Atmos. Chem. Phys. Discuss., 11, C9043–C9047, 2011
www.atmos-chem-phys-discuss.net/11/C9043/2011/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Aqueous phase processing of secondary organic aerosols" *by* Yao Liu et al.

Anonymous Referee #1

Received and published: 17 September 2011

General Comments

This manuscript describes a set of cleverly designed chamber experiments on aqueous photochemical processing of dissolved secondary organic aerosol (SOA) material. The authors generate SOA in a chamber, extract the water-soluble fraction in water to achieve environmentally relevant concentrations, add H2O2 to the solution, photolyze it, and re-aerosolize the solution. The composition of the organic material is followed with an aerosol mass spectrometer (AMS) and thermal desorption atmospheric pressure ionization mass spectrometer (TD-API-AMS). In addition, selected compounds are measured quantitatively in the photolyzed solutions. Finally, the hygroscopic growth factors of the particles are measured at 90% RH using a tandem differential mobility analysis (tandem-DMA) approach. The message of the paper resonates with other recent reports in the literature that aqueous (photo)chemical processing of SOA is a potentially important mechanism of aging.

The AMS detected a fairly insignificant change in composition, especially when compared to the recent study of Lee et al. (2011). However, both the dark and photochemical processing in the presence of H2O2 appeared to increase the hygroscopicity of the organic material. The authors ascribe this effect to the production of soluble carboxylic acids during oxidation by H2O2 and photooxidation by OH. This would have been a very important result were it not for potential caveats in the experiment, which need to be better discussed by the authors. Specifically, I am not convinced that the authors were measuring relevant growth factors for the particles generated from the processed solutions. The atomized solution was dominated by H2O2 (see specific comment 3 below), and although H2O2 is volatile it is also sticky, and a significant fraction of it could remain in the particle and affect the measured hygroscopic factors. The authors should definitively have included hygroscopic measurement for the atomized water + H2O2 solution for comparison. (This is a quick experiment to do; perhaps it can be added to the ACP version of the paper).

While reading this manuscript, I could not shake the impression that the authors could have done a more thorough job in planning their experiments and in analyzing and discussing their data, but for one reason or another did not. For example, they only conducted four chamber runs, which is on the lower end of most chamber experiments. They appear to have forgotten to do a dark blank experiment for the alpha-pinene system. The paper appears to be hastily written: one could do much more with the discussion of the very nice set of the APCI-MS and HPLC data the authors have at their disposal. Perhaps it is a matter of personal preference but I would rather see a more systematic study of one type of SOA than several disjoint experiments for three types of SOA. For the ACP submission, I would highly recommend to get rid of the TMB data entirely (since it is so insoluble, see comments below), perhaps also get rid of the alpha-pinene data (because of the issue with the missed dark H2O2 sample), and focus on the data set for isoprene SOA. The strength of the isoprene SOA data is that isoprene SOA experiments were repeated 2 times, the minimal number required to estimate the experimental uncertainties. Furthermore, a lot of data reported in this paper (such as Table 2) are more relevant for isoprene SOA, not to alpha-pinene or TMB SOA.

Specific Comments

1. The abstract is written in rather disorganized way making it difficult to follow. I would rewrite it, avoid repetition, and focus on the main message of the paper.

2. Not that something can be done about this at this point but the VOC mixing ratios chosen for this study appear to be unnecessarily high. In the alpha-pinene case, the concentration was so high that the size distribution drifted outside the SMPS measurement range. Why was it necessary to obtain "large quantities of SOA" as the experimental section states on page 5? Was there a limitation on the signal-to-noise ratio presented by one of the measurement methods? I suspect the primary limitation was the need to re-aerosolize solutions after processing (atomizers typically need a lot of solution). The authors should explain their choices clearly.

3. I was surprised by the very large disparity in the concentrations of SOA and H2O2 used in these experiments. The authors try very hard to make the SOA concentrations environmentally relevant. Their 1 mg/L mass concentration corresponds to 0.5 uM molar concentration, which is lower than the values used in most previous experiments. However, their H2O2 concentration is orders of magnitude higher, between 15 and 100 mM, and quite high compared to typical cloud water concentrations. Although this is not an issue for the mass spectrometry experiments, the high H2O2/organics ratio makes the interpretation of tandem-DMA experiments difficult.

4. Pages 6-7 and 8-9: there is no real need to have sub-titles for the paragraphs devoted to different instruments. This makes writing fragmented.

5. Page 12: what fraction of SOA was extracted in water? The TMB photooxidation aerosol is not especially soluble. In all likelihood, only a fraction of the TMB aerosol dissolved in these experiments. Indirect support for this can be found on page 15, where the authors state that AMS signals were too low after nebulization of the TMB SOA solutions. Also the lack of correlation between TD-API-AMS spectra of the original and dissolved & aerosolized TMB SOA suggest that it is poorly soluble in water. The solubility does not appear to be a limitation for the isoprene or alpha-pinene SOA due to their (well-known) high solubility in water.

6. Page 12: with the aerosol size distribution falling outside the range of the SMPS measurements, how was the particle mass concentration in the chamber estimated? As this number is used to calculate the mass concentration of the organic material in the extract, it is important to know it accurately.

7. Page 13: It is hard to see how a 300 W Xe lamp can result in a low intensity of actinic radiation in the aqueous phase reactor. Even if the lamp is on its last breath, and if used in the geometry described by Monod (2005), it should still supply more actinic photons than the fluxes existing under typical tropospheric conditions. Perhaps the resistance of the dissolved compounds to photochemistry is real and has to do with lower concentrations used in this study compared to that in Lee et al. (2011)?

8. Page 21: “In the mass range 150-300 Da” is a poor choice for a section title.

9. Page 23. In isoprene SOA, there is a prominent pattern in the mass spectra based on 2-methylglyceric acid (e.g., Edney (2005), Surrat (2006), Nguyen (2001), Zhang (2011), many other papers) leading a repeated difference of 102 Da. In contrast, differences of 12 Da and 28 Da rarely dominate in oxygenated organics.

10. Page 25: there are earlier references to tetrols as markers of isoprene SOA than the one cited.

11. Table 1: were alpha-pinene and TMS experiments done just once? This makes it

difficult to judge the reproducibility of the results, especially in view of the differences between experiments 1 and 2 in isoprene SOA described on page 14. It is not clear whether RH and T values pertain to all four experiments or experiments 2 and 3. It is also not clear why there is no H2O2 concentration specified for the dark alpha-pinene value. Judging from Fig. 3, this experiment has been skipped. Please provide a justification for skipping it.

12. Table 2: the title states that the data are for experiment 3; it should be experiment 2.

13. General comment about the figures: in my opinion, the authors attempt to put too much information in the figures and it makes some of them essentially unreadable. For example, it is very hard to see mass labels in the mass spectra shown in Figure 4. If is also hard to visually see the difference between the mass spectra; this difference could be shown better using different colors or inverted y-axis for the spectrum of processed SOA. Labels in several other figures are more visible but in general are quite small (this applies to legend in Figure 2, panel labels in Figure 3, and more or less everything in Figure 4). I would have expected a bit more care in figure preparation from the authors, who are for the most part very experienced writers.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 21489, 2011.