

Interactive comment on “Hygroscopicity of secondary organic aerosols formed by oxidation of cycloalkenes, monoterpenes, sesquiterpenes, and related compounds” by V. Varutbangkul et al.

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We would like to thank the reviewers for their valuable comments and suggestions to improve the manuscript. Below is our point-by-point reply to reviewer #1's concerns or suggestions (which appear in italics).

Reviewer #1:

The statement in the introduction that the low-hygroscopicity fraction in ambient aerosol is likely attributed to the presence of secondary organic aerosols, whether in urban or rural areas, is not correct. I agree that this may be the case in rural areas, however, in urban areas this is mainly due to the presence of primary soot particles.

We agree with the reviewer that in urban areas, the low-hygroscopicity fraction could also be due to primary soot particles (although, of course, the contribution from SOA cannot be ruled out altogether). The sentence was modified accordingly.

I understand that the ozonolysis experiments were run dry (relative humidity $RH < 10\%$) while the terpene photooxidation experiments were performed at an RH of about 50%. I suggest that the motivation for this difference is added along with a sentence on the consequences that this may (or may not) have on the chemistry and thus on hygroscopic properties of the corresponding SOA.

The ozonolysis experiments were performed in a dry chamber in order to keep the chemical mechanisms as simple as possible for a concurrent set of particle-phase chemical speciation analyses. The terpene photooxidation experiments were performed in a humid chamber in order to achieve a more atmospherically relevant environmental condition for the PTR-MS gas-phase composition measurement. Because the cycloalkene family was meant to be a set of “model compounds” rather than representative of atmospherically relevant species like the biogenics, we felt that the dry condition was sufficient for the hygroscopicity and yield measurements.

Hypothetically, the reaction mechanism of the cycloalkene ozonolysis could be dependent on humidity. For example, higher RH could increase the reaction rate of stabilized Criegee intermediates with water molecules, potentially changing the distribution of semivolatile species. However, it has been suggested that the effect of water on the stabilized Criegee intermediate of smaller cycloalkenes (carbon number of 8 or less) would be minor, since the dominant reaction pathway is through that of the excited Criegee intermediate that readily breaks down into other products (Chuong et al., 2004). In the end, it is unlikely that such minor effects on chemical composition would be captured by the hygroscopicity measurement. (This discussion has been added to the manuscript.)

The bimodal droplet distributions in the seeded cycloalkene ozonolysis experiment

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(Fig. 4) are indeed interesting. The authors explain this observation with differences in the organic volume fractions, and provide three different potential explanations for this. Their first explanation relates to the fact that the seed is not ideally monodisperse. Thus, particles of a certain size selected in the first DMA might have a varying organic fraction and thus a varying growth factor (GF). I agree that a spread of the seed particles over a certain size range results in a spread of the corresponding GF, however, a bimodal GF distribution is not possible in this way. This would only be possible with a bimodal seed size distribution. As the authors will have recorded the size distributions also for the seed particles this reason can probably easily be excluded.

The reviewer brings up several good points in this discussion of the reasons for the bimodal droplet distribution. It would indeed be unlikely that particles consisting of a smooth range of organic fractions would exhibit a clear bimodal GF distribution, and this counter-argument has been added to the manuscript. Our $(\text{NH}_4)_2\text{SO}_4$ seed size distributions are entirely unimodal, and information on the mode diameter and standard deviation of this initial distribution has been added to the paper for both wet and dry seed.

The third reason relates to the fact that large, doubly charged particles would have a lower organic fraction. These would then exhibit a higher GF. However, as the seed particles have probably a mean geometric diameter of less than 180 nm (no size distributions are given) the probability of doubly charged particles with a higher GF would increase with time opposite to what is observed. (The authors mention that about 10% of the particles are doubly charged, however, this number will vary with time, due to the change of the particle size relative to the dry diameter of 180 nm; this should be mentioned). In any case, this effect is not likely to explain the bimodality.

There are some competing effects when considering the time evolution of the relative contribution of the doubly-charged particles with lower organic fraction in the classified particle population. The fraction of 10% (of doubly-charged particles in the total classified particles) was estimated for early times in the experiment. The reviewer is

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correct in that the number of doubly-charged particles (at 289 nm) transmitted at the same voltage as the 180-nm singly-charged particles would increase with time due to shifting size distribution (this has been added to the text). However, as the experiment progresses, the difference between the organic fractions at 180 and 289 nm also decreases quickly, and the organic fractions of both sizes quickly approach unity for most compounds. This translates to the droplet distribution becoming more unimodal at the less-hygroscopic mode. Therefore, even though the bimodality disappears at larger times when one would expect there to be higher contribution of doubly-charged particles, it does not necessarily mean that the doubly-charged particles do not play a role in introducing some bimodality at early times. In general, however, we agree with the reviewer that the primary reason for the bimodality is probably the inhomogeneity of the chamber induced by the slow ozone injection.

