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 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, line 132:

"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^{o}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" in the Results & Discussion section (line 300) 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:

"However, 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 m^3) 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). IEPOX and ISOPOOH were present in the gas-phase during the SOAS campaign (Nguyen et al., 2015). They have relatively high Henry's Law constants (i.e., ($H_{L,IEPOX}$=2.7 x 10^6 M atm^{-1}). IEPOX was readily detected in ambient samples spiked with 3000 μM, 300 μM, and 30 μM of IEPOX, indicating that it can be ionized in our sample matrix. (Authentic trans-β-IEPOX, which is the predominant isomer of IEPOX, was synthesized for this purpose (Zhang et al., 2012).) However, it was not found in our ambient samples since it is not stable when stored in water."

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, line 346:

"Together, the ions discussed herein account for 30% of the total ion abundance."

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 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.)

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 that 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 + 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.

The reviewer's suggestion to sample "zero air" is challenging, because of the high flow rates. However, in addition to sample + H2O2 and sample + UV, we conducted a field water + H2O2 + 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 + H2O2 + UV control experiment.

We added to section 3.1, line 246:

"*In control experiments where we generated OH radicals in field water blanks, these ions were not observed, 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 on line 200.

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, line 168:

"While we can calculate the OH production rate from hydrogen peroxide photolysis (1.25×10^{-2} μM [OH] s^{-1}), the concentration of OH in the reaction vessel depends also on the reactivity of the organics. If the WSOG mix behaves similarly to glyoxal, OH concentrations would be on the order of 10^{-12} M (i.e., similar to Tan et al 2009)"

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.

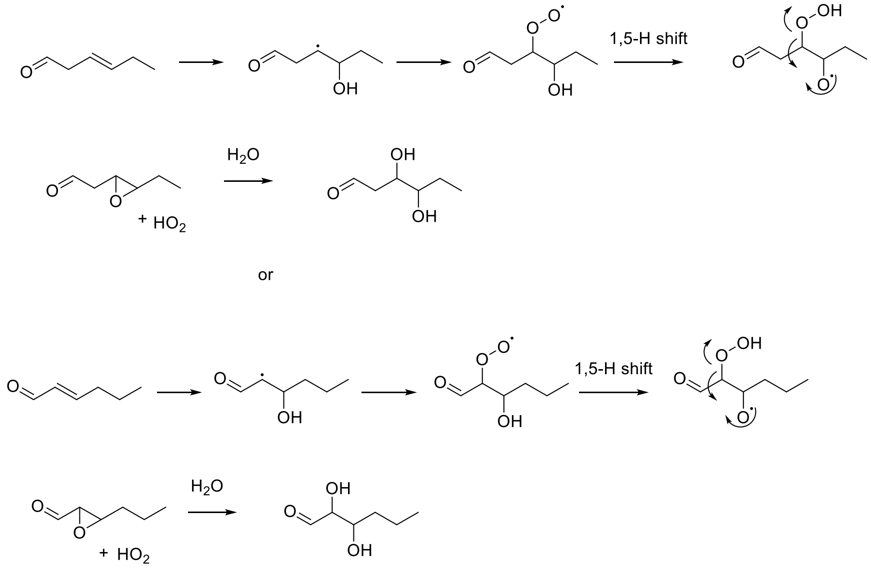
Figure 2: the positive ion (Na+) should be given here, as it is in Figure 4.

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 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 –OH and –OCH3 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/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.

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 HRToF-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 ($C_5H_{10}O_3$) is discussed in the paper (but see my comments above).

As per the reviewer's suggestion, we have changed line 415 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, line 346:

"Together, the ions discussed herein account for 30% of the total ion abundance."

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 µM-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, line 152:

"In general, mist chamber samples on intensive sampling days had higher organic content (TOC = 92-179 µM-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 200.

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 MS-MS shows loss of methanol, to give a product ion at m/z 155.0680 corresponding to the neutral molecular formula, $C_6H_{12}O_3$., consistent with expectations for a sodium ion complex of a dihydroxy hemiacetal in methanol solution, shown in Figure 2..*"

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, line 318:

"However, 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 m^3) 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). IEPOX and ISOPOOH were present in the gas-phase during the SOAS campaign (Nguyen et al., 2015). They have relatively high Henry's Law constants (i.e., ($H_{L,IEPOX}$=2.7 x 10^6 M atm^{-1}). IEPOX was readily detected in ambient samples spiked with 3000 µM, 300 µM, and 30 µM of IEPOX, indicating that it can be ionized in our sample matrix. (Authentic trans-β-IEPOX, which is the predominant *isomer of IEPOX, was synthesized for this purpose (Zhang et al., 2012).) However, it was not found in our ambient samples since it is not stable when stored in water."*

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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Identifying precursors and aqueous organic aerosol formation pathways during the SOAS campaign

Neha Sareen[1], Annmarie G. Carlton[1, a], Jason D. Surratt[2], Avram Gold[2], Ben Lee[3], Felipe D. Lopez-Hilfiker[3, b], Claudia Mohr[3, c], Joel A. Thornton[3], Zhenfa Zhang[2], Yong B. Lim[1, d], Barbara J. Turpin[2]

1. Department of Environmental Sciences, Rutgers University, 14 College Farm Road, New Brunswick, New Jersey 08901, United States

2. Department of Environmental Sciences and Engineering, Gillings School of Public Health, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States

3. Department of Atmospheric Sciences, University of Washington, Seattle, Washington 98195 United States

[a] Now at Department of Chemistry, University of California, Irvine, CA 92697, USA

[b] Now at Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

[c] Now at Institute of Meteorology and Climate Research, Atmospheric Aerosol Research, Karlsruhe Institute of Technology, Karlsruhe, Germany

[d] Now at Center for Environment, Health and Welfare Research, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea

