

REVIEWER 1

Review of “*Identifying precursors and aqueous organic aerosol formation pathways during the SOAS campaign*” by Sareen et al.

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 a 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 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.

We thank the reviewer for their helpful feedback and suggestions. We address each point in order below.

1) *The authors point out that there are some large discrepancies between in-situ measurements of gas-phase water-soluble organic gases (e.g., ISOPOOH, 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 ISOPOOH 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?

These suggestions to better characterize and discuss potential losses are helpful.

The length, diameter and material of the inlet tubing has been added to the first paragraph of methods section 2.1:

“Samples were collected from June 1 – July 14, 2013 from 1 m above the trailer roof through a 1.3 cm OD PTFE inlet (approximately 1.7 m in length).”

The reviewers' comments have been helpful in clarifying our thoughts on losses.

There are three major ways to lose water-soluble organic gases during sampling/storage:

1. Losses in tubing. Recent work by Krechmer et al highlight the uncertainties associated with quantifying the loss of gas-phase organic compounds to Teflon (Krechmer et al., 2016). This limitation is now acknowledged.
2. Ozone could also be collected during sampling and could react with certain organic gases during mist chamber collection.
3. Storage and sample handling. As described in the text, at the end of each collection day, the samples were separated into experimental sized aliquots and frozen immediately. They were shipped overnight with ice packs to the laboratory at Rutgers, where they were placed in the freezer at -20°C upon arrival. Before an experiment the sample was thawed at room temperature.

IEPOX does not survive extended storage in water (confirmed with our organic synthesis collaborator). We expect that this is also the case for ISOPOOH. This explains why we did not see IEPOX and ISOPOOH in our collected samples.

We have added a section called “Methodological Limitations” to address losses. We had already addressed losses to the quartz fiber filter, so that text has now been moved down to the new paragraph, which reads:

“It should be noted that WSOGs can be lost during sampling and storage through: 1) losses in tubing and by adsorption to the QFF during collection, 2) reactions in the mist chamber during collection with water-soluble ambient oxidants capable of penetrating the inlet (e.g., ozone), and 3) losses during storage post collection. The QFF removes particles upstream of the mist chambers. In the early stages of sampling, on the clean filter, adsorption of gases on the filter will reduce the concentrations of gases sampled by the mist chamber until these gases reach gas phase – adsorbed phase equilibrium. Using glyoxal as a WSOG-surrogate and the work of (Mader and Pankow, 2001) we predict that the measured WSOG in the mist chamber will be depleted for less than 2% of our sampling time (after <0.1 m³) due to loss to the filter. Thus, we expect water-soluble gases to penetrate through the QFF very efficiently for collection in the mist chamber water. Losses to Teflon inlets and chamber walls (Krechmer et al., 2016)

can be significant and variable and may reduce the number of species we are able to collect and identify in this work. While OH radicals are unlikely to penetrate the inlet, ozone might. Thus some ozone could be scrubbed by the mist chambers and could result in oxidation of some WSOGs during collection. Though many organics are stable when stored frozen in water, IEPOX does not survive extended storage in water (confirmed with our organic synthesis collaborator). We expect this to be the case for ISOOPOH also. ISOOPOH is an OH oxidation product of isoprene, which is further oxidized by OH under low-NO conditions to form isomeric IEPOX (Paulot et al., 2009). Both IEPOX and ISOOPOH are prevalent at the SOAS ground site due to the abundance of isoprene emissions in this forested region. These losses constitute the major limitation of the work in that they restrict the number of reactive water-soluble compounds we are able to identify.”

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

As the reviewer suggests, we do observe other organic species (not discussed in the text) that do not react with OH. Woods Hole high-resolution instrument time is expensive and valuable. We used our instrument time to focus on the reactive organic compounds, and we therefore do not have tentative identification of the other organics present in the samples. Since we have not chemically characterized these species, we cannot hypothesize why these ions are not oxidized by OH. The organic species with “reactant-like” trends make up about 30% of the ESI-MS total ion abundance in the analyzed samples. We now say this in section 3.1:

“Together, these ions make up roughly 30% of the positive mode total ion abundance in the experiment samples.”

