

Interactive comment on “Characterization of aerosol and cloud water at a mountain site during WACS 2010: secondary organic aerosol formation through oxidative cloud processing” by A. K. Y. Lee et al.

Anonymous Referee #2

Received and published: 22 April 2012

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

C1725

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 $R^2 > 0.9$). 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.

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

C1726

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.

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?

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?

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.

C1727

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.

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

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?

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).

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6019, 2012.

C1728