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Atmospheric Chemistry and Physics
Discussions

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.

Anonymous Referee #2

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Alfarra et al. present measurements of hygropscopic 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. 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.

Major comments:

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. 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 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. 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 a-pinene (by multiple studies) but not in this study. This is a significant result that shouldn't be passed over. 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.

Specific comments Pg 10712: A flow rate of 3 m3 min-1 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?

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 O3 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 O3 during the reaction. The section on the observed chemical half-life should be expanded to explicitly discuss these issues.

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.

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 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.

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

Editorial:

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

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