Review for: acp-2012-115

Characterization of aerosol and cloud water at a mountain site during WACS 2010: Secondary organic aerosol formation through oxidative cloud processing

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General comments:

This paper reports a series of measurements of the composition of cloud water and interstitial aerosols collected from Whistler mountains in Canada. In addition to comparing the aerosol vs. aerosolized/dried cloud water composition using aerosol mass spectrometry (AMS), the authors performed aqueous OH oxidation of the samples and characterized the degree of chemical change induced by the aqueous photochemical processing. The experiments described in this paper are novel, and the information is highly relevant to the atmospheric chemistry community. The main message of the paper is that aqueous oxidation of relatively volatile organics by OH produces oxidized organics with sufficiently low volatility to remain in residual particles after the cloud dissipation. The paper is well-written and the figures are appropriate. The following comments and suggestions are aimed at further improving the readability and the logical flow of the paper.

Specific comments:

Abstract

- According to the experiments described in the text, the enhancement of organics was observed only during the initial stages of the aqueous OH oxidation; this was followed by a decline with the amount of organics in aerosol extracts decreasing. The statement made in the abstract does not accurately reflect this point, and may give the false impression that organic mass always increases as a result of photooxidation.

Introduction

- Page 6021, line 5: it would be helpful to insert a citation to support the “usually hygroscopic” nature of atmospheric aerosols. The authors' group have a conducted a number of comprehensive studies on this topic in the past, so they should be in a good position to point the readers to appropriate references.

- Page 6022, line 18: the authors assert that “cloud water” in this work actually refers to fog water and that they are expected to be similar for a given elevation. This is not entirely accurate. There have been numerous measurements of cloud vs. fog water composition for a given site, and the conclusion is that the composition is not necessarily similar. Fog waters tend to contain more dissolved material. For example, concentration of dissolved inorganic compounds in fog water can be an order of magnitude greater (Fisak et al. 2002), possibly due to smaller drop size. Fog water has a wider range of pH values compared to cloud water (Collett et al. 2002). Finally, the OH concentration in clouds is expected to be higher than that in fogs (Ervens et al. 2011), especially in the interstitial areas of clouds where OH may be enhanced (Maudlin et al. 1997). The authors should elaborate on the justification of their assumption.

- For the completeness of the introduction, a few other studies should be mentioned. Bateman et al. (2011) focused on direct photolysis of dissolved organics, but they probably could not have avoided oxidation by OH. They observed fragmentation of dissolved organics accompanied by an increase in the O/C ratio – this is similar to the observations of the authors for the later stages of the photooxidation. Chang and Thompson (2011) found that OH oxidation of phenolic compounds in water produced complex molecules that absorbed light. There might be other relevant papers this reviewer is not aware of, I would check a recent comprehensive review on this topic by Ervens et al. (2011). References to these and other papers are supplied at the end of this review.

Experimental

- The aqueous OH oxidation experiments are performed with irradiation of H_2O_2. However, this irradiation happens in the presence of sulfate, nitrate, and ammonium in the cloud water and aerosol extracts. Can the authors estimate the degree of possible interference from these ions? Sulfate UV photolysis can produce radicals that generate organosulfates in the presence of organics (Nozierre et al. 2010). Nitrate is also a photolytic source of OH and other reactive species in water. Ammonium ion can be oxidized by OH to form hydroxylamine which is quite reactive. One way to assess the contribution from these ions is kinetics modeling; another way is conducting control studies with inorganic ions intentionally added to (or removed from) the solution. The reviewer's guess is that the contribution of other OH precursors is negligible because of the high concentration of H_2O_2.

- Please state the actual mass resolving power of the HR-AMS achieved in these measurements.

- The authors state that only one sample is analyzed from the peak site, so the discussion is focused on RN site. But data from the peak site are included in figures (e.g. Fig 1, 2, 3…) and the discussion includes this site. Also it is not clear how many samples from the RN site are included in the analysis.

