

Interactive comment on “Volatility and hygroscopicity of aging secondary organic aerosol in a smog chamber” by T. Tritscher et al.

Anonymous Referee #3

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This manuscript describes laboratory experiments aimed at understanding the “aging” (chemistry that lead to changes in physical properties) of secondary organic aerosol (SOA). In a very nice set of chamber experiments, α -pinene is oxidized by ozone, and after some time the resulting reaction mixture is then oxidized further by OH radicals. The data (including volatility, hygroscopicity, aerosol growth, and O:C ratio) are interpreted in terms of both condensation (SOA-forming) processes and “ripening” reactions. The overall goal of this work (understanding OA aging) is very important, the experimental approach is quite nice, and the data seem to have been very carefully collected and analyzed. However I have several concerns about the interpretation of the data – the authors make many assertions about the underlying chemistry that either are not explained well or do not appear to be supported by the experiments. Additionally, I had difficulty following the various arguments made; a large number of

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experiments with several variables (pinene concentration, O₃ concentration, light, OH source...) are described, but without enough organization to make the key points of the work clear. (The Summary and Conclusions section certainly helped with this, but many of the previous sections, like 3.1, 3.4.1, and the first part of 3.5 still seem tangential.) This paper thus needs major revision (possibly with additional experiments) before it can be published. Specific comments follow.

1) Throughout the paper, the authors assert that observed physical/chemical changes are related to the presence of oxidants, but no control experiments (studies of what happens in the absence of these oxidants) are ever described. For example, references are made to “O₃ mediated ripening”, but with no evidence that ozone has anything to do with it – possible processes that come to mind include oligomerization, or loss of certain species to the chamber walls. The authors provide no evidence that O₃ is in any way involved, so I don’t see why this can be called “O₃ mediated”. The proper control experiment would be to run the experiment in an excess of α -pinene, so that SOA in the absence of O₃ can be studied. Similarly, for OH: what happens when the lights are turned on, with no HONO added? How are the authors sure that the extra organics added to the chamber (pentanol and TME) are playing no role in the observed physical/chemical changes?

2) I don’t understand the need for introducing the new term “ripening” to the SOA lexicon. In addition to it being a rather silly word, it’s unclear how it is in any way different from “aging” (which is in the title of the paper). If the authors insist on using this term, its definition needs to be laid out in detail, and the differences between “ripening” and “aging” need to be explicitly discussed.

3) Based on the data presented it’s not clear to me that “ripening” (from O₃, OH, oligomerization, etc) ever actually occurs. It’s defined (p. 7424, lines 17-18) as changes in the properties of the aerosol that are not accompanied by changes to particle mass. But given that the authors feel their wall loss estimates are “conservative” (p. 7740, line 3), is this criterion ever actually met? Might the flat mass loading in the ozonolysis

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reactions actually be increases in aerosol mass? Even without an increase in the wall loss correction, for OH aging, mass very clearly goes up continuously (top right corner of Fig 6). Why is this interpreted as ripening?

4) The figures are very busy and hard to read/interpret. Part of this arises from the differences in y-axes, x-axes, and symbol/color conventions, even when the figures were quite similar (e.g., Figures 5-9). Standardization of these would help a lot. Additionally, many of the changes in the various parameters measured (O:C, kappa, VFR, loading, etc) are quite subtle, and are very hard to make out given the highly condensed y axes and overlain datasets. Multiple side-by-side plots with aspect ratios of $\sim 1:1$ would be far easier to read and interpret; some data averaging could help as well.