It is possible that some compounds that appear to be unreactive are instead both formed and reacted by the complex mix in such a way that a trend cannot be observed.

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 ISOOPOH) 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.)

Yes, there are masses identified by the CIMS and not the mist chamber and vice versa. We have only plotted masses that were reported by both. The comparisons with the

CIMS are less useful than we had hoped. A major advantage of the CIMS is the much better time resolution. However, the CIMS is not able to distinguish between multiple compounds with the same elemental formula and each CIMS ionization reagents is sensitive to some compounds and not to others (Lopez-Hilfiker et al., 2016). The advantage of the mist chamber is that it collects a much wider range of water-soluble organic compounds (WSOCs) and that samples are available for off-line analyses, such as FT-ICR MS-MS. The MS-MS fragmentation helps us to distinguish between compounds with the same elemental formula but different structures. We expect some overlap between species measured by the two methods, but we also expect differences, and just because the two methods measure compounds with the same elemental formula does not mean they are measuring the same compounds. For example, we expect to find several isoprene-derived compounds with the same elemental composition at SOAS, and the relative ionization efficiencies of these compounds using CIMS are very different. Thus, even if the mist chamber collected all these compounds perfectly and there were no losses during storage, we would not expect the correlation between the CIMS and mist chamber ESI-MS signals to be strong. This is due to the different ionization methods used. All the species that are detected in the mist chamber using the ESI-MS are not necessarily detected using the CIMS. Additionally, collection/storage losses could mean that the CIMS detects some compounds that the mist chambers do not.

To make this clearer, we now have placed the CIMS comparisons under a separate header called “**Comparison of CIMS and ESI-MS results**,” and moved this section to SI. We added

“The sensitivity of the I CIMS depends strongly on compound structure. Thus, we expect to find compounds in the mist chamber samples that are not detected by I CIMS , and it is likely that real-time CIMS analysis facilitates measurement of some species that we will not be able to detect in integrated mist chamber samples.”

4) Throughout the paper, oxidation results (sample + H_2O_2 + UV) are compared to results from two blanks: sample + H_2O_2 and sample + UV. A third one that is at least as important is oxidation (UV+ H_2O_2) 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.

The reviewer’s suggestion to sample “zero air” is challenging, because of the high flow rates. However, in addition to sample + H_2O_2 and sample + UV, we conducted a field water + H_2O_2 + UV control experiment. The field water blanks were handled, transported and stored identically to samples. The OH-reactive water-soluble ions identified in the sample + OH experiments were not found in the field water + H_2O_2 + UV control experiment.

We added to section 3.1: “*In field water + OH control experiments, these ions were not seen, confirming that they are not contaminants.*”

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 atmosphere.

We have clarified this sentence in the main text to explain that the discrepancies refer to key atmospheric observations not explained by semi-volatile partitioning theory, as follows:

“Inclusion of aqueous chemistry of clouds, fogs, and wet aerosols in models and experiments helps to explain discrepancies *in atmospheric observations of SOA that aren’t explained by semi-volatile partitioning theory, ...*”

This is a good suggestion by the reviewer to separate out the references, but since quite a few of the references would include multiple features highlighted in these lines, we have opted to leave it as is. Following is an abbreviated list of some references pointing to the features:

- high atmospheric O/C ratios: Volkamer et al., 2007; Carlton et al., 2006
- enrichment of organic aerosol aloft: Heald et al., 2006; Sorooshian et al., 2010
- formation of oxalate, sulfur- and nitrogen-containing organics and high molecular weight compounds: Kawamura and Ikushima, 1993; Kawamura et al., 1996; Crahan et al., 2004; Kalberer et al., 2004; Herrmann et al., 2005; Altieri et al., 2006; Galloway et al., 2009

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

Other standards also showed a behavior similar to glyoxal. Glyoxal variance as mentioned in the text is <6%; for the other two standards, methylglyoxal and glycolaldehyde, the variance is 7% and 4%, respectively.

