Anonymous Referee #3

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This study reports on aqueous phase processing in cloud water samples and filter samples from aerosols collected near clouds. It is complemented by laboratory studies that explore the oxidative processing of water-soluble cloud water constituents (aldehydes). The authors confirm prior studies that oxidative processing yields highly oxidized material that will remain in the particle phase after cloud evaporation but in addition, they show that continuous processing leads to the formation of volatile compounds that likely partition to the gas phase upon drop evaporation. This study is clearly highly interesting as it is the first one that indeed analyses AMS spectra of ‘real’ cloud water and cloud-processed aerosol and, thus, exceeds the numerous laboratory studies that were performed under controlled conditions with selected precursors. I have several comments below that should be addressed prior to publication that focus on the atmospheric relevance of the experimental conditions.

Major comments:

1) Possible salt formation: In ambient aerosol samples there are considerable concentrations of dicarboxylates that do not have gas phase sources. While the acids are indeed to volatile to remain in the particle phase, it has been shown that they likely form salts or metal complexes (e.g. ammonium oxalate, calcium oxalate, . . .[Yang et al., 2009; Furukawa and Takahashi, 2011]) and thus are not available anymore for any further processing upon drop evaporation. – Did the analysis of particles or cloud water give any evidence of such compounds? – Could they have been detected at all by the applied method? Smaller dicarboxylates tend to form more stable salts. It is known that oxidation of larger diacids yields smaller acids – thus, an apparent increase in volatility of the acid products might under atmospheric conditions actually help forming less volatile material. – Some discussion along these lines should be added.

Response:
We entirely agree with the reviewer's comment that salt formation may affect the volatility of small acids formed in the atmosphere. However, our measurement technique cannot provide enough information to comment on the extent of salt formation in our experiment. The following information has been added at the end of the manuscript to highlight this issue for future investigation.

Page 17, line 21-26: “Lastly, our observation suggests the increasing importance of fragmentation reactions on organic acids at the later stage of both aerosol filter extract and cloud water oxidation with smaller acids as the major condensed-phase products. Since smaller acids tend to form more stable and less volatile salts (e.g., ammonium oxalate) under ambient atmospheric conditions, it would be interesting to further investigate how the salt formation process affects the overall volatility of the organic products produced via aqueous oxidation.”

2) OH(aq) concentrations: The initial concentration of H2O2 (70 mM) seems very high as compared to H2O2 in cloud water. Can you give an estimate of the resulting OH(aq)

concentration? Are the oxidation rates k[OH][Org] comparable to those in cloud droplets? Given that a cloud droplet lives on the order of a few minutes, these rates should be discussed in the context of realistic time scales. It seems that the loss processes might have been overestimated

Aldehyde + OH -> SOA + OH -> volatile compounds

since at too high OH concentrations all aldehydes are likely very quickly consumed and thus OH might be available to further oxidize SOA (acids) to volatile compounds. In real clouds the turn-over rates of the individual steps might be much slower (due to lower OH) and thus less SOA will be oxidized before drops evaporate and possibly salt formation occurs.

Response:
We agree that it is important to present our result in a more quantitative manner. The steady state OH concentrations are now estimated using a simple model as shown in supplementary material. The results have been used to estimate the atmospheric timescale of OH exposure in aqueous cloud droplets. We believe that the real cloud droplet oxidation is likely represented by the data observed at the very low OH exposure of our oxidation experiments. The following discussion has been added to the revised manuscript.

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.”

Minor comments:

p. 6021, l. 29: This sentence reads as if the oxalic acid formation rate (microg /m3/s) might exceed sulfate formation which was likely not the case since sulfate concentrations are always much greater than oxalate levels. I assume that the authors refer to the statement that relatively oxalate formation increases later (i.e. higher in the cloud where LWC is higher) due to the multistep formation as opposed to the one-step formation of sulfate.

Response:
The sentence has been revised as follows.

