Anonymous Referee #2

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This paper describes investigations of the evolving chemical composition of ambient organic aerosol and cloudwater organics, using an Aerodyne aerosol mass spectrometer (AMS) deployed at the Whistler Aerosol and Cloud Study. The chemistry of the organics is described in terms of the AMS spectra of the atomized samples, as well as the spectral changes that occur after aqueous-phase oxidation. The oxidation experiments confirm that aqueous-phase oxidation leads to the formation of oxidized particulate species, but also (for the first time I think) demonstrate that much of the oxidized products are volatile, and thus that aqueous-phase oxidation can lead to a net loss of condensed-phase organics. Additionally it is shown that the relatively volatile components of cloudwater (those that would partition into the gas phase after cloud droplet evaporation) can oxidize to form lower-volatility species that can contribute to secondary organic aerosol (SOA). These last two conclusions are particularly important and novel, and this study represents an important advance in our understanding of atmospheric aqueous-phase oxidation chemistry. The paper is well-written and easy to follow, and the figures are excellent and capture the important points of the work. I recommend publication after the following concerns are addressed:

Throughout the paper (abstract line 8, P. 6027 line 20), it is argued that the similarity in AMS spectra of the organic aerosol and the cloudwater residuals “indicates” that the cloudwater organics derive from secondary organic aerosol. I do not think such a strong conclusion is warranted, for two reasons:

(1) since one of the results here is that aqueous-phase processing can form more highly oxidized organics, it would seem that an alternative conclusion could be that the aerosol was formed from cloud processing of less-oxidized material (i.e., the “fresh biogenic” SOA). Is there any reason to think one type of organic (aerosol or cloudwater) necessarily precedes the other?

(2) AMS spectra of oxidized organics tend to be extremely similar (because of the large m/z 44 peak for all organic acids), even for organics from very different sources. For example, aged biogenic aerosol, aged anthropogenic SOA, and fulvic acid – which come from three very different sources – look nearly identical in the AMS (with Rˆ2 > 0.9). Thus the similarity between spectra really does not indicate any commonality in sources. It might suggest a connection, but the AMS is not the right analytical technique for differentiating sources of oxidized organics.

Response:
Yes, we agree with both points. One, the organic aerosol that is observed may have already undergone cloud processing, and so it is impossible to assume that the character of fresh biogenic SOA translates directly to the composition of cloud water organics. And, two, the high similarity between the aerosol and cloud organic spectra does not necessarily lead to the strong conclusion made in the paper. The related sentences have been deleted in the revised manuscript.

P. 6024, line 27: What were the AMS organic levels of these blanks? Were the blank values (and spectra) subtracted from all other data? Moreover, it is not mentioned whether blanks were carried out for the oxidation reactions. Two important blanks would be clean water after oxidation in the photochemical reactor (to examine photochemical formation of low-volatility species in the background), and photolysis of cloudwater/aerosol extracts in the absence of added H2O2 (to examine the role of direct photolysis) - were such blanks carried out? If not, this needs to be mentioned, and uncertainties associated with these effects discussed.

Response:
We thank the reviewer for his suggestion. We didn’t carry out all the control experiments mentioned by the reviewer. The following paragraph has been revised in the manuscript.

Page 6, line 17-31: “To determine the background organic level contributed from water that was used for filter extraction, we atomized a few blank water samples and quantified their organic level using the experimental approach described above. Because of the low organic aerosol loading within the pre-biogenic period, a few aerosol filter extracts with total organic levels comparable to the background organic level of blank water were excluded from our data analysis. Eleven aerosol filter extracts with organic loadings at least 5 times higher than the average of the background organic level were included in the analysis. Note that it is not straight forward to subtract the spectra of water blanks from aerosol filter samples because the aerosol loadings measured by the CToF-AMS in each experimental run depend on the atomizer output as well as solute concentration. Due to the limited sample volume of aerosol filter extracts and cloud water, the effects of direct photolysis on our measurement were not examined. However, we believe that the organic composition of the reacting solution was mainly modified by OH oxidative reaction under such a high level of oxidant. Oxidation of water blanks were performed in the laboratory after the field campaign and there was no significant changes in organic loading.”