This has been added.

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.

As per the reviewer recommendation, we have removed this discussion from the text.

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

We provided the OH production rate from hydrogen peroxide photolysis. In order to estimate an aqueous OH concentration in these experiments, we would need to be able to

model the chemistry occurring in the reaction vessel. Tan et al. conducted OH oxidation experiments of glyoxal at cloud water condition and modeled the reaction vessel chemistry to predict the OH concentration (Tan et al., 2009). If we assume that all the water-soluble organic gases collected in the mist chamber behave similarly to glyoxal, since our TOC values for the mist chamber are within the range of the experiments conducted by Tan et al., and OH production rate was similar as well, we estimate OH concentrations to be similar to those of Tan et al., i.e. 3×10^{-12} M to 6×10^{-12} M.

We now say this in section 2.2:

“Note, while we can calculate the OH production rate from hydrogen peroxide photolysis (1.25×10^{-2} μ M [OH] s^{-1}), the concentration of OH in the reaction vessel depends also on the reactivity of the organics. If the WSOG mix behaved similarly to glyoxal, OH concentrations would be on the order of 10^{-12} M (i.e., similar to Tan et al) ”

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.

We thank the reviewer and have corrected the text to read Figure 4 instead of Figure 3 and have removed part of the text as suggested.

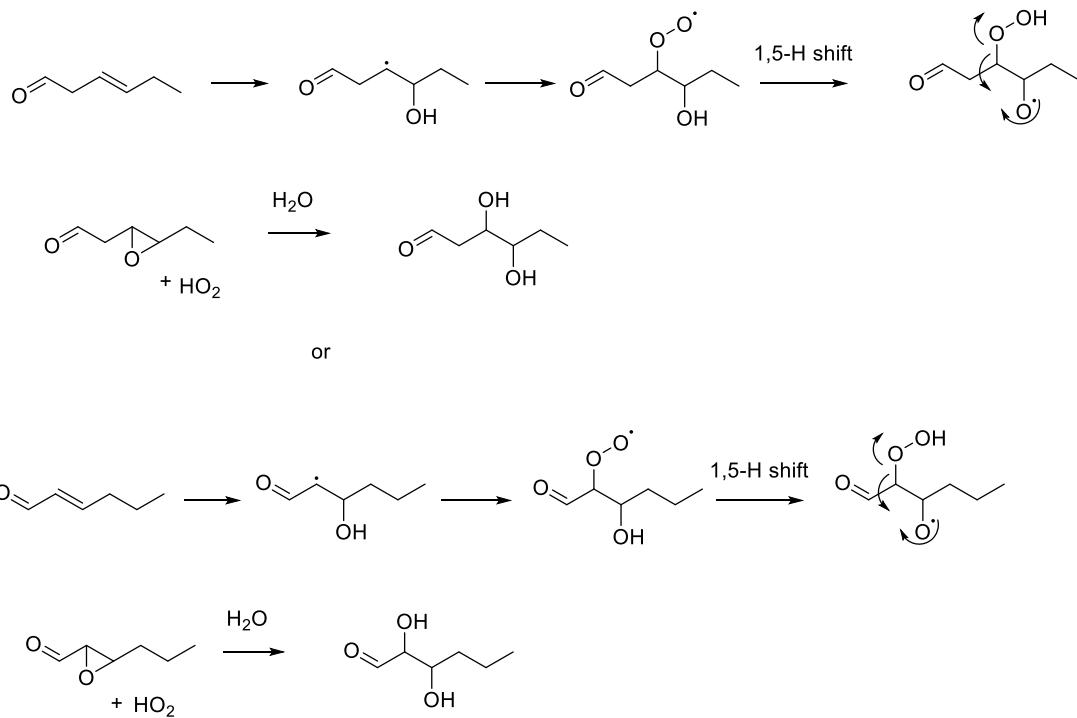
Figure 2: the positive ion (Na⁺) should be given here, as it is in Figure 4.

