Anonymous Referee #1
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The authors appreciate many important comments raised by Reviewer 1 which have been considered in the new version of the manuscript. The authors' answers to the questions/comments of Reviewer 1 are presented below.

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 H_2O_2 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 H_2O_2 appeared to increase the hygroscopicity of the organic material. The authors ascribe this effect to the production of soluble carboxylic acids during oxidation by H_2O_2 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 H_2O_2 (see specific comment 3 below), and although H_2O_2 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 + H_2O_2 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 H_2O_2 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.

Answers :

- For the reasons raised in the general comments by reviewer 1 and also reviewer 2, we have focused the new version of the manuscript on isoprene: we modified the title to "Aqueous phase processing of secondary organic aerosol from isoprene photooxidation". Also, the discussions were extended compared to the previous version.
- Regarding the H_2O_2 issue: The experiment proposed by the reviewer does not work. Firstly, water and H_2O_2 does not produce aerosol : the very small quantities of small particles (< 10 nm) that can be observed during nebulization of water are due to water impurities, and the presence of H_2O_2 does not modify the results. Secondly, prior to entering the H-TDMA, the aerosol is dried in a diffusion dryer to <15% RH such that water and the similarly volatile H_2O_2 evaporate and is rapidly destroyed on the walls of the stainless steel tubings.

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.

Answer : the abstract was rewritten as follows:

Transport of reactive air masses into humid and wet areas is highly frequent in the atmosphere, making the study of aqueous phase processing of secondary organic aerosol (SOA) very relevant. We have investigated the aqueous phase processing of SOA generated from gas-phase photooxidation of isoprene using a smog chamber. The SOA collected on filters was extracted by water and subsequently oxidized in the aqueous phase either by H_2O_2 under dark conditions or by OH radicals in the presence of light, using a photochemical reactor. Online and offline analytical techniques including SMPS, HR-AMS, H-TDMA, TD-API-AMS, were employed for physical and chemical characterization of the chamber SOA and nebulized filter extracts. After aqueous phase processing, the particles were significantly more hygroscopic, and HR-AMS data showed higher signal intensity at *m/z* 44 and a lower signal intensity at *m/z* 43, thus showing the impact of aqueous phase processing on SOA aging, in good agreement with a few previous studies. Additional offline measurement techniques (IC-MS, APCI-MS^2 and HPLC-APCI-MS) permitted the identification and quantification of sixteen individual chemical compounds before and after aqueous phase processing. Among these compounds, small organic acids (including formic, glyoxylic, glycolic, butyric, oxalic and 2,3-dihydroxymethacrylic acid (i.e. 2-methylglyceric acid)) were detected, and their concentrations significantly increased after aqueous phase processing. In particular, the aqueous phase formation of 2-methylglyceric acid and trihydroxy-3-methylbutanal was correlated with the consumption of 2,3-dihydroxy-2-methyl-propanal, and 2-methylbutane-1,2,3,4-tetrol, respectively, and an aqueous phase mechanism was proposed accordingly. Overall, the aging effect observed here was rather small compared to previous studies, and this limited effect could possibly be explained by the lower liquid phase OH concentrations employed here, and/or the development of oligomers observed during aqueous phase processing.

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.

Answer : The limitation was the need to dilute the SOA into 160 mL of water: 100 mL for "H_2O_2 + hν" samples (because this was the minimum liquid volume in the photoreactor); and 60 mL for both "control" and "dark H_2O_2" samples as the atomizer needed at least 30 mL of solution to nebulize during at least 90 minutes. This information was added in the new version of the manuscript.

3. I was surprised by the very large disparity in the concentrations of SOA and H_2O_2 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 H_2O_2 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 H_2O_2/organics ratio makes the interpretation of tandem-DMA experiments difficult.

Answer: The use of high concentrations of H_2O_2 was necessary to produce relevant concentrations of OH radicals. We estimate that our OH radical concentrations were 10^{-15} - 5 x 10^{-15} M, corresponding to typical concentrations in urban cloud droplets (Anastasio and McGregor, 2001; Herrmann et al., 2010). For the H-TDMA measurements, see our answer to the general comments.

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.

Answer : We agree, this was corrected in the new version of the manuscript

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.

Answer : Because we have deleted all the TMB and α-pinene experiments, the question remains for isoprene experiments only. It should be noted that the solubility of secondary organic aerosol strongly depends on the actual conditions; therefore the water soluble fraction is always tied to an operational definition. Under our experimental conditions, we have previously determined that the collection efficiency in water extracts is approximately 80%. This estimate was used to calculate the range of dissolved organic mass (DOM) concentrations in aqueous solutions (see answer to the next question)

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.