Page 3, line 8-11: "On the basis of aircraft measurements, Sorooshian et al. (2007) suggested that the source of oxalic acid in aerosol particles above cloud was a result of aqueous-phase processing, in which oxalic acid formation was shown to be enhanced with increasing amounts of both liquid water content and pH in droplets."

p. 6029, l. 3f: A sentence could be added that compares the O/C ratios derived from typical aqueous phase oxidation experiments (e.g., Lee et al., 2011, Lambe et al., 2011).

Response:
This information has been added to the revised version as shown below.

Page 10, line 25-32: "In general, the O/C ratios of our aerosol and cloud water samples are higher than those of chamber SOA produced by gas-phase oxidation chemistry as summarized in some previous studies (e.g., Aiken et al. 2008; Chhabra et al. 2010; Ng et al. 2011) but much lower than those obtained from aqueous SOA oxidation and glyoxal uptake experiments (Lee et al. 2011a; Lambe et al. 2011; Chhabra et al. 2010). Note that the O/C ratios of aerosol filter samples collected within the biogenic period are comparable to those measured from the Amazon Basin (0.42-0.49) (Chen et al. 2009), which is also strongly influenced by biogenic sources."

p. 6029, l. 14: Have similar experiments been performed (in other studies) under dry conditions? How quickly does mz44 increases if it is only formed from processing on/in dry particles or in the gas phase? Acid functionalities are usually formed quicker in the aqueous phase because of different mechanisms (gem-diol oxidation in the aqueous phase versus slower aldehyde oxidation if no water is present). Such a comparison would be highly interesting in order to confirm this trend for atmospheric constituents.

Response:
We agree this comparison would be interesting. We have conducted the heterogeneous OH oxidation experiment of biogenic SOA using a flow tube approach in the same field study and observed significant mass loss (~25%) and formation of LV-OOA with O/C values comparable to those formed via aqueous oxidation in the current study (Slowik et al. 2012). The timescale of OH exposure is equivalent to 3 days of atmospheric processing. However, due to the experimental techniques used, we cannot evaluate the reaction mechanism based on our observations. However, as a reference for the reader, the following additional information has been added to the section of the paper on conclusions and atmospheric implications.

Page 16, line 9-13: "In particular, heterogeneous OH oxidation of biogenic SOA using TPOT in the same field campaign (equivalent of ~3 days atmospheric processing) resulted in ~25% of organic mass loss and produced SOA with O/C values (~0.7-0.9) (Slowik et al. 2012)."

p. 6030, l. 18: Can you do a rough estimate of sulfate production during oxidation based on measured S(IV) and used H2O2 concentrations?

Response:
We thank the reviewer for their suggestion. We are unable to estimate the sulfate production based on our AMS measurement because the S(IV) related fragments can be also from S(VI) in particles and we cannot differentiate them using the AMS data alone. However, we believe that the effects of sulfate production from S(IV) are minimal because the measured sulfate mass by AMS is the total of S(IV) and S(VI) species, i.e. it does not matter if S(IV) is being converted to S(VI) because the AMS detects both species. This information has been added to the revised manuscript to clarify this point.

Page 12, line 9-14: "Note that oxidation of S(IV) species (mostly in the form of HSO_3^- at pH 2-7) may be transformed to inorganic sulfate in the oxidized cloud water samples, and hence the sulfate normalized results likely represent a lower limit of m/z 44 production. However, the S(IV) oxidation is expected to have minimal effects on our observations because the sulfate mass measured by the AMS is the total amount of S(IV) and S(VI) species."

p. 6032, l. 7: What is meant by 'cloud activation'?

Response:
This term has been deleted in the revised version.

p. 6032, l. 25: I assume that you imply that low volatility acids (e.g. dicarboxylic) are oxidized to form more volatile compounds. Such compounds (as stated corrected earlier) might include formic and acetic acid. In a recent study a potential role of SOA formation by acetic acid has been suggested and should be cited here [Tan et al., 2012]

Response:
Yes, it is important to include this reference in the revised manuscript. We decide to add the following sentence in the section of atmospheric implication, where we have some discussion of potential aqueous SOA precursors in the atmosphere.