- The experimental section could benefit from clarifying sentences to introduce sampling techniques and explain why they are used. For example, it would help to briefly explain the benefit of sampling techniques like CVI.

- The high 70 mM concentration of H_2O_2 may pose a problem because hydrogen peroxide has oxidative potential on its own. This concentration will be further increased during evaporation, and result in chemistry that the authors attribute to OH chemistry. Have the authors performed a control measurement wherein the solution with added H_2O_2 was aerosolized without prior photolysis?

- An estimation of the steady state OH radical concentration during irradiation, and an estimation of the total organic concentration achieved from extraction in 30 mL of water would be useful.

- Acronym “CToF” should be spelled out the first time it is used.

- As samples with low organic loadings were excluded, it would be a good idea to mention explicitly how many samples of each kind were used for analyses.

Results/Discussion

- Page 6026, line 14: volatile aldehydes account for a significant portion of the WSOC. However, upon droplet evaporation, they need not volatilize. De Haan et al. (2009) showed that methylglyoxal when evaporated in the presence of ammonium (which is present in ambient samples) results in low volatility nitrogen compounds. Nguyen et al. (2012) observed similar behavior during evaporation of solutions of more complicated aldehydes. To what extent such reactions occurring during atomization of solutions may contribute to the authors' observations? Perhaps they can be ruled out with appropriate control measurements (e.g., atomization without any irradiation and without H_2O_2 addition)?

- The authors discuss nitrate and sulfate extensively throughout the paper and use quantities like nitrate to sulfate ratios to characterize filter samples and cloud water. However, they do not discuss ammonium ion. Ammonium ion concentration can be quite high in cloud and fog water, as also demonstrated by Figure 1 of this work. Ammonium ion has been shown to be catalytic in the formation of oligomers from glyoxal (Noziere et al. 2009) and participate in complex chemistry during droplet evaporation (De Haan et al. 2011, Nguyen et al. 2012), so it may be interesting to expand upon this discussion.

- The reviewer is not an expert in the analysis of AMS data, and as a result, has some reservations about the ability of AMS to achieve the degree of chemical specificity implied by the discussion in paper. For example, it is not obvious that information on functional groups can be unequivocally derived from generic fragments. The fragment f29 was linked to carbonyls on page 6028, line 3 and fragment f44 was linked to carboxylic acids. These assumptions might work well for relatively simple mixtures (e.g., SOA prepared from a single precursor), but a number of complicated interferences are expected for ambient SOA. For example, m/z 29 can be either CHO^+ or $C_2H_5^+$, m/z 44 can be CO_2^+ or $C_2H_4O^+$, and m/z 43 can be also be $C_3H_7^+$. These interferences must have been discussed extensively in the AMS literature. It would help to cite appropriate examples from the prior work to help the readers better understand the level of confidence in the attribution of peaks to different functional groups.

- Page 6027, line 13 (and also abstract). Because the mass spectra are similar you conclude that there must be a common biogenic source of particles. Please insert a reference to previous AMS studies confirming that biogenic origin can be deduced unequivocally from the AMS spectra.

- Page 6020, line 4-5. It would be useful to compare the O/C ratios in this work with other lab and ambient SOA studies.

- Page 6029, line 27-28: The authors state that the differences from OH oxidation in filter and cloud samples are almost identical but when the spectra are normalized with respect to sulfate there is a only “minor production of m/z 44” or even a small reduction in the filter sample and not the cloud samples. This reviewer thinks that this point is confusing and can be better explained.

- Page 6030, line 2-3: Please explain what f18 and f28 are. They must correspond to H_2O^+ and CO^+, respectively. H_2O^+ and CO^+ are not specific fragments, so this reviewer has reservations about the statement that they are “indicating organic acids are predominant condensed-phase products…”.

- Page 6030, line 20-21: The authors state that the organic composition of cloud organics is different than that of WSOC in aerosols, which contradicts previous points that “in general, the aerosol and cloud organic spectra were very similar, indicating that the cloud water organics likely originated from secondary organic aerosol.” Please explain.