Correspondence to: Neha Sareen (neha.sareen15@gmail.com), Barbara J. Turpin (bjturpin@email.unc.edu)

Abstract. Aqueous multiphase chemistry in the atmosphere can lead to rapid transformation of organic compounds, forming highly oxidized low-volatility organic aerosol and, in some cases, light-absorbing (brown) carbon. Because liquid water is globally abundant, this chemistry could substantially impact climate, air quality, and health. Gas-phase precursors released from biogenic and anthropogenic sources are oxidized and fragmented, forming water-soluble gases that can undergo reactions in the aqueous phase (in clouds, fogs, and wet aerosols) leading to the formation of secondary organic aerosol (SOA$_{AQ}$). Recent studies have highlighted the role of certain precursors

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like glyoxal, methylglyoxal, glycolaldehyde, acetic acid, acetone, and epoxides in the formation of SOA_{AQ}. The goal of this work is to identify additional precursors and products that may be atmospherically important. In this study, ambient mixtures of water-soluble gases were scrubbed from the atmosphere into water at Brent, Alabama during the 2013 Southern Oxidant and Aerosol Study (SOAS). Hydroxyl (OH•) radical oxidation experiments were conducted with the aqueous mixtures collected from SOAS to better understand the formation of SOA through gas-phase followed by aqueous-phase chemistry. Total aqueous-phase organic carbon concentrations for these mixtures ranged from 92-179 µM-C, relevant for cloud and fog waters. Aqueous OH-reactive compounds were primarily observed as odd ions in the positive ion mode by electrospray ionization mass spectrometry (ESI-MS). Ultra high-resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) spectra and tandem MS (MS/MS) fragmentation of these ions were consistent with the presence of carbonyls and tetrols. Products were observed in the negative ion mode and included pyruvate and oxalate, which were confirmed by ion chromatography. Pyruvate and oxalate have been found in the particle phase in many locations (as salts and complexes). Thus, formation of pyruvate/oxalate suggests the potential for aqueous processing of these ambient mixtures to form SOA_{AQ}.

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1 Introduction

Aqueous multiphase chemistry has the potential to alter the climate-relevant properties and behavior of atmospheric aerosols. It is well established that a major pathway for secondary organic aerosol (SOA) formation is via the partitioning of semi-volatile products of gas-phase photochemical reactions into preexisting organic particulate matter (Seinfeld and Pankow, 2003). Semi-volatile partitioning theory is widely used to model SOA (Odum et al., 1996; Seinfeld and Pankow, 2003; Donahue et al., 2006). However differences between organic aerosol mass/properties predicted via this formation mechanism and those measured in the atmosphere suggest that other processes (e.g., aqueous chemistry) may also contribute (Foley et al., 2010; Hallquist et al., 2009).

Recent studies have highlighted the importance of water-soluble organic gases (WSOGs), liquid water, and condensed-phase reactions to SOA formation and properties (Ervens et al., 2011; Monge et al., 2012; Carlton and Turpin, 2013). Biogenic and anthropogenic gas-phase precursors are oxidized to form WSOGs such as glyoxal, methylglyoxal, glycolaldehyde, and acetone (Spaulding et al., 2003). These WSOGs are too volatile to form SOA through absorptive partitioning, but they can undergo aqueous reactions in clouds, fogs, and wet aerosols to form low-volatility products and "aqueous" SOA (SOA$_{\mathrm{AQ}}$) (Blando and Turpin, 2000; Ervens et al., 2004; Kroll et al., 2005; Liggio et al., 2005; Lim et al., 2005; Heald et al., 2006; Loeffler et al., 2006; Sorooshian et al., 2006; Volkamer et al., 2006; Volkamer et al., 2007; Ervens et al., 2008; De Haan et al., 2009a; El Haddad et al., 2009; Ervens et al., 2011; Rossignol et al., 2014). Inclusion of aqueous chemistry of clouds, fogs, and wet aerosols in models and experiments helps to explain discrepancies in atmospheric observations of SOA that are not explained by semi-volatile partitioning theory, particularly high atmospheric O/C ratios, enrichment of organic aerosol aloft, and 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; Carlton et al., 2006; Heald et al., 2006; Volkamer et al., 2007; Nozière and Cordova, 2008; De Haan et al., 2009b; El Haddad et al., 2009; Galloway et al., 2009; Shapiro et al., 2009; Volkamer et al., 2009; Lim et al., 2010; Lin et al., 2010; Nozière et al., 2010; Perri et al., 2010; Sareen et al., 2010; Schwier et al., 2010; Sorooshian et al.,

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2010; Sun et al., 2010; Ervens et al., 2011; Lee et al., 2011; Tan et al., 2012; Ervens et al., 2013; He et al., 2013; Gaston et al., 2014; Ortiz-Montalvo et al., 2014). Although uncertainties are large, modeling studies show that SOA_{AQ} is comparable in magnitude to "traditional" SOA (Carlton et al., 2008; Fu et al., 2008; Fu et al., 2009; Gong et al., 2011; Myriokefalitakis et al., 2011; Liu et al., 2012; Lin et al., 2014). However, SOA_{AQ} precursors and their chemical evolution remain poorly understood.

Much of what we know about aqueous chemistry leading to SOA_{AQ} formation is derived from laboratory studies with single precursors hypothesized to be important; however, the most important precursors for SOA_{AQ} formation in the ambient environment may remain unidentified. A small number of studies conducted with ambient mixtures have provided insights into the pathways of SOA_{AQ} formation. For example, photochemical oxidation of aerosol filter samples and cloud water from Whistler, British Columbia suggest that water-soluble organic compounds of intermediate volatility (e.g. *cis*-pinonic acid) can be important precursors for SOA_{AQ} (Lee et al., 2012). Pyruvic acid oxidation experiments in Mt. Tai, China cloud water suggested a slowing of pyruvic acid oxidation presumably due to competition for OH radicals with the complex dissolved cloud water organics (Boris et al., 2014). However, further ambient measurements are needed to identify precursors important for ambient SOA_{AQ} formation in atmospheric waters.

