Anonymous Referee #2
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The authors appreciate many important comments raised by Reviewer 2 which have been considered in the new version of the manuscript. The authors' answers to the questions/comments of Reviewer 2 are presented below.

General comments:
This paper investigated the aqueous phase processing of secondary organic aerosols (SOA) generated from gas-phase oxidation of isoprene, α-pinene and TMB using a smog chamber. The SOA collected on the filters were extracted by water and subsequently oxidized by H_2O_2 under dark condition and OH radicals in the presence of light using a photochemical reactor. Numerous online and offline analytical techniques including AMS, TD-API-AMS, HPLC-API-MS, API-MS2, IC-MS, SMPS and HTDMA were employed for physical and chemical characterizations of the chamber SOA and nebulised filter extracts. This is one of a few studies to investigate the aqueous phase oxidation of a complex organic aerosols, and the presented results are interesting. However, the objective of the paper is not clear, and some of the results can be discussed in more details. Some expected results (e.g., TD-API-AMS spectra in a positive mode, and aqueous oxidation of TMB SOA) were omitted in the manuscript without providing any explanations. Furthermore, the reproducibility of the data for α-pinene and TMB aqueous oxidation is another concern. The specific comments are shown below.

Answer: For the reasons raised in the general comments by reviewer 2 and also reviewer 1, we 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.

Specific comments:
1. Introduction: Page 21492, line 19-20: The sentence describing the objective is too general. Actually, the overall goal of this paper is not clear after reading through the paper.

Answer: The two last paragraphs of the introduction of the manuscript were re-written as follows:
"…A number of recent studies have focused on the ability of aqueous phase reactivity of some single organic compounds to form oligomers, and potentially new SOA (Altieri et al., 2006 and 2008; Carlton et al., 2006 and 2007; Perri et al., 2009; El Haddad et al., 2009; Tan et al., 2009 and 2010; Zhang et al., 2010; Liu et al., 2012). However, the effects of aqueous phase photooxidation of a complex mixture of organic compounds, such as those encountered in SOA, have only very recently been experimentally investigated by a few authors (Lee et al., 2011; Bateman et al., 2011) who have shown that this type of approach reveals a number of new aspects of SOA aging, that can be more atmospherically representative than the classical dry heterogeneous reactivity. However, none of these studies have dealt with SOA formed from isoprene photooxidation.
Although isoprene is the most abundant non-methane hydrocarbon emitted in the atmosphere, it was not considered as a significant contributor to SOA until recently. Nevertheless, some of its gas phase photooxidation products (such as methacrolein) are more direct precursors of SOA (Surratt et al., 2010; Lin et al., 2012), inducing isoprene photooxidation as one of the largest sources of atmospheric SOA (Hallquist et al., 2009; Carlton et al., 2009). Because most of the photooxidation products of isoprene are water soluble, it is likely that their aqueous phase processing has an important influence on SOA aging. The aim of this work

was to investigate a detailed study of the aging of isoprene SOA by photooxidation in the aqueous phase."

2. The experimental section is confusing. It is not clear that which instruments were employed to analyze organic aerosols from the smog chamber and nebulized solution droplets from the aqueous-phase photooxidation reactor. Figure 1 should show all the instruments being used. After read through the text, I think CPC and AMS were connected to the smog chamber, and IC-MS was utilized for aqueous characterizations as well. To make readers easier to follow, the authors should make it clear in each subsection and Figure 1. I also suggest to reorganize the flow of this section by moving the descriptions of both online and offline characterization after Section 2.5.

Answer: The experimental section and Figure 1 were clarified in the new version according to the reviewer's comment, and the descriptions of both online and offline characterization were moved after section 2.5.

3. Page 21498, line 9-18: The criteria used to decide the initial H_2O_2 concentration was presented in this paragraph. So, what is the expected OH levels in each experiment?

Answer: For isoprene experiments, using two different methods, we estimated that our OH radical concentrations were 10^{-15} - 5×10^{-15} M, corresponding to typical concentrations in urban cloud droplets (Anastasio and McGregor, 2001; Herrmann et al., 2010; Ervens and Volkamer, 2010). This estimation was added in the new manuscript.