We have included Na⁺ in Figure 2.

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?

The putative dihydrodiol can form via an epoxide by a reaction analogous to that published for the formation of dihydroxyisopentanol (DHIP) from 2-methyl-3-buten-2-ol (MBO) (Zhang et al., 2014). In water, the epoxide hydrolyzes to the corresponding dihydrodiol. The formation of 2,3-dihydroxypentanal can thus be explained by the scheme below.

Scheme: Formation of 2,3-dihydroxypentanal from pent-2,3-enal



DHP, in fact, can be cited as an example of a diol generated from an alkene measured both in laboratory and field studies.

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

"Mechanisms" has been removed from the text.

Lines 290-319, Figure 4: When MeOH is added to the sample (for ESI analysis), might there be an exchange between $-\text{OH}$ and $-\text{OCH}_3$ groups? If so, this species might simply be from an isoprene tetrol.

Unactivated alcohol OH, such as the hydroxyl groups of 2-methyltetrol will not exchange with methanol in solution to give a methoxy substituent, unlike the situation for carboxylic acids where formation of the corresponding methyl ester is possible. The exchange suggested by the reviewer has not been reported in any of the numerous LC/ESI-MS analyses of 2-methyltetrols in isoprene SOA. The MS^2 data are best explained by formation of a hemiacetal via addition of methanol to an aldehyde, which is a well-known reaction.

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.

Since Figure 5 is purely speculative and we do not have supportive fragmentation data to back up any of the proposed structures, we have decided that it would be best to remove this figure and the related text from the manuscript and avoid any confusion or

misinformation for the readers.

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)?

As stated in the previous comment, this figure has been removed from the text.

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/ISOPPOOH, 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.

We have edited this paragraph for clarity. Two or more compounds are detected with the same elemental composition but with different sensitivities in the CIMS. Thus the CIMS signal might contain the compound we tentatively identified, but we cannot be sure. Also, the ion discussed here is a fragment and not a parent ion.

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.

The reviewer is correct and we have removed this statement from the draft.

Figure S2: Plots need axis labels and units.

Units are normalized ion abundance. We have included the label for sampling dates as per the reviewer’s suggestion and added the following text to the figure caption:

“Normalized ion abundance from ESI-MS and HRTToF-CIMS for compounds with the same elemental formula.”

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.

The reviewer correctly points out that CIMS measurements can help determine the gas to particle ratio of oxalic acid. However, similar high quality gas-particle partitioning measurements have been conducted earlier using other techniques such as those used by Martinelango et al. during the Bay Region Atmospheric Chemistry Experiment (BRACE) (Martinelango et al., 2007). Their measurements show that particle-phase oxalate concentrations are much greater than gas-phase concentrations. Additionally, field

measurements of dicarboxylic acids in atmospheric particles in Hong Kong find only about 6-12 % of total oxalic acid in the gas-phase (Yao et al., 2002). We reference these papers.

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

As per the reviewer’s suggestion, we have changed this line to read:

“...and some are tentatively gas-phase oxidation products of green leaf volatiles..”

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?

We agree with the reviewer that it would be helpful to provide an upper limit for the amount of aqueous SOA that can be formed from cloud/fog processing in a given sample. In doing so, we would have to make quite a few assumptions such as collection of all gas-phase WSOC (as the reviewer suggests), conversion of all SOA to oxalate/pyruvate etc. that could greatly distort the results and mislead the community, and hence we have opted to not provide such an estimate. A technique that could provide a better estimate would be to conduct droplet evaporation experiments on the collected samples.