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This work reports, for the first time, results of aqueous OH radical oxidation experiments conducted in ambient mixtures of water-soluble gases. Ambient mixtures were collected in the Southeast US during the Southern Oxidant and Aerosol Study (SOAS) in the summer of 2013; experiments were used to identify water-soluble gases that may serve as precursors of atmospheric aqueous SOA. This region has experienced an overall cooling trend in surface temperature over the second half of the twentieth century, compared to the warming trend observed elsewhere in the US (Robinson et al., 2002; Goldstein et al., 2009; Portmann et al., 2009). Biogenic sources dominate emissions in this region with varying degrees of impact from anthropogenic sources. Measurements by Nguyen et al. (2014) and model results by (Carlton and Turpin, 2013) indicate the significance of anthropogenic aerosol liquid water (ALW) in this region and support a role for ALW in SOA_{AQ} formation. In the Southeast US, photochemistry and abundant liquid water coexist, making it an ideal location to study SOA_{AQ} formation through gas-phase followed by aqueous-phase chemistry. The objective of this work is to identify WSOGs important to SOA_{AQ} formation. Since OH oxidation experiments were conducted in dilute solution, we will also identify products expected through cloud/fog processing of ambient WSOG mixtures. Products may differ in aerosols, where solute concentrations are higher, and radical-radical chemistry and acid-catalyzed reactions (e.g. epoxide ring-opening reactions yielding tetrols and organosulfates from isoprene epoxydiol, IEPOX) are important. We expect that aqueous chemistry in clouds, fogs and wet aerosols is a sink for reactants identified herein, and that this work will motivate laboratory studies and chemical modeling of newly identified aerosol/cloud precursors.

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2 Methods

Samples of ambient water-soluble mixtures collected in mist chambers during the SOAS field study were used to conduct controlled aqueous OH radical oxidation experiments. Mass spectral techniques were used to tentatively identify compounds with decreasing abundance in aqueous OH oxidation experiments, but not control experiments with the aim of identifying new aqueous chemistry precursors for further study. Ion chromatography was used to identify selected products.

2.1 Mist chamber field sampling at SOAS (in Brent, AL)

Water-soluble gases were scrubbed from filtered ambient air at the Centerville ground site in Brent, AL during SOAS. Samples were collected from June 1 – July 14, 2013 from 1 m above the sampling station roof through a 1.3 cm OD Teflon inlet (approximately 1.7 m in length). Four mist chambers (Anderson et al., 2008a; Anderson et al., 2008b; Dibb et al., 1994; Hennigan et al., 2009) were operated in an air-conditioned trailer (indoor temperature, 25^{o}C) at 25 L min^{-1} in parallel for 4 hours, typically 2-3 times each day between 7 AM and 7 PM CDT. Particles were removed by passing the ambient air through a pre-baked quartz fiber filter (QFF) (Pall, 47mm) prior to introduction into the mist chamber.

The mist chambers were operated with 25 mL of 17.5 ± 0.5 MΩ ultra-pure water; additional water was added during the run to replace water lost by evaporation. Samples from all four mist chambers were composited daily and frozen in 35 – 40 mL (experiment-sized) aliquots. Total organic carbon (TOC) concentrations ranged from 45 – 180 µM-C (Supplementary Table S1). Prior to and at the end of a sampling day, each mist chamber was cleaned using a 5-minute DI water wash step.

Based on daily forecast predictions, certain days were selected for intensive sampling (Supplementary Table S1). Intensive sampling during SOAS was conducted on days when high levels of isoprene, sulfate, and NO$_x$ were predicted by the National

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Moved down [1]: 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

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Moved down [5]: (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 m^3). Thus, we expect water-soluble gases to penetrate through the QFF very efficiently for collection in the mist chamber water.

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Center for Atmospheric Research (NCAR) using the Flexible Particle dispersion model (FLEXPART) (Stohl et al., 2005) and the Model for Ozone and Related Chemical Tracers (MOZART) (Emmons et al., 2010). In general, mist chamber samples on intensive sampling days had higher organic content (TOC = 92-179 μM-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).

2.2 Aqueous OH radical oxidation in a cuvette chamber

Ambient SOAS field samples were exposed to OH radicals in a custom built photochemical temperature-controlled (25°C) quartz cuvette reaction chamber. Ten screw-capped quartz cuvettes (Spectrocell Inc., Oreland, PA) containing 3 mL of sample were placed equidistant around a 254 nm mercury lamp (Heraeus Noblelight, Inc. Duluth, GA) housed in a quartz sheath (Ace Glass Inc., Vineland, NJ). A solar spectrum lamp was not used because the objective was to produce OH radicals by H_2O_2 photolysis, rather than to mimic tropospheric photolysis. The chamber was protected from ambient light by covering in aluminum foil. OH radicals (1.25×10^{-2} μM [OH] s^{-1}) were generated *in situ* by photolysis of 125 μM H_2O_2, added to each cuvette prior to inserting the lamp. While we can calculate the OH production rate from hydrogen peroxide photolysis (1.25×10^{-2} μM [OH] s^{-1}), the concentration of OH in the reaction vessel depends also on the reactivity of the organics. If the WSOG mix behaves similarly to glyoxal, OH concentrations would be on the order of 10^{-12} M (similar to Tan et al., 2009). Cuvettes were removed at t = 10, 20, 30, 40, 60, 80, 100, 120, 150 min and any remaining H_2O_2 was destroyed by addition of 36 μL of 1% catalase (Sigma; 40,200 units/mg). A duplicate

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Moved down [3]: This is consistent with the one measurement we have of breakthrough at SOAS, where we ran two mist chambers in series and found TOC concentrations within +/- 11% of each other.