4. AMS measurements: (a) The arrows shown in Figure 2 may be misleading. They give an impression that the evolution of organic compositions during aqueous oxidation are following their trajectories on the f_{44}-f_{43} space. Some recent studies have demonstrated that the aging pathways of lab and ambient SOA usually have a curvature in another direction (i.e., f_{44} increase continuously and f_{43} initial increase and then decrease via oxidative aging) (Ng et al., 2010; Lambe et al., 2011; and Lee et al., 2011a). (b) What are the reasons to omit the discussion of all TMB samples and the "dark H_2O_2" samples of isoprene SOA. Please either state the reason or discuss the data in this section.

Answer: (a) Figure 2 was modified: the arrows were deleted and TMB and α-pinene experiments were deleted. (b) In the new version, all TMB experiments and discussions were deleted, but all samples were discussed for isoprene SOA, including "dark H_2O_2" samples.

5. HTDMA measurements:(a) The f_{44}/f_{43} ratio can generally explain the observed changes in organic hygroscopicity after aqueous processing. Nevertheless, it is possible to further examine whether there is any correlation between organic kappa and O:C ratio, which can be determined by the elemental analysis of HR-AMS data or estimated from the relationship between f_{44} and O:C established by Aiken et al. (2008). It would be interesting to compare the results with the correlations recently reported by Lambe et al. (2011) and Massoli et al. (2011). (b) Page 21503, line 5-6: The concentration of TMB SOA in aqueous solution (> 0.9 mg/L) is much higher than that of isoprene SOA (0.4 mg/L). What is the possible reason to have low AMS signal for nebulised TMB SOA extracts? Is it related to the water solubility or volatility of the SOA?

Answers:

a) In the new version of the paper, we added the following figure (see Figure 4) representing the κ values as a function of the corresponding f_{44} values for the two isoprene experiments, and we added the following text:

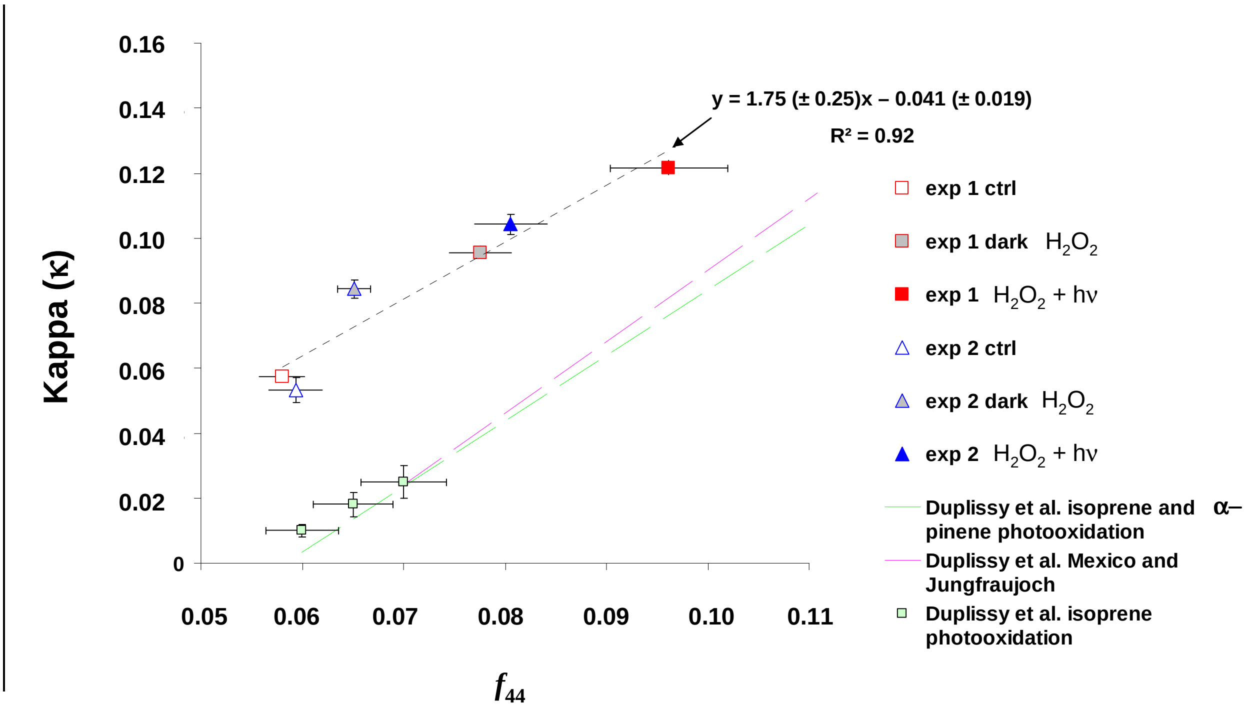

Figure 4 : Relationship between f_{44} (obtained from HR-AMS measurements) and κ (obtained from H-TDMA measurements) for experiments 1 and 2 during nebulization of “control”, “dark H_2O_2” and “H_2O_2 + hν” samples, obtained after aqueous phase processing of SOA formed from isoprene photooxidation. Comparisons with previous smog chamber and field data obtained by Duplissy et al. (2011).

