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Atmospheric
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Discussions

Interactive comment on "CCN activity and droplet growth kinetics of fresh and aged monoterpene secondary organic aerosol" *by* G. J. Engelhart et al.

G. J. Engelhart et al.

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(1) *Referee: The Abstract should be rewritten.*

Response: The abstract has been revised for increased clarity and the discrepancy in soluble material values has been corrected.

(2) *p. 98, lines 5-8: Previous work on SOA: all of the cited references here are to CCN studies of pure organic compounds, some of which may indeed be minor components of SOA. I do not understand why they are cited as previous work on SOA;, when there are several studies that actually did look at SOA systems. In the sentence prior to this one, the King et al (2007) study is cited: they did actually generate monoterpene SOA,*

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and compare their findings of CCN activity to prior work also cited here. Again those values are generally in agreement, within the experimental uncertainties, with this work and with prior work.

This has been rewritten to indicate that the studies cited used single or multiple known SOA components without generating SOA. The reference to the SOA work of King et al. has been added to the rewritten section that follows.

(3) *p. 98. The Van Reken et al. study did find lower CCN activity toward the end of their experiment, but similar or higher near the beginning. See the plotted comparison of some of the Van Reken data against other work that appears in Prenni et al. (2007).*

This point has been added to the paper.

(4) *p. 98, l 17: The Prenni et al. study is mentioned, but unlike the discussions of the Van Reken and Huff-Hartz papers, no quantitative information is given about our findings. These are easily accessible, especially since we compared our data to both of those studies. The values from King et al. (2007) should be added here as well. There may be additional studies of CCN activity of monoterpene SOA that have recently appeared; the authors should check that they have gathered all of the relevant references. One issue that may arise with the intercomparison is that not all of the data are presented in a similar format as here, namely the critical dry diameter at a specified percent supersaturation. However, all of the data can be interconverted to these values. Such an update to the comparison presented by Prenni et al. would be a very beneficial addition to the literature and would serve to build confidence that monoterpene SOA CCN activity is now well-understood.*

In order to balance the comments by both reviewers we have revised the last part of the introduction to focus on the important points in a shorter more concise way as well as to expand the previous research cited to give a more accurate view of the body

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of evidence of monoterpene CCN understanding. The quantitative comparisons have been removed from the introduction.

(5) *One thing that is not mentioned in this discussion of prior work is that several different methods were used to determine CCN activity. For example, Van Reken integrated the size distribution to the 50 percent number activated to estimate the critical diameter, while Prenni et al used monodisperse particles and either scanned size or supersaturation. Different CCN counters were used as well. These differences in experimental approach should introduce some scatter into the findings.*

The different approaches used in the measurements are now mentioned in the discussion of previous work.

(6) *p. 100, l 20: Parameterization of the CCN properties of this important class of SOA is missing. This statement is not true. Petters and Kreidenweis (2007) give a parameterization, in terms of kappa, of CCN activity of a-pinene and b-pinene SOA (they are the same). We include the observations of Van Reken and Huff Hartz in the estimate. The equivalent kappa values I calculate for King et al. and for this work (see below) are within these estimates.*

The fitted hygroscopicity parameter is now introduced at the beginning of the paper. While the parameterization proposed here is different the reference to missing past parameterizations has been removed.

(7) *Section 2: Experimental methods: It seems the monodisperse aerosol was generated using a 5:1 flow ratio (it is not clear from p. 102, lines 1-3 what the flow ratio was, but this is the ratio quoted earlier in this section for the SMPS). This is the same flow ratio used by Prenni et al (2007) to sample smog chamber SOA and by Petters et al. (2007) to sample aged organic aerosol from a smog chamber. In those studies, we* *found that it was necessary to account for multiply charged particles in the CCNc inversion to determine correct critical diameters, and developed the approach described in Petters et al. (AST, 2007). In that paper we show that the correction is most important for large critical diameters (low hygroscopicity), but depends on the input size distributions. They were measured in this study (p. 100, line 14-15) but not reported. I expect that the multiplet correction is not critical for the findings here, but the authors should explain whether it was applied, and if not, justify why it is not needed.*

A brief description of this has been added to the paper. The sigmoidal fit for the DMT CCN counter is only conducted on the particles above the early activation hump, which can be attributed to the multiply charged particles exiting the DMA and entering the CCN counter and the CPC. This is apparent in Figure 2 as the fit drops off to zero rather than following the multiply charge early activators. A non-linear least-squares fit is used for the static CCN counter fit to the sigmoidal curve. There are very few data points in the region of concern for multiply-charged particles and thus the fit is not changed much due to these particles.

(8) *Also in Section 2, I may have missed a discussion of how uncertainties in the measurements were generated. This should be included. Finally, one very important consideration that I think belongs in Section 2 is described in Section 3, Results: namely, the findings for ammonium sulfate test aerosol.*

This uncertainty discussion has been moved to the experimental methods section, which was then broken into subsections for clarity and emphasis on the use of two distinct CCN measurement tools.