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cuvette was removed at t = 40 min to calculate method precision. The following control experiments were performed: 1) sample + H_2O_2, 2) sample + UV, 3) H_2O_2 + UV, and 4) field water blank + OH. Replicate experiments were performed on selected samples. Ambient conditions for sample collection are given in Table 1 for samples used in experiments.

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2.3 Analytical methods

Samples and field water blanks from all collection days were characterized by total organic carbon analysis (TOC; Shimadzu 5000A) and electrospray ionization mass spectrometry (ESI-MS; HP – Agilent 1100). Ion Chromatography (IC; Dionex ICS 3000) was used to analyze organic anions and track the formation of products and intermediates. Samples at each reaction time were analyzed by ESI-MS in positive and negative ion modes to identify precursors and products. Selected samples were also analyzed by ultra-high resolution electrospray ionization Fourier-transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS) and tandem MS (MS-MS) on a Thermo-Finnigan LTQ-XL at Woods Hole Oceanographic Institute, MA to determine elemental composition and extract structural information on precursors. Analytical details and quality control measures have been described previously (Perri et al., 2009). Briefly, the ESI quadrupole mass spectrometer was operated in positive and negative ion modes over a mass range of 50-1000 amu. In the negative ion mode, the mobile phase consisted of 1:1 methanol/0.05% formic acid in water; and in the positive ion mode, 0.05% formic acid in water. The fragmentor and capillary voltages for the ESI-MS were set at 40 V and 3000 V (nitrogen drying gas; 10 L min^{-1}; 350 °C), respectively. Nitrobenzoic acid in the

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negative ion mode and caffeine in the positive ion mode were used as mass calibrants. Standard mixtures were analyzed with each experimental sequence: acetic acid, pyruvic acid, nitric acid, succinic acid, tartaric acid, ammonium sulfate, and oxalic acid in the negative ion mode and glyoxal, methylglyoxal, and glycolaldehyde in the positive ion mode.

ESI ionization efficiency varies with sample mix and over time. However, the mass spectra of the mist chamber samples were similar across experimental days and the variability in the glyoxal, methylglyoxal, and glycolaldehyde standard ESI signals were 4-7% across analysis days, suggesting that ion abundance trends (Figure S1-S2) will reflect concentration trends. Six injections were averaged for each sample and data retained for each ion abundance greater than zero within 95% confidence intervals. Ions were considered to be above detection limits if peaks were greater than the average plus three standard deviations of the water blank.

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Organic acids were measured by IC (IonPac AS11-HC column; 30 °C, AG11-HC guard column) with conductivity detection (35 °C), using a Milli-Q water eluent and KOH gradient method. For oxalate, the method precision is 22%, calculated as a pooled coefficient of variation (CV) from pairs of cuvettes removed at t=40 min. The analytical precision for oxalate is 19% (pooled CV) based on replicate analysis of 30% of samples. Analytical accuracy for oxalate is 7%. The limit of detection (LOD) for oxalate by this protocol has been previously determined to be 0.1 µM (Perri et al., 2009).

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Samples from June 15 and June 30, 2013 were analyzed using ultra-high resolution FT-ICR-MS in the positive ion mode using 1:1 methanol/water as the mobile phase at 4 µL min^{-1}, capillary temperature of 260 °C and spray voltage 3.8-4.2 kV.

Weekly analysis of standards (caffeine, peptide-MRFA, ultramark, SDS, and sodium taurocholate) verified the mass accuracy < 2 ppm. Previously pyruvic acid and peroxyhemiacetal standards analyzed with the same protocol were within 2 - 10 ppm. Five precursor masses were isolated (isolation width: *m/z* = 2) and fragmented by collision-induced dissociation (CID) (normalized collision energy: 26-33%) with helium in the ion trap (IT) and infrared multi photon dissociation (IRMPD) with a CO_2 laser. Elemental composition (within ±1 ppm) and double bond equivalents of ions were calculated by Midas Molecular Formula Calculator (v1.1). No restrictions were placed on the number of carbon, hydrogen, oxygen, nitrogen, sodium and sulfur atoms included in the molecular formula calculations.

Compounds are detected in the ESI-MS by forming cluster ions with hydrogen, sodium, or ammonium in the positive ion mode; compounds are sometimes hydrated with water or methanol. In the negative ion mode, ions are deprotonated.

3 Results & Discussion

OH oxidation experiments at concentrations relevant to cloud/fog water were conducted on samples collected June 11, 12, 15, 16, 20, 21, 29, and 30 of 2013, days on which total organic carbon (TOC) was highest, ranging from 92-179 µM-C in samples.

3.1 Precursors in SOAS samples

The concentration dynamics in experiments conducted with the 8 daily composites were similar. Positive ions at *m/z* 125, 129, 143, 173, and 187 exhibited reactant-like trends (Figure 1; June 30 sample + OH), showing decreasing signal intensity

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with increasing exposure to OH. These ions disappeared after 40 minutes of oxidation. Together, these ions account for roughly 30% of the total ion current in the positive mode in the experiment samples. In control experiments the abundance of these ions did not change over time, as illustrated in Figure 1 (sample + UV and sample + H_2O_2) for the positive ion at *m/z* 187 in samples collected on June 15 and 30. Hence, reaction with UV or H_2O_2 alone does not explain the decreasing signals in the presence of OH radical. In control experiments where we generated OH radicals in field water blanks, these ions were not observed, confirming that they are not contaminants. Experiments conducted on all sample days showed the same reactants decreasing with exposure to OH, indicating that the water-soluble organics captured from the ambient daytime air in the mist chambers varied little across the study.