P. 6034, line 7 (and Fig 6b): This finding that the aqueous oxidation of glyoxal and methylglyoxal leads to a decrease in aerosol mass is an important one, as it seems to be in stark contrast with the emerging view that such reactions can serve as a major source of SOA. (This work suggests that they do indeed form SOA, but in rather small yields). This needs to be highlighted here, and probably even included in the abstract. The formation of highly oxidized but volatile products of aqueous-phase oxidation has received relatively little attention so far.

The mechanism of this mass loss should be discussed in more detail. Fragmentation to formic acid is mentioned as one possibility, but oxalic and glyoxalic acids are also known to be important products of glyoxal oxidation. These are probably too volatile to remain in the particle phase also. Perhaps the glyoxal and methylglyoxal are in the cloud water primarily as oligomers, and the oxidation degrades such oligomeric species, forming smaller and more volatile acids?

Response:
This is a very good point and we can understand why the reviewer may interpret the data in Figure 6b as indicative of glyoxal and methylglyoxal as giving rise to less and less SOA when oxidized in the atmosphere. In short, we do not believe this behavior would occur in the atmosphere for reasons described below. And so, to avoid confusion and to make the point more

clearly, we have removed the results and discussion pertaining to glyoxal and methylglyoxal from the paper, focussing instead on the more easily interpreted laboratory results for cis-pinonic acid and the ambient measurements instead. Also, the points related to glyoxal and methylglyoxal have been made in our earlier publications, as described below.

For the sake of discussion, however, it is important to discuss the glyoxal and methylglyoxal measurements presented in the ACPD paper. In particular, Figure 6b shows large organic mass reduction for both dicarbonyls, indicating continuous production of volatile species such as formic acid. The details of the reaction mechanisms and comparison to the studies from other research groups have been reported in our previous publications and hence are not described here. However, in brief, the rapid drop of organic mass at the early period of the oxidation is probably due to the formation of hydroxyhydroperoxides (HHP) (Lee et al. 2011b; Zhao et al. 2012). The HHP formed by glyoxal and H_2O_2 may be too volatile or unstable to be retained in the particle phase during droplet evaporation but it could be an important intermediate for producing glyoxylic and oxalic acid in the bulk solution (Lee et al. 2011b). The accumulation of glyoxalic and oxalic acid in the particle phase led to increase of organic mass at the later stage of oxidation. Loeffler et al. (2006) showed that glyoxal and methylglyoxal primarily remain in the particle phase due to self-oligomerization in the evaporating droplets. It is, however, not clear whether the formation of HHP may limit the self-oligomerization and thus enhance the overall organic volatility. Furthermore, oligomer formation was not significant in our experiments perhaps due to insufficient initial organic radicals for radical-radical oligomerization (Lee et al. 2011b; Tan et al. 2009; 2010; Zhao et al. 2012).

And so, with regards to the results in Figure 6b, we point out that this figure is not inconsistent with glyoxal and methylgloxal being good SOA precursors, i.e. each gives rise to significant aerosol mass at long oxidation times. As described in our earlier study (Lee et al. 2011b; Zhao et al. 2012), the mass loss at early times is related to the formation of HHP that is too volatile to be retained in the particle phase and may limit the self-oligomerization of the dicarbonyls as described above. HHP formation is more important in the lab experiments than in the real atmosphere. As well, gas-particle partitioning in our experiments does not precisely match that which will occur in the atmosphere.

Finally, the paper could be improved with a more quantitative estimate of the atmospheric relevance of the aging via aqueous-phase processing. The oxidation experiments demonstrate very nicely how the amount and degree of oxidation of condensed phase organics change upon photochemical processing, but there is no discussion of kinetics. Over what sort of rough timescales would the changes observed (mass increase, mass loss, change to oxidation state) be expected in the atmosphere?

Response:
Yes, we agree that the paper would benefit from an estimate of the atmospheric timescale of OH exposure used in the experiment. And so the steady state OH concentration has been estimated using a simple chemical model as shown in the supplementary materials. The follow discussion has been added to the revised version.

Page 6, line 4-6: “We estimated the steady state OH radical concentration to be about 10^{-11} M using a simple chemical model with a calculated H_2O_2 photolysis rate constant of 6.9×10^{-4} s^{-1} (see details in supplementary material).”