(9) *Page 105, Section 3.2: Using the parameters from classical Kohler theory given here, I compute kappa=0.15. From Figure 3, rough estimates of the variation in kappa that these points represent are 0.1 < kappa < 0.2 for 0.33 percent supersaturation. Especially considering the offset in calibration from Prenni et al., their value of 0.1 +/-*

0.04 (as summarized in Petters and Kreidenweis, 2007) is in excellent agreement with this present estimate.

This is a very good point. We have added these calculations in section 4. This also allowed us to move some of the comparisons out of the introduction. We do agree that the kappa has the advantage of allowing readers to compare results across systems quickly.

(10) *Section 3.2, Aging of SOA particles: This section is interesting, and potentially quite useful to modelers. It would be good if the information could be made more quantitative, that is, the change in critical diameter with time in the chamber is given, but the relevant parameter for the atmosphere is the equivalent atmospheric aging, which is approximated as 2 days from the ozone levels used. It is also important to note whether the aging changes CCN activity appreciably, but to evaluate this, a common framework is needed, which could be the critical diameter or the molecular weight.*

The change in activation diameter due to oxidative aging in the chamber is modest for this system. We have added some discussion but given the small effect we would prefer not elaborate further.

(11) *p. 104, line 26: a DRY density of 1.77*

This has been amended.

(12) *p. 105, lines 19-21: The change in critical diameter in the initial part of the experiment might be due to higher uncertainty, rather than a real physical change, if low or rapidly-changing number concentrations of appropriate particle sizes are present. (The multiplet correction may be more important at the start of the experiment as well.) As the size distribution stabilizes by coagulation, there are more particles in the 50-100 nm size range, which is where the CCNc needs to sample from. Can the authors comment on this possibility?*

If the multiple charge correction were more important at the beginning of the experiment then the activation diameter would be smaller than real conditions. In this case we saw a slightly increased activation diameter. Also, as the reviewer notes there are fewer larger particles in the system which reduces the opportunity for doubly charged particles. There is a greater uncertainty in the activation diameters for the first 30 minutes due to the rapidly changing size distribution. This is especially true for the static CCN counter which requires 7.5 minutes for a sample, which is on the timescale of the reaction, condensation, growth and coagulation. The higher uncertainties in the data during this time period have been noted in the paper.

(13) *Figure 7 is a very nice summary. I would suggest to use ln sc- ln diameter axes, because these yield nearly straight lines and the relationships are easier to see. The authors could also, similar to Prenni et al., show prior work on the same figure to demonstrate the agreement (or lack thereof) between the various monoterpene SOA CCN studies. I think the information shown here is essentially the same as that in Figure 14 (or could be made the same by including the 15 percent uncertainty in the Kohler fit parameters in the SOA line in Figure 7). If that is the case, then Figure 14 is not really needed.*

The axes have been changed as suggested. Since we are already comparing two instruments and two types of precursors we believe adding previous work to the figure would make it rather confusing. Figure 14 is a comparison of the very simple classical Koehler theory to the experimental calculations and is therefore important to demonstrate this. The use of a priori knowledge to estimate the CCN activity of these SOA particles is quite interesting and is highlighted by this figure.

(14) *Section 3.4: In this section (and also Section 4, and whenever else the best-fit parameters, especially molecular weight, are quoted), ALL of the assumptions that are needed to get to an estimate of molecular weight must be clearly identified.*

This information has been added.

(15) *Section 4: lines 6-8: here it is omitted that also values for vant Hoff factor and solubility have to be assumed for the parameterization.*

This has been added.

(16) *Page 112, lines 20-23: similar to activation diameters estimated from classical Kohler theory: I do not see how this is possible, since the classical theory assumes a single component with known properties, or at least multiple components with known properties. Clearly, SOA does not meet these criteria. Kohler theory was FIT to these data, as well as in prior studies, but no a priori estimate is possible. Perhaps the authors are referring to single-component organic studies. Table 1 in Petters and Kreidenweis (2007) attempts to summarize and compare these, for the data available up to the time that paper was prepared.*

This is precisely why we find this approach so interesting. In the KTA analysis we fit the data, but here for the parameterization we base our estimates for parameters on assumptions/previous information. For example, the average molecular weight for known alpha-pinene SOA species is approximately 175 g/mol (Huff Hartz et al., 2005). This is based upon a priori knowledge, but this maps quite nicely on the 180 g/mol MW determined in this work through KTA analysis. We used 180 g/mol throughout this work for the molecular weight of this SOA species. The simplest assumption is that the SOA contains many acids with very low acid dissociation constants, so we use an estimate for the number of dissolution ions of 1. We assume the surface tension of water and complete solubility based upon the small amount of solute in the CCN droplets. The KTA analysis tells us that this assumption introduces some error, but it still allows to a nice a priori estimation that matches the data quite well.

(17) *The final paragraph of the paper should be modified to reflect the comments* *above, namely: how this work fits in with other monoterpene studies that together already suggest a single CCN-parameter (whether that be kappa, molecular weight, or critical diameter) value for monoterpene aerosol; and how that value compares with other particle types (i.e., a more quantitative estimate of good CCN activity).*

We have followed the suggestion of the reviewer and rewritten the last paragraph.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 95, 2008.

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