REVIEWER 2

The authors of this manuscript collected gas phase compounds during the SOAS measurement campaign and measured their reaction progress in the presence of OH to understand the aqueous phase chemistry that occurs as a result of gas-to-particle partitioning of these compounds. They measured loss rates of several oxidized compounds and formation rates of four organic acids as a result of reaction of these ambient compounds with OH and monitored the formation of highly oxidized oxalate, pyruvate, acetate, and glycolate over time. This indicates that the aqueous phase oxidation of water soluble organic compounds may be very important for the formation of these compounds, possibly followed by repartitioning back to the gas phase after oxidation. This study is important for the atmospheric chemistry because it uses ambient compounds as precursors for oxidation, instead of single “proxy” compounds or simple mixtures of such. The authors were able to track both precursor and product compounds, which could lead to mechanistic conclusions about the formation of organic acids in atmospheric waters. However, more details are needed about both the sampling method (e.g., recovery of compounds through the mist chambers and instrumental precision, see comments below) and about other compounds besides those discussed here. This will give the reader a better sense of the significance organic acid formation from the compounds discussed here.

The five masses that exhibited “reactant-like trends” are discussed in detail. Are these the only compounds observed in the initial mixtures? If not, were there others that

reacted with OH or that stayed constant over the course of the experiment? It seems unlikely that these are the only compounds detected, and more detail would be appreciated to give the reader a sense of the concentrations of these compounds as compared to others. How significant were these five compounds in terms of the percentage of organic matter? Why wouldn't other compounds react with OH? How likely is it that compounds that are not detected contribute to organic acid formation? If these are the only compounds that displayed "reactant-like trends," then this will allow for the conclusion that oxalate, pyruvate, acetate, and glycolate are directly produced from these compounds and not from others. Otherwise, this argument is hard to make. A similar comment can be made for the oxidized species formed from the OH reaction. Only four organic acid products are mentioned in the manuscript. Were others observed? If not, is this expected? The reaction of OH with organics is likely to produce these small organic acids eventually, but I would expect to see other acids formed as intermediates in this process as well.

Discussion of the significance of these compounds in WSOC would strengthen this manuscript. As is, the authors make some interesting conclusions about the formation of aqueous SOA formation, but it is difficult to determine the magnitude of their contributions to aqueous phase chemistry. An upper bound estimate of this contribution might also be interesting to see.

As the reviewer suggests, we do observe other organic species (not discussed in the text) that do not react with OH. Since the focus of our investigative effort and chemical characterization was on compounds that reacted, we do not discuss "non-reacting" ions. In fact, FT-ICR-MS time is expensive and analyses are time consuming. Thus we focused our instrument time on the reactive compounds. Since we have not chemically characterized these species, we cannot hypothesize why these ions are not oxidized by OH. The organic species with "reactant-like" trends account for about 30% of the total ion abundance observed in the mist chambers. This is now indicated in the text:

"Together, these ions make up roughly 30% of the positive mode total ion abundance in the experiment samples"

The organic acids observed in this study are formed as intermediates or products and as the reviewer says, OH oxidation will lead to their formation. It is certainly possible that other acids could be formed.

We agree with the reviewer that it would be helpful to provide an upper limit for the amount of aqueous SOA that can be formed from cloud/fog processing in a given sample. In doing so, we would have to make quite a few assumptions such as collection of all gas-phase WSOC, conversion of all SOA to oxalate/pyruvate etc. that could greatly distort the results and mislead the community, and hence we have opted to not provide such an estimate. A technique that could provide a better estimate would be to conduct droplet evaporation experiments on the collected samples.

Specific comments

The authors state in the methods section that intensive days were chosen because of high concentration predictions by NCAR and that during those days, they observed higher than usual TOC content in general. However, in examining Supplementary Table S1, it seems that the days marked "intensive" are not much higher than others, if at all. The range given in the text (92-179 $\mu\text{M-C}$) does not match the range of TOC on intensive days. Can this be clarified? Does this range only represent the days that were used in further measurements?