- Two assumptions are used in this paper: (1) high O/C compounds have in general lower volatility (e.g. page 6029, line 11); (2) high O/C is indicative of significant fragmentation, which leads to mass loss through the production of high volatility products (e.g. page 6032, line 19 and page 6036, line 14). These two seemingly contradictory ideas need to be reconciled. Strictly speaking, O/C is not well correlated with volatility. Many other factors such as molecular size and degree of chemical interaction with other organics contribute to volatility.

- Page 6033, line 26: This statement can be made in a clearer way. The authors are probably trying to say that when one atomizes pinonic acid solution some of the compound will volatilize. But when one oxidizes it in solution, and then atomizes the solution, more mass will be in the particle phase due to the less volatile products and therefore the particles will appear to have accumulated mass.

- It is interesting that the authors found a decrease in organic mass from aqueous OH oxidation of glyoxal and methylglyoxal. This seems to be in contrast to other reports, for example from Barbara Turpin group, where oligomer formation was observed for this same system. What can the origin of the discrepancy?

Figures

- Figure 2: Is there a reason the cloud-influenced sample collected on July 12 was not included in Figure 2? The authors should insert a brief explanation.
- Figure 4: The difference spectra look very similar for filter and cloud samples when they are normalized with respect to the organic mass. However, when normalization is done with respect to sulfate, the difference spectra are no longer similar, for example large peaks at m/z 28 and m/z 44 essentially disappear from panel c but not from panel f. This approach is a little confusing; it would be a good idea to explain the normalization procedure in the text and expand on why it is beneficial.

Technical corrections

- In general, the use of “WSOC compounds” is redundant. Please use just “WSOC,” e.g., on page 6026, line 3 you can write “WSOC rapidly increased…”
- The term “peak site” that is used in figure captions and further in the text needs to be defined first in Section 2.1.
- Page 6024, line 10: change “ml” to “mL”
- Page 6024, line 10: change “18 MΩ water” to “purified water (18 MΩ cm)”
- Page 6024, line 17: change “colume” to “volume”
- Page 6029, line 9: delete “as described”
- Page 6034, line 4 and Page 6036, line 7: correct the spelling of “pinonaldehyde”
- Figure 2: the labeling scheme is confusing as the letters a-h are not arranged in order by column nor by row. Please fix.

References

Bateman et al., Photolytic processing of secondary organic aerosols dissolved in cloud droplets. *Phys. Chem. Chem. Phys.* **2011,** *13* (26), 12199-12212.

Chang, J. L.; Thompson, J. E., Characterization of colored products formed during irradiation of aqueous solutions containing H_2O_2 and phenolic compounds. Atm. Environ. 2010, 44 (4), 541-551.

Collett et al., The chemical composition of fogs and intercepted clouds in the United States. *Atmos. Res.* **2002,** *64* (1), 29-40.

De Haan et al., Secondary organic aerosol formation by self-reactions of methylglyoxal and glyoxal in evaporating droplets. *Environ. Sci. Technol.* **2009,** *43* (21), 8184-8190.

Ervens et al., Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies. *Atm. Chem. Phys.* **2011,** *11* (21), 11069-11102.

Fisak et al., Pollutant concentrations in fog and low cloud water at selected sites of the Czech Republic. *Atmos. Res.* **2002,** *64* (1-4), 75-87.

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Nguyen et al., Formation of nitrogen- and sulfur-containing light-absorbing compounds accelerated by evaporation of water from secondary organic aerosols. *J. Geophys. Res. D* **2012,** *117*, D01207, doi:10.1029/2011JD016944.

Noziere et al., Radical-initiated formation of organosulfates and surfactants in atmospheric aerosols. *Geophys. Res. Lett.* **2010,** *37* (5), L05806, doi:10.1029/2009GL041683.

Noziere et al., Products and kinetics of the liquid-phase reaction of glyoxal catalyzed by ammonium ions (NH_4^+). *J. Phys. Chem. A* **2009,** *113* (1), 231-237.