Elemental formulae assigned to precursor ions by Midas with corresponding MS-MS fragmentation data for the ions from June 15 and 30 samples are shown in Table 2. Both sampling days showed similar fragmentation spectra, consistent with the presence of the same parent compounds on both days, despite potential differences in the air mass on these days. MS-MS spectra were not obtained under the acquisition conditions of this work for positive ions at *m/z* 143, 129 and 125. Proposed structures for the positive ions at *m/z* 187 and 173 based on MS-MS data are shown in Figures 2 and 3. The O:C ratio for the reactant masses range from 0.1 - 0.8. In the following sections, we discuss individual reactants observed by ESI-MS. The discussion below is focused on the molecular formulas, rather than the detected ions, i.e. Na^+ or H^+.

***m/z* 187:** This is the ion with the highest *m/z* observed by ESI-MS in the positive ion mode that follows a precursor-like trend (Figures 1 and 2). The composition

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Deleted: Na^+ or H^+.) The daughter ion peak seen during fragmentation of the positive ion at *m/z* 187 corresponds to *m/z* 155.0680, CH_3OH loss, corresponding to the molecular formula, $C_6H_{12}O_3$. We propose that this compound is present in the gas-phase as the $C_6H_{12}O_3$ aldehyde and in water as the $C_6H_{14}O_4$ tetrol shown in Figure 2. $C_6H_{12}O_3$ is consistent with an oxidation product of *E*-2-hexenal and *Z*-3-hexenal, both being unsaturated aldehydes that have frequently been detected during field studies and are emitted to the atmosphere from vegetation due to leaf wounding (O'Connor et al., 2006). The oxidation mechanism of these two green leaf volatiles to form $C_6H_{12}O_3$ is shown in Figure 3.

$C_7H_{16}O_4Na$ is assigned by the Midas molecular formula calculator based on the exact mass 187.0942 from FT-ICR MS, corresponding to the composition $C_7H_{16}O_4$ for the neutral compound. The MS-MS shows loss of methanol, to give a product ion at *m/z* 155.0680 corresponding to the neutral molecular formula, $C_6H_{12}O_3$, consistent with expectations for a sodium ion complex of a dihydroxy hemiacetal in methanol solution, shown in Figure 2. In the absence of methanol, this compound would appear hydrated with water as the $C_6H_{14}O_4$ tetrol, as shown in the blue box in Figure 2. The corresponding gas-phase compound is shown in the tan box in Figure 2. *E*-2-hexenal and *Z*-3-hexenal are unsaturated aldehydes that have frequently been detected during field studies and are emitted to the atmosphere from vegetation due to leaf wounding (O'Connor et al., 2006). The gas-phase oxidation of these two green leaf volatiles, as shown in Figure 4a and 4b, could explain the presence of $C_6H_{12}O_3$ in the gas phase and $C_6H_{14}O_4$ in the aqueous phase (Figure 2).

***m/z 173*:** On most sampling days this reactant mass has the highest abundance in the positive mode ESI mass spectra (Supplementary Figure S1). Similar to other reactant peaks, it reacts away within the first 40 minutes of exposure to OH in the cuvette chamber (Figure 1). The Midas-suggested molecular formula for this parent ion (*m/z* 173.0782) and its two fragment ions at *m/z* 141.0523 and 129.0524 are $C_6H_{14}O_4$, $C_5H_{10}O_3$, and $C_4H_{10}O_3$, respectively (a reactive parent ion with the formula $C_4H_{10}O_3$ was also observed, and is discussed below).

A likely structure for positive mode *m/z* 173 is shown in Figure 3. In this case the compound is proposed to be a $C_5H_{10}O_3$ aldehyde in the gas phase (tan box in Figure 3) and a $C_5H_{12}O_4$ tetrol in water (blue box in Figure 3). In the FT-ICR-MS it is seen

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Deleted: A compound with a molecular formula of $C_5H_{10}O_3$ (the same mass as a fragment ion discussed above) was observed in the gas-phase in the same location (Centerville field site) by high-resolution time-of-flight chemical ionization mass spectrometry (HRToF-CIMS) (Lee et al., 2014), coupled to a filter inlet for gases and aerosols (FIGAERO) (Lopez-Hilfiker et al., 2015; Lopez-Hilfiker et al., 2014). This could be the same compound that we measure as *m/z* 173.0782, as explained below. Note that the HRToF-CIMS employed iodide ionization, which forms organic-iodide adducts, resulting in a virtually fragmentation free ionization. Gas phase measurements from the HRToF-CIMS were made in real time through a 3/4" PTFE inlet operated at 16 standard L min^{-1}. Isoprene hydroxy hydroperoxide (ISOPOOH) and isoprene epoxide (IEPOX) are both detected at this mass, but HRToF-CIMS is more sensitive to ISOPOOH. ISOPOOH is an OH oxidation product of isoprene, which is further oxidized by OH under low-NO conditions to form isomeric isoprene epoxydiols (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, but it is likely that *m/z* 173 is not indicative of these two compounds in our samples. As discussed below in detail, based on ESI-MS measurements with an IEPOX standard, it can be confirmed that IEPOX was not detected in the mist chamber samples. The O-O peroxide bond in ISOPOOH is the weakest bond in the molecule, and hence when undergoing MS-MS, should be the first to fragment. There is no evidence of this bond breaking in the fragmentation spectra for *m/z* 173, leading to the conclusion that the detected compound is not ISOPOOH. IEPOX and ISOPOOH were present in the ambient air at the field site. We expect that they were lost during sampling or storage.

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hydrated with methanol. The parent ion at *m/z* 173 loses methanol to form $C_5H_{10}O_3$ (*m/z* 141.0523), and it also loses C_2H_4O to form $C_4H_{10}O_3$ (*m/z* 129.0524). The aqueous oxidation precursor observed as m/z+ 173 and tentatively identified as the $C_5H_{10}O_3$ aldehyde shown in tan in Figure 3, could be derived from another green leaf volatile. Specifically, $C_5H_{10}O_3$ is consistent with the gas-phase oxidation product of (*E*)-2-methyl-2-butenal, another green leaf volatile (Figure 4c) (Jiménez et al., 2009; Lanza et al., 2008). It has also been reported as an isoprene oxidation product (Yu et al., 1995).