Figure 4 shows a linear dependency between κ and f_{44} (which can be converted into O:C ratio using the relationship established by Aiken et al., 2008) in good agreement with the studies of Chang et al., (2010), Massoli et al., (2010), Duplissy et al., (2011) and Lambe et al., (2011) who investigated a large panel of gas-phase SOA precursors including alkanes, aromatics, terpenes and isoprene, but also field samples collected at different types of sites (urban, elevated, rural…). Comparing our “control” samples with the smog chamber data obtained by Duplissy et al. (2011) during isoprene photooxidation (performed under similar conditions as ours), we observed a shift of the kappa values to higher values in our study (Fig. 4). This increase in hygroscopicity (with constant f_{44} values) may be due to water extraction of SOA and subsequent nebulization carried out in our study, while Duplissy et al. (2011) performed direct measurements in the smog chamber. Meanwhile, the slope obtained here (Fig. 4) (1.75 ± 0.25) is in very good agreement with the ones obtained by Duplissy et al. (2011) (who selected κ values measured under similar conditions as here, i.e. obtained from hygroscopic growth factors (HGF)) for gas-phase smog chamber aging of biogenic SOA (2.02 ± 0.04) and also for field data (Jungfraujoch and Mexico city: 2.2 ± 0.4). These observations show that, compared to gas-phase aging, aqueous phase aging of biogenic SOA did not substantially modify the correlations between the hygroscopicity (derived from HGF) and oxidation levels of biogenic SOA. Finally, the good agreement between our slope and those obtained for the field data selected by Duplissy et al., (2011) from Mexico City and and Jungfraujoch, is encouraging.

b) It is probable that the water solubility of TMB SOA was much lower than that of the biogenic SOA, and thus, our estimated concentration in the liquid phase was a maximum concentration. In the new manuscript, the TMB experiments were deleted.

6. Section 3.3: (a) I think the smog chamber was operated in batch mode, and hence
the chamber SOA composition should keep changing throughout the experiment. I am
wondering if the authors attempted to determine the 2-h average TD-API-AMS spectra
of chamber SOA measured on-line. Because the TD-API-AMS spectra of nebulised
aqueous extracts also represents the 2-h average organic composition, this approach
may improve all spectral correlations between chamber SOA and their corresponding
aqueous extracts (Figure 4). (b) What are the results of AMS analysis and TD-APIAMS
operated in positive mode for biogenic SOA and negative mode for TMB SOA?
Are they come up with the same conclusion made in this section? (c) The meaning of the last
paragraph is not clear.

Answers:

a) We agree with the reviewer on the fact that 2-h average TD-API-AMS spectra of chamber SOA measured on-line should improve the correlations with the TD-API-AMS spectra of nebulised aqueous extracts. Unfortunately, during the 2h of filter sampling, only 2 to 3 mass spectra (which are very similar) were performed in each mode during the 2nd hour.

b) In the new version of the paper, we have added all the TD-API-AMS data obtained in the positive mode for the isoprene SOA, and we come up with the same conclusions. The HR-AMS is only operated in the positive mode as the ionisation proceeds via electron impact.

c) The last paragraph has been deleted.

7. Section 3.4: (a) It is necessary to extend the discussion of the α-pinene results in
this section. In particular, Figure 5 shows the positive spectral differences to demonstrate
the formation of aqueous oxidation products. Similarly, the negative differences
should be able to indicate the consumption of some specific SOA materials during the
oxidation. Although the comparison is only qualitative, this information may improve our
understanding on aqueous oxidation mechanism of α-pinene SOA. (b) Again, what are
the results of TD-API-AMS operated in positive mode for both isoprene and α-pinene SOA? I
expect to have the TMB results in this section too.