Page 17, line 13-16: "Nevertheless, V-CWO usually consists of many short chain carbonyls and organic acids (e.g. formic acid and acetic acid) with high O/C ratio. Tan et al. (2012) recently demonstrated that aqueous OH oxidation of acetic acid can produce organic acids with lower volatility, such as glyoxylic, glycolic and oxalic acid, forming additional SOA materials."

Section 3.5: Even though the methodology is described in a previous study, the general conditions should be briefly noted (e.g., H2O2 and OH concentrations, duration of experiments)

Response:
The general conditions of the experiment were added to revised manuscript.

Page 14, line 26-30: "The aqueous-phase OH oxidation of *cis*-pinonic acid was performed in the photochemical reactor (~1 L) for 5 h and ammonium sulfate salt was added to the reacting solution as an internal standard for normalization of organic signals. The initial concentrations of *cis*-pinonic acid and H_2O_2 concentrations were 500 µM and 13.3 mM, respectively. The estimated steady state OH concentration was 10^{-12} to 10^{-13} M."

p. 6034, l. 5: Bateman et al.[2011] have shown that aqueous phase processing of terpene-derived SOA actually acts as a sink due to photolysis. These findings mentioned should be mentioned here.

Response:
The following sentence has been added to the revised manuscript.

Page 15, line 16-18: "Likewise, Bateman et al. (2011) recently proposed that photolytic processing of cloud droplets can act as a sink of d-limonene derived SOA and can lead to increases in the O/C ratio of the processed solution."

p. 6036, l. 10: Using only the Henry's law constant (KH) as a measure for a potential role on SOA formation is somewhat too simplified. A KH of 9000 M/atm implies that a few % of the compounds are partitioned to the aqueous phase at typical cloud LWC. While this is a first requirement for the importance of aqueous phase processing, it is the further reactivity in the aqueous phase that determines whether this material is efficiently oxidized. A high KH does not necessarily imply a high reactivity.

Response:
We agree with the reviewer's comment. The sentence has been revised as follow.

Page 17, line 9-12: "Gelencser and Varga (2005) have suggested that organics having Henry's law constant greater than 10^3 $Matm^{-1}$, such as pinonaldehyde (9 x 10^3 $Matm^{-1}$), can be potential precursors of SOA formed via aqueous processing, depending on their reactivity towards atmospheric oxidants."

Technical comments:

p. 6024, l. 17: should that be 'column'?

Response:
Done

p. 6026, l. 21: monoterpene oxidation (not monoterpeneS)

Response:

Done

References:

Bateman, A. P., S. A. Nizkorodov, J. Laskin, and A. Laskin (2011), Photolytic processing of secondary organic aerosols dissolved in cloud droplets, Phys. Chem. Chem. Phys., 13(26), 12199-12212.

Furukawa, T., and Y. Takahashi (2011), Oxalate metal complexes in aerosol particles: implications for the hygroscopicity of oxalate-containing particles, Atmos. Chem. Phys., 11(9), 4289-4301, 10.5194/acp-11-4289-2011.

Tan, Y., Y. B. Lim, K. E. Altieri, S. P. Seitzinger, and B. J. Turpin (2012), Mechanisms leading to oligomers and SOA through aqueous photooxidation: insights from OH radical oxidation of acetic acid and methylglyoxal, Atmos. Chem. Phys., 12, 801-813.

Yang, F., H. Chen, X. Wang, X. Yang, J. Du, and J. Chen (2009), Single particle mass spectrometry of oxalic acid in ambient aerosols in Shanghai: Mixing state and formation mechanism, Atmospheric Environment, 43(25), 3876-3882.