

Interactive comment on “Relating CCN activity, volatility, and droplet growth kinetics of β -caryophyllene secondary organic aerosol” by A. Asa-Awuku et al.

A. Asa-Awuku et al.

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We thank the reviewer for the positive feedback and the thoughtful comments.

This reviewer agrees with reviewer #1, in that the manuscript would be significantly improved by a more detailed description of the experimental plan and objectives (i.e. what was the purpose of each experiment, how were instruments chosen for each experiment, why was the specific progression in experiments chosen, etc.) As much of this information as is appropriate should be included in an enhanced version of table 1.

There are two key sets of experiments required for our analysis, online and offline measurements. The purpose of the offline measurements is to characterize the water-

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soluble component whereas the online measurement looks at the properties of aging beta-caryophyllene SOA. For offline measurements, the SOA formed in the chamber is entirely devoted for filter collection, so enough mass can be collected and regenerated for offline measurement. We have clarified these points in the text.

One concern is that it was not clear to me which experiment(s) included filter sampling. I gather that a filter sample was only obtained during one experiment. Table 1 indicates that filter collection occurred during experiment 3, in which no OH was present. The text (p. 10113, lines 15-17), however, indicates that the filter was collected during an experiment in which oxidation was by OH and O₃, suggesting that it was collected during experiment 2. This is an important distinction, since (as noted on p. 10109, lines 26-27), the nature of water-soluble oxidation products from the O₃ and O₃ + OH systems are likely different. If filter samples were indeed collected during just one experiment, the conclusions drawn later about WSOC may not necessarily apply to other experiments in the series. The authors found OH-experiments to produce less volatile SOA, and it is entirely possible that there was significantly different (character and volume fraction) WSOC present in the non-OH experiments. This distinction about when filter samples were taken and the implications and limitations for conclusions about WSOC should be made clearer.

Indeed, the filter sample was collected during Experiment 3, where SOA was formed in the presence of OH and O₃ (the text had a typo and is now corrected). All graphs and data consistently reflect that conclusions about the WSOC fraction were obtained from filter experiment 3.

Next, chamber experiments are generally carried out at VOC concentrations above ambient. One consequence is that, at these higher VOC loadings, some semivolatile oxidation products that might otherwise remain predominately in the gas phase will partition to the aerosol phase as SOA. The presence of this more volatile SOA can significantly alter hygroscopic properties (Duplissy et

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al. GRL 2008). One would expect this more volatile fraction to be less polar, and therefore less hygroscopic. This is the opposite of what is observed in the present study, with more volatile species appearing to be more hygroscopic.

Duplissy et al (2008) studied illuminated α -pinene NO_x SOA, which is quite different from the dark/ β -caryophyllene/ O_3 system studied here. Despite the large differences between the two, both show an increasing hygroscopicity/CCN activity with ageing of SOA. The precursor concentrations in both studies are under 50 ppb, and we use about 3 times greater than the “preferred condition” of Duplissy et al, (2008). Given this, and that we carry experiments under excess O_3 , the SOA in this study is likely atmospherically relevant. With that said, future work should focus on lowering the precursor concentrations to as low levels as possible.

Oxidation reduces volatility if occurs through addition (i.e., does not affect the “backbone” structure, or carbon number of the molecules). Fragmentation however, could give increase both hygroscopicity and volatility. If occurring, the WSOC would have reduced average MW (compared to the parent hydrocarbon) and increased volatility of the soluble fraction; both effects are seen in this study. We have added this comment in the manuscript.

Oligomerization is briefly mentioned in the manuscript, but it is not considered a reasonable explanation for the observed trends, nor is a real explanation for the trends advanced. While the reviewer feels that this finding is inherently valuable and understands that a thorough explanation would require much more detailed experiments, one is left without a compelling reason to believe that semivolatile hygroscopic material fully explains the observed discrepancies between the two instruments. For example, can one distinguish any changes in MW as time progresses? If not, the authors may more firmly rule out oligomerization.

Oligomerization may contribute the insoluble (less volatile) material, which could partially dissociate into (more volatile) monomers upon heating. Hydrolysis of the

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oligomers is also possible, which could contribute the soluble fraction. The data at hand is not sufficient to support or rule out the latter, and is left for future work.

The findings about semivolatility of the hygroscopic components, and the implications for measurements of CCN, are important. This is perhaps the strongest part of the paper, and the authors may consider emphasizing these findings further. Specifically, these results are significant for field measurements of CCN.

We have further emphasized these findings in the abstract and conclusions of the paper.

It would be of value to emphasize the error that could be introduced by measuring CCN at elevated temperatures in the field. This is touched on (p. 10126, lines 23-24), but I envision a line reading something like: “If the volatility observed here is applicable to the real atmosphere, It is possible that CCN measurements made at 10 degrees above ambient could introduce an overestimation in CCN activity on the order of ____%”. This inclusion certainly isn’t necessary, but would be nice for framing the significance of this study’s volatility findings.

The degree of overestimation is a strong function of instrument temperature, particle size and oxidation state; this prohibits making a general statement on the bias. However, we have emphasized that volatility of the organic fraction could decrease the soluble fraction, i.e., underestimate the CCN activity of the aerosol, and included a statement (in the abstract) describing the % error found in activation diameter.

Overall, the rest of the conclusions are nicely presented and explained (particularly the kinetic arguments). One other minor suggestion is that the figures should include legends wherever possible, as opposed to descriptions of marker shapes and colors in the caption. It can be hard to move back and forth between text and figure, while at the same time trying to determine what the data show. This may be an issue of personal preference, but I think it would make the figures easier to follow.

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We have attempted to do this as much as possible in the revised manuscript. Adding legends to some figures made them too “cluttered”, so for those only, symbols were defined in the caption.

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