Answers:

a) For isoprene and α-pinene, we chose to show the positive spectral differences because the negative differences showed fewer (less than 10) and much less intense peaks (by a factor of 2 to 8). It is true that these comparisons are only qualitative, but they indicate that the most striking result from our analyses is the formation of aqueous oxidation products, on which we focus our discussion. We added some discussion on that point in the new manuscript.

b) Because we decided to focus on isoprene experiments in the new version, we added all the TD-API-AMS data obtained in the positive mode for the isoprene SOA, but the α-pinene and TMB results were deleted

8. Page 21508, line 22-28: Lee et al. (2011b) recently showed that the reaction between
glyoxal and H_2O_2 can produce 2-hydroxy-2-hydroperoxyethanal (HHPE), which
can be decomposed in the presence of UV light. Therefore, 1-HEHP was possibly

produced via the reaction between acetaldehyde and H_2O_2.

Answer: Yes, we agree on the fact that the reaction of acetaldehyde with H_2O_2 produces 1-HEHP as for identification purposes, we performed the synthesis of 1-HEHP via this reaction (see section "reagents"). However, acetaldehyde is highly volatile and was not present on the collected SOA. It is possible that the formation of 1-HEHP in the "dark H_2O_2" samples occurred via the dissolution of larger carbonyl and/or gemdiol compounds, followed by H_2O_2 oxidation. The sentence was modified as follows: "This behaviour can be explained by the dissolution of larger carbonyl and/or gemdiol compounds, followed by H_2O_2 oxidation in the dark, leading to the formation of hydroperoxides such as 1-HEHP, and by further OH oxidation and/or direct photolysis of 1-HEHP (which is highly photosensitive as it was shown by Monod et al., 2007) in the "H_2O_2 + hv" sample."

9. Section 3.5.2: Some high mass peaks were observed in the "dark H_2O_2" samples (Figure S2). Furthermore, Tan et al. (2009, 2010) did not observe significant formation of oligomer in their experiment when cloud-relevant concentration (10^{-6} M) of glyoxal and methylglyoxal were used. Compared to Tan et al. (2009, 2010) (10 mM), much higher initial H_2O_2 concentration (100 mM) was used in the aqueous oxidation of isoprene SOA. For the case of α-pinene, the initial H_2O_2 concentration was only 15 mM and no formation of oligomers was observed. Is it possible that high H_2O_2 (and probably OH radical) concentration also favours the oligomerization process?

Answer: OH radicals concentrations in the liquid phase favour the oligomerization process because they initiate organic radical formation, which can then contribute to radical mechanisms of oligomerization as it was shown by Guzmán (2006); Lim et al. (2010); Tan et al. (2012) and Liu et al. (2012). For "dark H_2O_2" experiments (shown in Figure S2), the formation of high mass peaks is more surprising. It may be explained by the formation of organic hydroperoxides, which further react with aldehydes to form peroxyhemiacetal compounds that can be attributed to oligomers (Kroll and Seinfeld, 2008).

Minor comments:

1. Page 21494, line 5: What kind of filter was used for aerosol collection?

Answer: We used Teflon filters for the collection. This information was added to the manuscript.

2. Page 21494, line 17: Please change "AMS" to "AMS: Aerosol mass spectrometer"

Answer: Following comment 4 by reviewer 1, we deleted all the sub-titles for the paragraphs devoted to different instruments, in order to minimize writing fragmentation.

3. Page 21500, line 7-9: Please briefly explain how to calculate the organic concentrations in aqueous solution from the SMPS data.

Answer: The dissolved organic mass (DOM) concentrations in aqueous solutions were calculated as follows (now described in the new version of the manuscript (in supplementary information S1)):

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

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.

4. Page 21506, line 5: I am not sure if "HPLC-MS" used here is equal to the "HPLCAPI-MS" mentioned in the experimental section. If yes, please use "HPLC-API-MS" throughout the paper.

Answer: All "HPLC-MS" expressions were replaced by "HPLC-API-MS"

5. Table 2: (a) Please add a few columns to indicate the production pathways of the identified organics (e.g., chamber vs. aqueous oxidation). (b) The chemical structures shown in Page 21523 are not well displayed.

Answers:

a) In the new manuscript, Table 2 was cut into three parts:

- one table (Table 1) including only the chemical structures of the molecules, and the analytical conditions employed for their identification and quantification in water extracts,
- 2 figures (Figure 7 and Figure S5) showing the evolution of the quantity of the identified molecules in the aqueous phase after H_2O_2 oxidation in the dark and after photooxidation by OH.

Finally, some discussion was added in the text concerning i) the detection of these molecules in water extracts after sampling from the chamber and ii) their evolution after aqueous phase processing, and their production pathways.

b) This was improved in the new version.

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