

Interactive comment on “Identifying precursors and aqueous organic aerosol formation pathways during the SOAS campaign” by N. Sareen et al.

Anonymous Referee #1

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The paper describes measurements of the oxidative chemistry of atmospheric water-soluble organic compounds (WSOC). Mist chamber samples were taken during the SOAS campaign, for the collection of gas-phase WSOC. Collected organic species were then oxidized offline by OH radicals (generated by addition of H₂O₂ followed by UV irradiation), and oxidation chemistry was tracked using ESI-MS and IC. A small number of organic species were found to decrease with OH oxidation, and a few oxidation products were found to be formed. These results are interpreted in terms of the formation of secondary organic aerosol (SOA) within cloud or fog droplets.

This is useful study on an important topic in atmospheric chemistry. The overall approach (collection and aqueous-phase oxidation of ambient WSOC) is a novel one, and has the potential to provide insights into the role of aqueous-phase oxidation in SOA formation. However, the actual measurements described in this manuscript raise

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a number of questions about the relationships of the organics collected/measured to those in the ambient atmosphere – examples include the fraction of ambient gas-phase WSOG that are actually collected, the possibility of loss of organic species during sampling, and the potential role of background organic species. These concerns are described below, and need to be addressed if this work is to be published in ACP.

1) The authors point out that there are some large discrepancies between in-situ measurements of gas-phase water-soluble organic gases (e.g., ISOP₂OOH, glyoxal) and the species measured within the mist chambers. This is attributed to “loss during sampling or storage” (line 319), with the possibility that they may have undergone oxidation within the water (line 360). Since such losses have major implications for the generalization of results, these need to be discussed more thoroughly. First, irreversible loss to the sample lines/inlets can be a major sink for IVOCs, so this needs to be considered. What was the sampling scheme used? (The length, diameter, and material used for the sample tubing needs to be given.) What is the sampling efficiency of water-soluble standards sent through this sampling setup? This is briefly touched on in the paper, in a discussion of glyoxal loss to the particle filter (lines 134-136), but this is based on rough calculations and not actual measurements, and doesn't consider the role of losses to tubing.

Further, if oxidation within the collected (non-irradiated) sample is occurring (lines 360-363), there is some important chemistry here that needs to be discussed. The authors appear to be arguing that glyoxal and ISOP₂OOH react with in-situ, non-OH oxidants (H₂O₂, etc). Is this consistent with previous studies, and the existing literature? Moreover such behavior would have to be different from that of compounds focused on in this study: they would have to be resistant to oxidation by any oxidants collected within the mist-chamber samples, but still reactive with OH. Is this the argument being made here? If so, what are the implications for atmospheric oxidation of these various species?

2) The paper focuses entirely with organic species that exhibit “reactant-like trends”.

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However there also should be some discussion of ions that do not exhibit such trends, if any. Were any of these observed? If so, what fraction of total WSOC signal do they make up? What are their formulas and characteristics? (Why are they not oxidized by OH?)

3) While there are some comparisons of mist-chamber species (collected WSOC) and CIMS (gas-phase compounds), this is only for a few select compounds. A more comprehensive comparison of the data from the two techniques is an important and necessary test of the hypothesis that these mist chambers are collecting WSOGs from the gas phase. For example, are there any WSOGs (other than ISOPOOH) measured by the CIMS (or PTRMS, etc.) that are not measured in the mist chamber? Conversely, what could explain any compounds measured in the mist chamber but not by the CIMS (e.g., m/z 125)? Finally, for the ions that are measured by both techniques, the ion intensities should be compared in all cases. (Figure S2 shows only a subset.)

4) Throughout the paper, oxidation results (sample + H₂O₂ + UV) are compared to results from two blanks: sample + H₂O₂ and sample + UV. A third one that is at least as important is oxidation (UV+H₂O₂) of the sample-blank (water from the mist chamber that was exposed to zero air rather than ambient air, ideally sent through the same sampling setup). This is necessary for assessing whether any organic species were introduced by the sample lines, glassware, or sample handling.

Other Comments:

Lines 68-79: This sentence would be more useful if the references were put throughout the sentence (connecting studies with individual features of SOA) rather than all at the end. This is particularly important because of the argument that there are "SOA discrepancies" involving high-MW, sulfur-containing, and nitrogen-containing species. I haven't read all 30 cited references closely, but I'm unaware of any such discrepancies (presumably between measurements and models?), since those organic types are usually not followed explicitly in models, nor are measured routinely in the ambient

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atmosphere.

Line 208: Glyoxal is just one of several standard compounds added. Did all the standards show a similar behavior?

238-240, 263-264: given that an FTICR is used in this study, these discussions of the implications of unit-mass resolution m/z values seem unnecessary.

251, Fig. 1, and elsewhere: What is the approximate aqueous OH concentration in these experiments?

269-273: I think the authors mean Figure 4 instead of Figure 3 here. This whole section could be removed, since it introduces a lot of information and raises questions that are not addressed until later in the paper.

Figure 2: the positive ion (Na⁺) should be given here, as it is in Figure 4.

Lines 284-285, 324-325; Figure 3: This chemistry all involves the formation of diols from C-C double bonds. However diols are not generally considered to be alkene oxidation products. The main routes for formation of diols are when RO₂+RO₂ reactions dominate (e.g., Ruppert and Becker 2000, Atmos. Environment, 34, 1529-1542) or in the oxidation of conjugated dienes (leading to the formation of isoprene tetrols). What is the mechanism proposed here? Similarly, have these diol species been measured in any laboratory product studies?

Line 288: These aren't "mechanisms" but simply measured compounds mapped back to potential reactants.

Lines 290-319, Figure 4: When MeOH is added to the sample (for ESI analysis), might there be an exchange between -OH and -OCH₃ groups? If so, this species might simply be from an isoprene tetrol.

Figure 5: I would think some of these structures could undergo fragmentation during MS-MS analysis. As stated in line 315, O-O bonds should break in this case.

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Figure 5: The structures given for m/z 125 are quite non-polar, with only one functional group in an eight-carbon molecule. Are they sufficiently water-soluble that they would be expected to be trapped in the mist chamber (or in cloud/fog droplets in the atmosphere)?

297-319: The argument in this paragraph was hard to follow. First it is stated that the CIMS and ESI measurements could “be the same compound”. But then it’s argued that CIMS is measuring IEPOX/ISOPOOH, which is not measured in the mist-chamber samples by ESI. But yet this ion is given as one of the CIMS-ESI comparisons in S2, suggesting the authors are arguing the species are in fact the same. This needs to be clarified.

Line 326: the structure given in Fig. 4 is not consistent with isoprene oxidation, since it has two methyl groups. The only plausible isoprene product (with one methyl group) of that formula that I can think of is IEPOX.

Figure S2: Plots need axis labels and units.

Lines 381-382: This observation may simply be a result of a historical lack of good techniques for measuring gas-phase pyruvate and oxalate (i.e., pyruvic acid and oxalic acid). These compounds can now be measured routinely with CIMS (with acetate ionization), so these sorts of comparisons haven’t really been able to be made well until now.

Lines 426: What were the “several” isoprene products? I think only one (C₅H₁₀O₃) is discussed in the paper (but see my comments above).

Overall: From the concentrations of oxalate/pyruvate formation, this work should give a rough upper limit for the amount of aqueous SOA that can be formed from cloud/fog processing in a given sample (assuming collection of all gas-phase WSOC). What is this value?

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