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Interactive comment on “Aging of secondary organic aerosol from small aromatic VOCs: changes in chemical composition, mass yield, volatility and hygroscopicity” by L. Hildebrandt Ruiz et al.

Anonymous Referee #1

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Overview

In this manuscript the authors report the results of toluene photochemical chamber oxidation experiments. The authors vary the photochemical oxidation conditions and measure the changes in aerosol oxidation state, volatility, and hygroscopicity. They also photochemically age the aerosol in the presence of NO_x and report the effects of aging on these properties. The topic is of general interest to the readers of ACP and the paper is generally clear and well written. However, there are two main issues that

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need to be addressed before the manuscript can be published.

First, it isn't clear what new scientific knowledge this paper adds to the literature and it is less clear what the implications of this work are for the atmosphere. In some experiments a particular property evolved with one trend while in another similar experiment the opposite trend is observed. Some experiments designed to be replicates of one another produced very different results. In the case of aerosol hygroscopicity, there is no clear trend among experiments with OA oxidation state. The authors don't provide a very convincing explanation of these differences and it is difficult for me as a reviewer to identify any unifying message the authors are trying to convey. The authors seem to struggle to come up with very substantial conclusions with the last two paragraphs of the conclusions section largely saying that aging remains a puzzle. After reading the paper, I didn't come away with any particular message regarding aerosol aging and am instead left wondering how or if this can be applied to the atmosphere. Second, the authors do not discuss irreversible wall loss of semi-volatile species, which has been shown to be substantial and important for this (and many other) chemical system. Wall loss has been offered in other manuscripts as an explanatory factor for many of the observations the authors present. Therefore, it is not clear that the many of the authors' observations are not biased by wall loss. Indeed, I suspect the authors struggle with their conclusions precisely because they are aware of this problem but are unsure of how to deal with it. Therefore, it is quite difficult as a reviewer to recommend this manuscript for publication in its current state. If these issues can be addressed the manuscript may be publishable, though the wall loss artifact will be difficult to evaluate.

Major Comments

The largest deficiency of this manuscript is that the irreversible loss of semi-volatile species to the walls of the chamber is not considered or discussed. Zhang et al. have recently shown that a significant fraction of SV species are lost to chamber walls during toluene photooxidation (Zhang et al., 2014). They report that this loss is substantial, with 50 – 80% of the products lost to the walls and they show that this effect depends

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on seed concentration and OH exposure, among other factors (Zhang et al., 2014). Other researchers have also concluded that faster chemistry (i.e., higher OH exposure) helps to minimize wall loss (e.g. (Kroll et al., 2007)) and that lower-volatility, more highly oxidized species are more likely to be lost (Matsunaga and Ziemann, 2010). Therefore, it seems plausible that the entirety of section 3.2 could/should be explained by variable wall loss driven by the different oxidation conditions. Figure 4 strongly suggests these effects, with lower yields found at similar aerosol mass loadings for the slower reacting, lower OH exposure experiment. Furthermore, the difficulty the researchers report in reproducing their observations during experiment designed to have identical oxidizing conditions (p 31458, second paragraph) suggests that wall loss is a contributing factor (probably the driving factor) to their measurements in these two experiments. The authors need to discuss wall loss and why they feel it isn't the explanatory factor in their experiments before publication. As it stands now, I'm not convinced that many of their observations and conclusions are not biased by an experimental artifact, albeit one that may very well be driven by the changes in the oxidizing conditions.

After reading the manuscript, it isn't clear what conclusions can be drawn from these experiments, what they contribute to the existing body of SOA literature, or what the implications of this work are for the atmosphere. There is no correlation between OA oxidation state (or O:C) and CCN activity. Sometimes the OA oxidation state decreased as the experiment progressed (Experiments 2 and 3) while sometimes the opposite was true (Experiment 9 and most others?). In some experiments OA oxidation state correlated with volatility in others it didn't (Figure 6). Sometimes experiments designed to have identical oxidation conditions produced very different results (Experiments 2 & 4). Most of the explanations the authors offer for these differences involve significant hand-waving and are not very convincing. If one considers the considerable uncertainties introduced by wall loss, it becomes even less clear what was learned from these experiments. The manuscript would be greatly improved if the authors can offer more definitive and clear conclusions and discuss what the atmospheric implications of this work are.

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Finally, before publication, the Materials and Methods section of the paper should be significantly shortened with much of the material either left out altogether or moved to the supplementary material. Often, the authors give lengthy descriptions of procedures that don't impact a readers understanding of the paper. For example, section 2.2.3 is approximately one page long, but the second sentence by itself is sufficient to describe what was done. At the same time, there are places where there are too few details, namely in terms of the "other small aromatic VOCs" that were used in the experiments. These other VOCs are mentioned in the title, abstract, and as footnotes in Table 1, but nowhere else in the manuscript. The hypothesis that these experiments were testing is not described and it certainly isn't clear. Therefore, it is impossible for reviewers to evaluate these experiments. The authors should either provide more details on the other VOCs (concentrations injected, how SOA was separated from toluene SOA, what fraction of SOA is from toluene vs. other, etc.) and how they affected the experiments or simply remove those experiments from the paper and make the associated changes to the title and abstract. It appears that only experiments 6 and 8 employed other VOCs and the conclusions of the paper don't rely on these experiments, so it is puzzling as to why the authors provide so many details on other aspects of the experiment but provide no description on this aspect of the experiment.

Technical and Editorial Comments

Title: Since the author don't separate aging from SOA formation and acknowledge this in the manuscript, shouldn't the title be changed to reflect this fact?

P 31455, Lines 3-5. It seems very unlikely that the mean carbon oxidations state is three, 20 minutes into the experiment. This would require approximately 10 oxygen atoms being added to the molecule in 20 minutes. The authors should remove this statement from the manuscript or justify how this could be possible. It seems more likely that the unreasonably high oxidation state is a result of low S/N or some other artifact.

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Figure 2, Experiment 2 panel: It appears that the organic aerosol concentration at the beginning of the experiment is not zero. Please comment on the source of the background aerosol.

P31455, lines 14-16 and 23-24. There is a contradiction here or else the message the authors are trying to convey is unclear. Lines 14-16 say that the aerosol oxidation state increased in experiment 9 and in all other experiments. A few lines later, experiment 3 is discussed and the oxidation state decreases during the experiment. Please correct this.

Figure 8. I recommend moving this figure to the supplemental material. It isn't discussed in the text, is only mentioned in one sentence, and only shows the fitting routine is adequate.

Figure 9. The trendline seems to be driven to a large extent by the single point at the upper left in the graph. How confident are the authors in this point? Without it, it appears that the fit would produce a very different slope and therefore conclusion.

References

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