Other comments:

Ozone has previously been shown to cause physical/chemical changes to organics with no C=C double bonds, presumably due to additional oxidation reactions [Shilling et al., JPCA 111:3358, 2007]. That earlier work seems highly relevant to the present studies, and should be discussed here

P. 7425, line 14: Volkamer et al 2006 utilizes a box model, not a chemical transport model.

P. 7426, lines 7-8 and P. 7427, lines 15-16 (and Table 1): for aging/ripening, an important set of reactions involve conversion of one functional group to another. Assuming this is considered a "functionalization" reaction, changes to volatility, hygroscopicity, etc are not always fixed: for example, the oxidation of an alcohol group to a carbonyl group involves an increase in vapor pressure and a decrease in hygroscopicity. Also, fragmentation reactions will generally increase solubility (consider acetaldehyde fragmenting to form formaldehyde), whereas oligomerization reactions will generally decrease it.

Table 1: what does the last column mean?

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P. 7427, line 27: these three processes are different than the three discussed in the previous several paragraphs.

P. 7428, lines 22-24: of what magnitude was the wall-loss correction? (20%? 100%? 300?)

P. 7428, lines 24-25: how was the collection efficiency (CE) of the AMS computed? Was the possibility of changes to the CE upon aging investigated?

Section 2.3: what are the temperature and RH of the chamber? Do these change with reaction time, lights, etc?

Fig. 3: The OH trace is misleading, as OH is not zero during the ozonolysis phase – it almost certainly plays an important role then.

P. 7434, line 11: The authors mention two mechanisms of "ripening", but several more seem possible. Slow oligomerization, photolysis, thermal decomposition, etc.

P. 7435, line 1: After a couple hours, pinene is no longer in excess, so OH will start reacting with other species. (OH+a-pinene is not terribly fast, with $k=5e-11$ cm³/molec/s, so OH+aldehydes will be able to compete). As a result, the assertions that there are only first-generation products around at the end of the "ozonolysis phase" of the reactions (e.g., p. 7440, line 14; p. 7447, line 20) is quite misleading.

P. 7435, line 18: what was the initial concentration of the TME?

P. 7435, lines 22+: the use of four separate metrics to describe reaction time is very confusing, and makes the reading of the plots (which use all four as x axes!) quite difficult to intercompare. Can these be simplified in any way?

P. 7436, line 2+: why was pinonaldehyde decay and not pentanol decay used? Were the data corrected for possible photolysis or wall loss of pinonaldehyde?

P. 7436: the units h/cm³ seem a little strange. I would recommend h molecules/cm³.

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Section 3.1 and Figure 4: I would suggest removing this section, as it seems only tangentially related to the overall paper (which is about aging). The key to this work is how the aerosol properties change in a given experiment (the “large vertical error bars”), not how they compare to each other or to results from other studies.

Fig. 6: why are similar plots for TME+O3 not shown?

Fig. 6: the grey dotted lines seem a bit misleading, as they don't always go through the data terribly well. Linear fits for the different regions are needed.

P. 7442-3, lines 28+, and P. 7448, lines 16-18: I simply don't agree with the authors' assertions that the OH source doesn't make a difference. From Table 2, the drop in VFR for the TME data is far less pronounced than for HONO. (This would be more obvious if a version of Figure 6 for the TME+O3 experiments was presented.)

Figure 8: why are no HONO data shown?

P. 7445, lines 16+: This paragraph seems unrelated to the title of the section it is in (“Ripening and size dependence”).

P. 7445, lines 23-24: I don't understand the chemistry here; to my knowledge there is no evidence that O3+TME generates more OH in the presence of light. Was there an inferred increase in OH from pinonaldehyde decay? If so, could this have arisen from pinonaldehyde photolysis? (If this is the case, it would suggest that light, and not necessarily OH, is responsible for the observed changes.)

P. 7447, lines 26-27: increased OA mass will lead to more volatile compounds partitioning into the aerosol, not necessarily “smaller” compounds. While the higher volatility can arise from smaller size, it can also be from lower polarity, which would imply a lower kappa value.

P. 7448, lines 4-5: the O:C changes are rather subtle, when compared to the changes in particle mass, so I think it's not accurate to call the newly condensed organics highly oxidized.

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The Summary and Conclusions section could be strengthened further with a “cartoon” that illustrates the key processes involved.

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