Answer : In the new version of the manuscript, we provide the particle mass concentrations in the chamber only for isoprene. In this case, during the filter collection, the particle size was in the range of the HR-AMS measurements (Figure S1), while it was slightly exceeding the ones of the SMPS (in volume). Here is the calculation of the dissolved organic mass concentrations in water extracts as it is now described in the new version of the manuscript (in supplementary information S1):

The dissolved organic mass (DOM) concentrations in aqueous solutions were calculated as follows:

$$DOM\,(mg/L) = \frac{1}{V_{water}} \times \frac{V_{sample}}{t_{sample}} \times \sum_{t_i} \left(\frac{m}{V}\right)_{t_i} \times \Delta t_i \times 80\%$$

Where:

- V_{water} = volume of water used for SOA extraction (160 mL of water)
- V_{sample} = volume of {air + particles} sampled from the chamber (0.720 m^3 of air)
- t_{sample} = Sampling duration (2 hours)
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- $\frac{V_{sample}}{t_{sample}} \times \sum_{t_i} \left(\frac{m}{V}\right)_{t_i} \times \Delta t_i =$ total mass of particles sampled on the filter (µg). The HR-AMS provided a mass of organic particles per m^3 every 2 minutes $\left(\frac{m}{V}\right)_{t_i}$. Integrating this data during the filter collection time, multiplied by $\frac{V_{sample}}{t_{sample}}$, yields the total mass of particles sampled on the filter.
- The collection efficiency of SOA in water extracts was approximately 80%, as determined during previous experiments for SOA derived from α-pinene and isoprene.

The resulting value (3 – 4 mg L^{-1} (there was an error in the calculation of the ACPD version)) is given as a range of concentrations because the water extraction collection efficiency (~ 80%) is an estimate for soluble SOA.

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)?

Answer: It is true that the intensity of the 300 W Xe lamp used for that campaign was particularly low, as we realized after the campaign, when it was replaced by a new one.

In our experiments, we do not think that the resistance of the dissolved compounds to photochemistry was particularly high as we observed a decrease of the concentrations of a hydroperoxide (1-HEHP) under irradiation.

The comparison with Lee et al. (2011) is difficult because they used a Hg lamp (i.e. mainly 254 nm). Photolysing H_2O_2 at this wavelength provides high amounts of OH radicals with low intensity, but this wavelength is not relevant to the troposphere, a number of organic compounds are photosensitive at 254 nm.

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

Answer : The two subsections were renamed as follows:
3.4.1 Influence of aqueous phase processing on the formation of reaction products in the mass range 60-150 Da.
3.4.2 Influence of aqueous phase processing on the formation of oligomers observed in the mass range 150-300 Da.

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.

Answer : Comparing our study to previous papers dealing with isoprene SOA, it is true that we observed (on-line in the smog chamber and in the “control” samples) substantially less large oligomers. Fig. 4 shows that we detected the corresponding monomers and some of the dimers, but nothing higher. Looking thoroughly at different papers (Edney at al. (2005), Dommen at al. (2006), Surratt at al. (2006), Nguyen at al. (2010), Nguyen at al. (2011)), it appears that several reasons can explain this difference:

- In the literature, large oligomers (higher than 300 Da) were observed at both low RH (< 5%) and high RH (50 or 90%), but they were more intense at low RH. So, under our conditions (RH = 50-60%), the expected signal was low.
- In the literature, the signal obtained for large oligomers was small (see for example Fig. 1a in Surratt at al. (2006)), even under optimal conditions, i.e. at low RH, and operating pre-concentration of the SOA prior to analysis.
- Compared to all the previous studies, our samples were not enough concentrated to observe large oligomers:
  - Our filters containing SOA were extracted into 160 mL of water, while :
    - in Surrat at al. (2006), the filters were extracted into 5 mL of methanol, evaporated until dryness, and then re-diluted into 1 mL of water / methanol / acetic acid prior to analysis
    - in Nguyen at al. (2010), the filters were extracted into 1 mL of acetonitrile
  - Our online analyses using the TD-API-AMS did not allow any pre-concentration treatment, while in all previous studies, off-line measurements were done, which included accumulation of the SOA material :
    - In Dommen at al. (2006), the use of MALDI-MS allowed the authors to get rid of extraction steps. 0.7–1.5 m^3 of air was sampled on stainless steel plates in an impactor, leading to a much higher SOA accumulation compared to our study.
    - In Nguyen (2011), the use of a nano-DESI coupled to a LTQ-ORBITRAP mass spectrometer, allowed the authors to get rid of extraction steps. SOA was sampled and accumulated on aluminum foils and PTFE substrates in a cascade impactor at 30 $l\ min^{-1}$.

We have added a discussion on this point in the new manuscript.

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

the one cited.

Answer : This reference was replaced by Claeys et al., 2004a and b.

11. Table 1: were alpha-pinene and TMB 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 H_2O_2 concentration specified for the dark alpha-pinene value. Judging from Fig. 3, this experiment has been skipped. Please provide a justification for skipping it.

Answer: Alpha-pinene and TMB experiments were done 3 times, but not under the same conditions. Only the selected ones were usable for the purpose of the paper. Also, it is true that the "dark H_2O_2" experiment is missing for α-pinene. For these reasons, added to those mentioned in the general comments, we decided to remove the TMB experiments, and focus the new version of the paper mainly on isoprene, and mention (in the conclusion) some of the results obtained for α-pinene that are regarded as preliminary results. Therefore also the title was changed to "aqueous phase processing of secondary organic aerosol from isoprene photooxidation".
The RH and T values are the same for all experiments, the chamber conditions were the same for all experiments. This was specified in the new version of the manuscript.

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

Answer : Yes, this was corrected in the new version.

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. It 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.

Answer : Focussing the paper mostly on isoprene allowed us to make the figures simpler and wider in the new version.

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