We apologize for this confusion. To clarify, we primarily focused on the intensive days that had the highest TOC contents; primarily the first three intensive periods highlighted in the table. Besides these days, we also chose to pick July 20th and 21st to perform experiments due to the high TOC values on these days. We have clarified this in the text:

"In general, mist chamber samples on intensive sampling days had higher organic content (TOC = 92-179 $\mu\text{M-C}$), and hence we focused our experiments on those days and included two additional days from the non-intensive period that had high TOC values (Table 1)."

Line 208: Why is glyoxal the only standard compared across all analysis days? Were the variabilities of the other standards on a similar scale? If so, this should be stated here.

Similar to glyoxal, the other standards also showed a similar behavior. Glyoxal variance as mentioned in the text is <6%; for the other two standards, methylglyoxal and glycolaldehyde, the variance is 7% and 4%, respectively. This is now noted in the text.

Line 215-219: Limit of detection and precision information is given here for oxalate, but this is not the only organic acid measured by IC. Can all the acids studied be considered to be similar to this or do they vary significantly?

Yes, we typically find the precision and detection limits of oxalate, pyruvate, and acetate to be similar. However, in this work we used ESI-MS for pyruvate.

In Figure 2, m/z 187 is actually the sodium cluster, which is not shown in the figure. However, Figure 4 makes it clear that this is the case. These should be changed to be consistent with each other.

We have included Na⁺ in Figure 2.

A predicted structure for m/z 187 is shown in Figure 2, along with the predicted gas- and aqueous- phase structures. However, the observed mass contains an extra methoxy group. From previous comments on the methodology and the discussion that follows about the compound at m/z 173, I assume this is a result of hydration by methanol in the FT-ICR-MS. However, this is not stated until after the discussion of m/z 187, and should be explained the first time it is seen.

We thank the reviewer for this suggestion and have included this information in the text for m/z 187 as follows:

“The positive ion at m/z 187 is seen hydrated with methanol and upon fragmentation, methanol is lost and the daughter ion peak is observed at m/z 155.0680, corresponding to the molecular formula, C₆H₁₂O₃.”

In line 319 and again in lines 360-364, the authors state that they expect IEPOX, ISOPOOH, and glyoxal were lost in their experiments during sampling or storage. Have any tests been done to quantify losses of other compounds during sampling or storage? If these compounds were lost, it seems likely that there are others that are either lost or not fully recovered. Were any recovery studies done with known amounts of standards instead of spiking the samples just before analysis?

We have not performed recovery studies, although this would be a good addition to our future work. However, we have now added a section called “Methodological limitations” of the work that focuses on issues such as losses:

“It should be noted that WSOGs can be lost during sampling and storage through: 1) losses in tubing and by adsorption to the QFF during collection, 2) reactions in the mist chamber during collection with water-soluble ambient oxidants capable of penetrating the inlet (e.g., ozone), and 3) losses during storage post collection. The QFF removes particles upstream of the mist chambers. In the early stages of sampling, on the clean filter, adsorption of gases on the filter will reduce the concentrations of gases sampled by the mist chamber until these gases reach gas phase – adsorbed phase equilibrium. Using glyoxal as a WSOG-surrogate and the work of (Mader and Pankow, 2001) we predict that the measured WSOG in the mist chamber will be depleted for less than 2% of our sampling time (after <0.1 m³) due to loss to the filter. Thus, we expect water-soluble gases to penetrate through the QFF very efficiently for collection in the mist chamber water. Losses to Teflon inlets and chamber walls (Krechmer et al., 2016) can be significant and variable and may reduce the number of species we are able to collect and identify in this work. While OH radicals are unlikely to penetrate the inlet, ozone might. Thus some ozone could be scrubbed by the mist chambers and could result in oxidation of some WSOGs during collection. Though many organics are stable when stored frozen in water, IEPOX does not survive extended storage in water (confirmed with our organic synthesis collaborator). We expect this to be the case for ISOPOOH also. ISOPOOH is an OH oxidation product of isoprene, which is further oxidized by OH under low-NO conditions to form isomeric IEPOX (Paulot et al., 2009). Both IEPOX and ISOPOOH are prevalent at the SOAS ground site due to the abundance of isoprene emissions in this forested region. These losses constitute the major limitation of the work in that they restrict the number of reactive water-soluble compounds we are able to identify.”

