part of the discussion to reflect the reviewer's comment, and have also expanded the discussion of the relationship between composition and kappa to refer to the other factors mentioned by the reviewer. However, we think the task of comparing with data from other studies using a number of precursors under different conditions would be better suited for a review article.

Comment: Pg. 10728: "Discrepancies between online measurements of composition and hygroscopic growth when particles contain substantial amounts of semi-volatile material show that correction for this fraction are required (Gysel et al., 2007) and discrepancies between measurements of sub-saturated hygroscopic growth and droplet activation in the laboratory (Good et al., 2010b) and atmosphere (Irwin et al., 2010) are likely attributable to this effect." This comment is speculative and should be removed. First, there is insufficient discussion on the evidence and proposed explanations of frequently observed discrepancy between sub- and super-saturated kappa for SOA systems (e.g. Prenni et al., 2007, Jurányi et al., 2009, Petters et al., 2009, Poulain et al., 2010, Massoli et al., 2011). From these works at least five proposed explanations for the gap can be obtained. The veracity of any of the explanations is questionable and semi-volatile material may be added to the list. However, this work presents no evidence for semi-volatile artifacts nor does it discuss how the abundance of semi-volatiles would produce the gap via the sample protocols used. Even if both points could be addressed here, the other proposed explanations need to be disproved before the statement made here ("discrepancies...are likely attributable to this effect")

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would be valid. The respective sentence should be removed from the abstract.

Response: We have modified our statement to acknowledge an element of the reviewer's comment. We agree that the observed discrepancies may not be fully attributable to the effect of semi-volatiles and this was sloppy wording on our part, but semi-volatiles must be considered as one of the factors that could contribute to the observed discrepancies. We do not need to disprove the other proposed explanations referred to by the reviewer, as we believe that they could contribute to the observed discrepancies as discussed in the literature. We have addressed the reviewer's comment on the contribution of semi-volatiles to this problem in our response to his/her previous comment above. The modified statement in the revised manuscript now reads as follow:

"Discrepancies between online measurements of composition and hygroscopic growth when particles contain substantial amounts of semi-volatile material show that correction for this fraction are required (Gysel et al., 2007) and the equilibration of semi-volatile material will likely contribute to discrepancies between measurements of sub-saturated hygroscopic growth and droplet activation in the laboratory (Good et al., 2010b) and atmosphere (Irwin et al., 2010)."

We agree with reviewer that the effect of semi-volatile should be included in the list of proposed explanations for the gap. The role of semi-volatiles should be considered as one of the known-unknowns that could be controlling kappa to an unquantifiable extent, but that other unknowns cannot have as large an effect within the known variability of their values (e.g. surface tension).

Editorial:

Tt has to be noted -> It has to be noted

This error has been corrected in the revised manuscript.

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