Thus, I agree with the authors that the second reason is the most likely one, i.e., an inhomogeneity in the bag due to the slow injection of ozone, which takes 2.5h to complete. The fact that this bimodality is not seen in the photooxidation experiments also points to this inhomogeneity induced by the ozone flushing. If the mixing in the chamber were fast this would just result in a broadening of the GF distribution. However, the fact that two distinct modes are formed indicates that the mixing is rather slow. This in turn results in important caveats in such ozonolysis experiments: Any chemical analysis that is not able to discriminate between individual particles and thus determines a bulk information of the particle ensemble or even a bulk information of a specific size cut (including the aerosol mass spectrometer!) may be prone to errors or misinterpretation.

We agree that the AMS is in fact prone to some errors due to different growth trajectories of particles at a certain size, due to slow ozone injection or otherwise. The measurement of size-resolved organic fraction is meant to be an average of a small range of organic fractions that probably exist in a monodisperse population at the end of the experiment. Nevertheless, in the large time limit, the organic fractions at all sizes

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are very close to unity, thus making this error minimal. Also, we did not present any hygroscopic growth curves from the seeded cycloalkene ozonolysis experiments that required AMS size-resolved organic fraction data. Nucleated SOA was generated for this purpose.

Table 3 gives the GF for each SOA. It should be mentioned for which time these numbers are given. Obviously, GF will grow over extended periods of time, in some cases resulting in lower limits, like in the 1-methyl cycloheptene experiment in Fig. 5, where the final state is not reached yet.

The growth curves of the cycloalkene ozonolysis experiments were determined after at least 150 minutes from the beginning of ozone injection, after the organic volume has at least leveled off, and continue to at least 400 minutes after start of reaction. When the RH is ramped up and down, we do not see a detectable change in GF with time at a certain RH, suggesting that the GF of most of the compounds has already leveled off by this time.

The result of Fig. 8, where a substantial decrease of the water content (or decrease of the GF) is shown is surprising (in fact this is the water content at 50% RH, which should be mentioned in the figure caption; the same applies to Fig. 11).

The notes have been included in the captions, and the chamber RHs have been added to each figure legend.

I agree that SOA oxidation and oligomerization are competing processes which may result in an increase or decrease of GF with time, depending on the relative importance. However, to my opinion it is unlikely that oligomerization should be so greatly different for alkene SOA and sesquiterpene SOA. How does the monoterpene SOA behave? Figure 11 only shows the GF change of total SOA (including the inorganic seed) with time, however it would be interesting to see the GF evolution of the SOA alone.

Unfortunately, we were unable to determine the change in GF of the “pure organic

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portion” of the monoterpene SOA because the AMS size-resolved organic fraction measurement was quite noisy, due to the fact that the organic condensation occurred quickly. We have rewritten some sentences in the abstract and conclusion, however, that could be construed as a claim that we observed the pure monoterpene SOA portion also becoming less hygroscopic with time.

There may be another reason for this behavior: To determine the GF the aerosol is dried with a Nafion dryer. It could be possible that some of the semivolatile material is also lost in this drying process. As the SOA gets less volatile with time (both through oxidation and oligomerization) this loss may become smaller, resulting in an erroneous decrease of the water content with time.

The possibility of losing some semivolatile species during the drying process in the Nafion dryer is certainly possible. However, we believe that it is unlikely to occur significantly enough to cause the observed magnitude of decrease in water content for two reasons. First, the particles never actually pass through the Nafion dryer itself; only the filtered air from the “excess” flow from the first DMA passes through it and recombines with the classified aerosol stream at the base of mixing column (please refer to the instrument schematic in Figure 1). Thus, the removal of any species in the dryer would only be from the gas phase in the particle-free air stream. While this could cause some repartitioning of semivolatile species from the particles once the two streams recombine, the overall effect would be small compared to if the particles actually pass through the Nafion dryer. Second, the Nafion membrane only allows transport of a few types of molecules across it: water, alcohols, ammonia, and primary and secondary amines. Ammonia and amines are not relevant to our systems, and alcohols are unlikely to be present in fractions as high as 90%, which is roughly the amount necessary to account for such a drop in water content in time (from a water content of 10% to 1%). Thus, we believe that the observed decrease in water content with time in sesquiterpene SOA is real.

Minor issues: The reference Lee et al. (2005) in the text should read Lee et al. (2006).

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Corrected, with updated reference of the published paper.

Fig. 6: the exponent 0.8842 should be -0.882 (the exponent A is mentioned to be a positive number, see Table 3; eq. 2 mentions -A as the exponent).

Corrected (from 0.3842 to -0.3842 to match the actual value).

References

Chuong, B., Zhang, J. Y. and Donahue, N. M.: Cycloalkene ozonolysis: Collisionally mediated mechanistic branching, *Journal of the American Chemical Society*, 126, 12363–12373, 2004.

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