In Figure 5, for m/z 125, how likely is it that the first structure shown (the aldehyde) is detected as such and not hydrated in the aqueous mixture? Is this a likely structure? The authors also state in the discussion of this figure that gas phase compounds are

seen at m/z 129 and 143. However, it seems unlikely that these compounds are the polyols found in Figure 5. Are there any compounds with those masses that may be found in the same form in both the gas- and aqueous- phase?

Since Figure 5 is purely speculative and we do not have supportive fragmentation data to back up any of the proposed structures, we have decided that it would be best to remove this figure and the related text from the manuscript and avoid any confusion or misinformation for the readers.

In the Figure 6 caption, special mention is made of the fact that oxalate is present in all samples. Is this not true for pyruvate as well?

This is true for both pyruvate and oxalate and have corrected this in the figure caption.

I'm not really sure why Supplementary Figure S3 is not included in the main portion of the manuscript. It is discussed in the main text and seems to be important to the overall conclusions of the paper. It is also hard to follow, mainly because there are so many points. It would be easier to see the trends if a general trend line was added as in Figure 6.

Acetate and glycolate are found in some samples, but in varying concentrations. Did the authors see any trends that might explain their formation on some days and not others? Also related, if acetate and glycolate co-elute on the IC, how can the statement be made that "Acetate formation is seen on some but not all days" when any signal seen is due to the combination of both? Was acetate also measured via another method? There seems to be a lack of discussion about the glycolate present. In the discussion of these results (lines 375-380), acetate is mentioned but not glycolate. Is this because it is expected that most of this combined signal is acetate or because glycolate is not expected to be an important oxalate precursor in these ambient mixtures?

Supplementary Figure S3 shows acetate and glycolate production during sample oxidation experiments. As shown in the figure, there are two experimental days where there is a higher production of these compounds, but there are no trends (e.g. relation to high initial sample TOC values) that we have observed to explain their higher formation on some days versus others. On some of the days with lower production of acetate/glycolate, the trend lines would be similar to the control experiments, not allowing us to conclusively assert that they are formed on all days, and hence we have not included this figure in the main text. The reviewer is correct that acetate and glycolate co-elute and we have no other way of distinguishing between the two. We have corrected the statement to include glycolate:

"Acetate/ glycolate formation is seen on some but not all days" and include glycolate in the results and discussion.

Were any measurements of oxalate in the particle phase taken at SOAS? in lines 421-423, the authors state that based on their conclusions, it is unlikely that oxalate will be

present in the particle phase, but it would be interesting to test this.

They do not seem to be published yet.

Technical Corrections:

Page 6, line 140: "ml" should be "mL"

Page 7, line 159: "Henry's law" should be "Henry's Law"

Page 12, line 270: Should this refer to Figures 2 and 4 instead of 2 and 3?

Page 13, line 288: Figure 3 does not show a mechanism, but only initial and final structures.

Page 14, line 327: It is unclear to me why the word "these" is italicized.

Page 16, line 363: There is an extra parenthesis at the end of the paragraph.

Supplementary Figure S2: This figure is missing axes labels.

Supplementary Figure S3 caption, line 2: "co-elude" should be "co-elute"

We thank the reviewer for these technical corrections and have addressed them in the final draft.

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