Page 16, line 19-32: “Based on the estimated steady state OH concentration in our experiments, the maximum OH exposure was equivalent to roughly a week in the atmosphere, assuming an aqueous OH concentration of 10^{-13} M in cloud droplets during the daytime (Jacob, 1986) and constant cloud water exposure. Given that cloud droplets exist for only minutes at a time, it is clear that the aqueous oxidative processing of V-CWO during each cycle is likely represented by the data observed at the very low OH exposure region of Figure 5a, where additional organic mass may be produced. Ambient aerosol particles may experience numerous aerosol-cloud cycles within their lifetime, thus increasing their total exposure to aqueous phase processing and thus the importance of V-CWO processing to SOA formation. At very high OH exposures, LV-CWO can be oxidized to produce higher volatility products as shown in Figure 5b.”

Other comments:

Section 2.2: some basic information on the photochemical reactor is necessary. For example, the lamp wavelength is not given anywhere in the manuscript.

Response:
Some basic information has been added.

Page 5, line 30 to Page 6, line 3: “Some of the aqueous samples were oxidized for 10 minutes using a custom-made photochemical reactor with an ozone-free Hg lamp (UVP, 254 nm) (Lee et al. 2011ab). The small glass tube with a volume of about 30 mL was inserted to the reaction glass vessel (~100 mL) for holding the aqueous solution samples.”

P. 6030, line 25: How meaningful is this spectral subtraction? If the absolute amount of carbon changes (as is shown in the following paragraph), the subtraction of fractional mass spectra will not yield any quantitative information (and instead can exaggerate small differences). For this reason I would recommend removing this paragraph (and the corresponding figures), instead focusing on the following paragraph related to absolute spectral and mass changes.

Response:
Thanks for the reviewer's suggestion. However, we have decided to keep the subtraction of fractional mass spectra because it provides the information about the relative composition changes in the reacting solution. For example, we know the mass loss of organic acids from the absolute spectral difference but we know that organic acids become more and more dominant after oxidation from the fractional spectral difference.

P. 6033, line 7: IVOCs by definition are found only in the gas phase and not in the particle phase.

Response:

We agree that IVOC are mainly in the gas-phase.

Page 14, line 17-22: "*Cis*-pinonic acid, a major first-generation product of α-pinene ozonolysis, is a moderately water-soluble organic acid with a vapor pressure close to the lower limit of intermediate volatile organic compounds (IVOC) (Donahue et al. 2011; Jimenez et al. 2009). Therefore, it predominantly exists in the gas phase and upon oxidation may give rise to SV-OOA and LV-OOA formation in the atmosphere (Donahue et al. 2012; Jimenez et al. 2009)."

P. 6033, line 21: this is confusingly written – presumably the observed growth is from the oxidation of pinonic acid. I think the point here is that the difference cannot come from functionalization reactions on the *measured* pinonic acid?

Response:
Yes, this is true. We revised the related sentence to make it clear as shown below.

Page 14, line 3-10: "Since the organic mass increased by a factor of 2.2 at its maximum, this cannot be realistically achieved by functionalization reactions of the AMS measured *cis*-pinonic acid alone (e.g., this would require addition of about 10 OH groups, without fragmentation occurring). However, due to the fact that a large fraction of atomized *cis*-pinonic acid escapes to the gas phase after droplet evaporation and aqueous OH oxidation of *cis*-pinonic acid can produce less volatile first- and/or second-generation oxidation products (Jimenez et al. 2009), it is expected that more organic mass can accumulate in the particle phase upon evaporation."

P. 6034, line 20-22: I don't understand the argument here. The paragraph is about organic mass loss via oxidation of glyoxal, but this sentence is about glyoxal itself (rather than glyoxal oxidation products).

Response:
We include this argument here because oxidation of these dicarbonyls and cloud water have totally different mass change responses. This is consistent with the fact that glyoxal and methylglyoxal only make small contributions to the total water-soluble organics.

Fig 6: The y-axis should span the full range (0-1.0) to give an accurate sense of the fractional change in aerosol mass.

Response:
Done