Positive ions at m/z 143, 129, and 125: No fragments were observed for these reactants under conditions of MS-MS acquisition in this work. The Midas-predicted molecular formulae for the ions at *m/z* 143.0676, 129.0520, and 125.096 are $C_5H_{12}O_3$, $C_4H_{10}O_3$, and $C_8H_{12}O$, respectively. Interestingly, the reactant detected at *m/z* 129 has the same mass as a fragment of the parent ion at *m/z* 173 discussed earlier (and the structure of the $C_4H_{10}O_3$ fragment shown in Figure 3 is a possible structure for *m/z* 129).

Methodological Limitations: In this work, we aim to collect the ambient mix of water-soluble gases into water at concentrations comparable to those found in clouds and fogs with the purpose of simulating cloud/fog-relevant OH oxidation chemistry and identifying previously unrecognized precursors of aqueous chemistry. Below we discuss limitations with respect to our ability to collect and store these aqueous mixtures and with respect to our ability to identify the OH-reactive compounds collected.

Mist chamber collection times (4 hr) were selected with the aim of collecting ambient mixtures of water-soluble gases near Henry's law equilibrium. Two pieces of evidence suggest that gas-aqueous partitioning of the water-soluble organic gases is close to Henry's Law equilibrium in our samples. In previous testing conducted in a different

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East Coast location that is a recipient of long-range transport (i.e., central New Jersey), we found that WSOG concentrations in the mist chamber leveled off after 1-3 hours of ambient sampling, suggesting that the collected WSOG mixture approaches Henry's Law equilibrium over these collection times. This is consistent with the one measurement we have of breakthrough at SOAS, where we ran two mist chambers in series and found TOC concentrations within +/- 11% of each other. These measurements suggest that a representative mixture of the water-soluble gases entering the mist chambers were collected.

However, 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 m^3). 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

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scrubbed by the mist chambers and could result in oxidation of some unsaturated 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 isoprene hydroxyhydroperoxide (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). IEPOX and ISOPOOH were present in the gas-phase during the SOAS campaign (Nguyen et al., 2015). They have relatively high Henry's Law constants (i.e., ($H_{L,IEPOX}$=2.7×10^6 M atm^{-1}). IEPOX was readily detected in ambient samples spiked with 3000 µM, 300 µM, and 30 µM of IEPOX, indicating that it can be ionized in our sample matrix. (Authentic *trans*-β-IEPOX, which is the predominant isomer of IEPOX, was synthesized for this purpose (Zhang et al. (2012).) However, it was not found in our ambient samples since it is not stable when stored in water.

Together, the ions discussed herein account for 30% of the total ion abundance. The remaining 70% did not exhibit a clearly decreasing trend during OH oxidation experiments. It should be recognized that some water-soluble OH-reactive compounds might not have decreased during experiments because they were intermediates of multiple precursors. Together, these methodological limitations suggest that additional OH-reactive water-soluble gases were likely present that we were unable to identify.

3.2 Product formation during aqueous oxidation experiments

Figure 5 shows significant formation of oxalate and pyruvate in OH radical experiments conducted with all samples but not during the control experiments (Sample + UV; Sample + H_2O_2). Pyruvate peaks around 60-80 min, which is earlier than the oxalate peak at 100-120 min (Figure 5). Acetate + glycolate (which co-elute in the IC) also forms in at least some samples and reacts away in the presence of OH (Supplementary Figure S3). Sulfate and nitrate concentrations remained constant throughout the experiment as measured by the IC. While there may be many sources of oxalate, aqueous OH radical oxidation of pyruvate in the aqueous phase is known to form oxalate at dilute (cloud-relevant) concentrations (Carlton et al., 2006). Aqueous acetate oxidation is also a source of oxalate (Tan et al., 2012). The concentration dynamics are consistent with a role for these compounds in the formation of oxalate in the ambient mixtures although the mechanisms by which pyruvate and acetate formed are not well constrained in these experiments. These observations suggest that oxalate, pyruvate, and acetate/glycolate can form in ambient mixtures of water-soluble gases in the Southeast US in the presence of clouds/fogs and oxidants. Pyruvate and oxalate have been observed primarily in the particle phase in the atmosphere (Saxena and Hildemann, 1996; Limbeck et al., 2001; Yao et al., 2002; Kawamura et al., 2003; Martinelango et al., 2007). Moreover, modeling studies of oxalate, the most abundant dicarboxylic acid in the atmosphere, suggest that aqueous chemistry is a large contributor of oxalate formation globally, making it a good tracer for SOA_{AQ} formed in clouds and fogs (Myriokefalitakis et al., 2011). Above versus below cloud measurements also support this (Sorooshian et al., 2010). Thus, the experiments suggest that aqueous oxidation of ambient (Southeastern US) water-soluble mixtures at cloud/fog relevant concentrations has the potential to form material that

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remains in the particle-phase species after droplet evaporation, i.e. SOA_{AQ}. However, the atmospheric prevalence of *particle-phase* oxalate can only be explained by the formation of salts and complexes, since oxalic acid is volatile and the volatility of oxalate salts is orders of magnitude lower than that of oxalic acid (Ortiz-Montalvo et al., 2014; Paciga et al., 2014). The aerosol at the SOAS ground site was acidic (campaign average pH~0.94) (Guo et al., 2015) and as a consequence oxalic acid may remain largely in the gas phase in this environment, but may eventually react on more basic surfaces, e.g., coarse particles. Note that we expect the products of aqueous chemistry in wet aerosols to be different from those in clouds and fogs because of the extremely high (molar) solute concentrations in wet aerosols (Surratt et al., 2007; Noziere et al., 2008; Galloway et al., 2009; Lim et al., 2010; Sareen et al., 2010; Nguyen et al., 2012).

