

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

### **Anonymous Referee #1**

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This is an impressive piece of work. The hygroscopicity of secondary organic aerosol (SOA) has been investigated for a wide variety of SOA precursors. The paper should be published in ACP after considering the following comments, which mainly concern the interpretation of results.

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.

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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 bimodal droplet distributions in the seeded cycloalkene ozonolysis experiment (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 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. 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

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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.

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 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). 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. 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. Certainly, experiments applying the traditional approach with the dryer placed before the sizing by the first DMA, followed by humidification will bring clarity to this point.

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

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