3.3 Atmospheric implications

We have tentatively characterized several water-soluble OH-reactive species collected at an isoprene-rich photochemically-active location in the southeastern U.S. In several cases compounds with the same elemental composition were measured in the gas phase by HRToF-CIMS. The tentative structures for the proposed reactants are consistent with formation from green leaf volatiles and isoprene oxidation. Aqueous OH oxidation under dilute conditions (TOC approx. 100 μM) relevant to fogs and clouds produced oxalate and pyruvate suggesting that cloud/fog processing of these compounds (and subsequent neutralization or complexation) is a potential source of SOA. The reactants characterized in this work are precursors for aqueous chemistry and are potentially important SOA_{AQ} precursors in all atmospheric waters, i.e. clouds, fogs, and wet aerosols.

The aqueous chemistry of these precursors is poorly understood and warrants further study.

4 Conclusions

We observed formation of pyruvate, oxalate, and acetate/glycolate during OH oxidation experiments conducted with ambient mixtures of WSOG from the southeastern US. The formation of these highly oxygenated organic acids indicates a potential for SOA_{AQ} formation (e.g., upon neutralization with NH_3, metal complexation or heterogeneous reaction on course dust/salt particles). Given the acidity of SOAS fine particles, we think it is unlikely that oxalate will be found in substantial quantities in the fine aerosol at the SOAS ground site.

We tentatively characterized several water-soluble reactive precursors which undergo aqueous chemistry and SOA_{AQ} formation in wet aerosols, clouds and fogs at this location. High resolution mass spectrometric analyses suggest precursors had O:C ranging from 0.125-0.80 and some are tentatively gas-phase oxidation products of green leaf volatiles. No distinct difference was seen in the aqueous oxidation of ambient samples collected across days during the SOAS field campaign. Further work involving organic synthesis, aqueous OH oxidation of authentic standards, and mass spectral analyses with pre-separation are likely to yield further insights into the aqueous chemistry of these compounds in the future.

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5 Acknowledgements

This research was funded by the EPA STAR grant 835412. The views expressed in this manuscript are those of the authors and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency. The authors acknowledge Melissa Soule and funding sources of the WHOI FT-MS User's Facility (NSF OCE-0619608 and the Gordon and Betty Moore Foundation). We also thank Jeffrey Kirland, Ronald Lauck, and Nancy Sazo for their invaluable assistance in the laboratory and field, and Louisa Emmons for the air quality forecasting during SOAS.

Supporting Information Available. Included are sampling and TOC data for all collection days (Table S1), time series of ESI-MS abundances for m/z+ 125, 129. 143. 173 an 187 (Figure S1), discussion and graphical comparisons with chemical ionization mass spectrometry (CIMS) (Figure S2), and concentration dynamics for acetate+glycolate during aqueous OH experiments and control experiments (Figure S3). The material is available free of charge via the Internet at http://pubs.acs.org.

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Tables & Figures

Table 1: Sample collection dates for which experiments were run and their sampling conditions. Temperature, relative humidity, and ozone ranges are shown both for the entire day and collection time period. Total organic carbon (TOC) accuracy and precision are verified with potassium hydrogen phthalate (KHP) standards to be better than 5% (Perri et al., 2009).

Collection date	**Collection time**	**µM TOC**	**T (^{o}C) all day (coll. time)**	**RH (%) all day (coll. time)**	**O_3 (ppb$_V$) all day (coll. time)**
11-Jun-2013	7am-7pm	139.5	22-32 (23-32)	53-99 (53-98)	9.9-38.2 (11.3-38.2)
12-Jun-2013	7am-7pm	179.7	23-33 (23-33)	48-94 (48-94)	13.1-41.8 (13.1-41.8)
15-Jun-2013	7am-7pm	117.0	17-31 (18-31)	45-94 (45-90)	11.6-53.4 (11.6-53.4)
16-Jun-2013	7am-7pm	108.2	22-32 (22-32)	53-93 (53-84)	2.6-41.7 (23.1-41.7)
20-Jun-2013	8am-5pm	131.5	20-30 (21-30)	55-98 (59-94)	4.8-52.2 (6.2-42.8)
21-Jun-2013	10am-6pm	104.4	20-30 (25-30)	50-93 (50-78)	16.6-45.2 (30.3-45.2)
29-Jun-2013	7am-7pm	92.0	21-31 (22-31)	43-100 (43-100)	16.3-53.7 (16.3-53.7)
30-Jun-2013	7am-7pm	98.7	20-30 (20-30)	38-100 (38-100)	1-53.5 (1-53.5)

Table 2: Elemental formulas assigned to precursor ions using ESI-FT-ICR MS in the positive ionization mode and Midas Molecular Formula Calculator. MS/MS fragmentation data is also shown.

Precursor peak using ESI-MS	Positive mode *m/z* (using FT-ICR)	$[M+Na]^+$ or $[M+H]^+$	Mol. Wt.	Double bond equivalents
187	187.0942	$C_7H_{16}O_4Na$	164.1043	0
	155.0680	$C_6H_{12}O_3Na$	132.0786	1
173	173.0782	$C_6H_{14}O_4Na$	150.0887	0
	141.0523	$C_5H_{10}O_3Na$	118.0625	1
	129.0524	$C_4H_{10}O_3Na$	106.0625	0
143	143.0676	$C_5H_{12}O_3Na$	120.0781	0
129	129.0520	$C_4H_{10}O_3Na$	106.0625	0
125	125.096	$C_8H_{13}O$	124.0883	3

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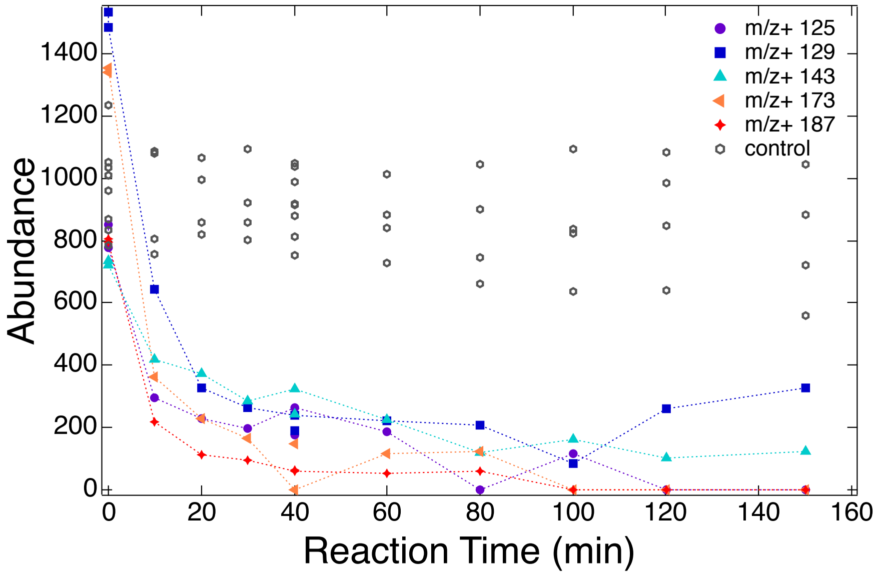

Figure 1. Positive ions (ESI-MS) exhibiting precursor-like trends during aqueous OH-radical oxidation experiments with the ambient mixtures collected on June 30. All days show similar trends, with all 5 reactant masses showing statistically significant decreasing trends as compared to the control experiments. Controls (sample + UV, sample + H_2O_2) shown for *m/z* 187; other masses show similar trends.

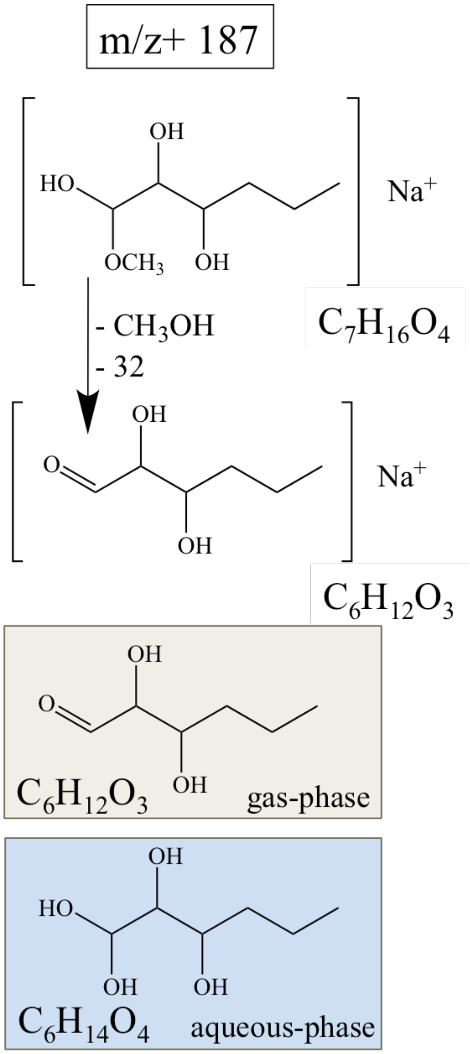

Figure 2. Proposed structure for the positive ion at *m/z* 187. The top structure is the parent compound detected as a reactant in the ESI-MS; the following structures show the MS/MS fragments. This compound would take the forms shown in the shaded boxes when present in atmospheric air and water.

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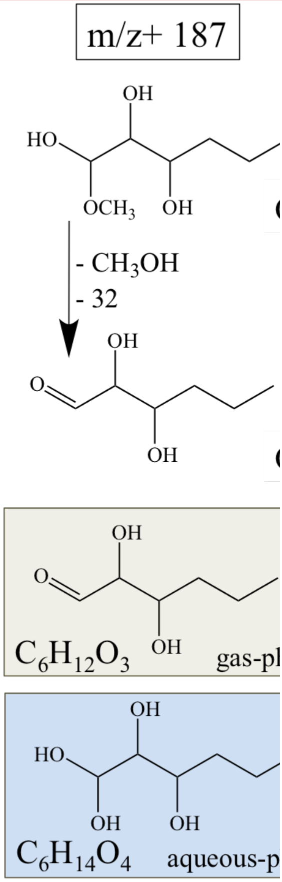

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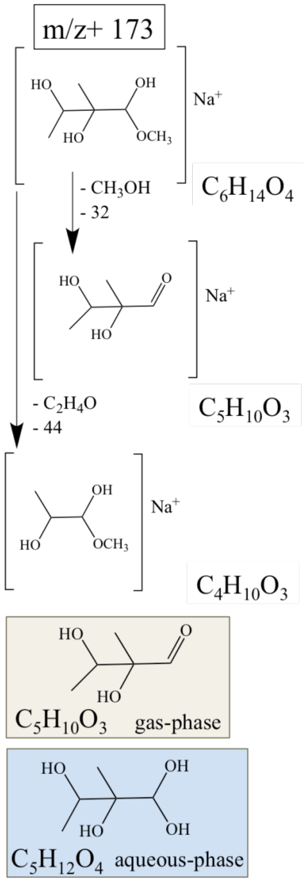

Figure 3. Proposed structure for the positive ion at *m/z* 173. The top structures in each panel are the parent compound detected as a reactant in the ESI-MS; the following structures show the MS/MS fragments. This compound would take the forms shown in the shaded boxes when present in atmospheric air and water.

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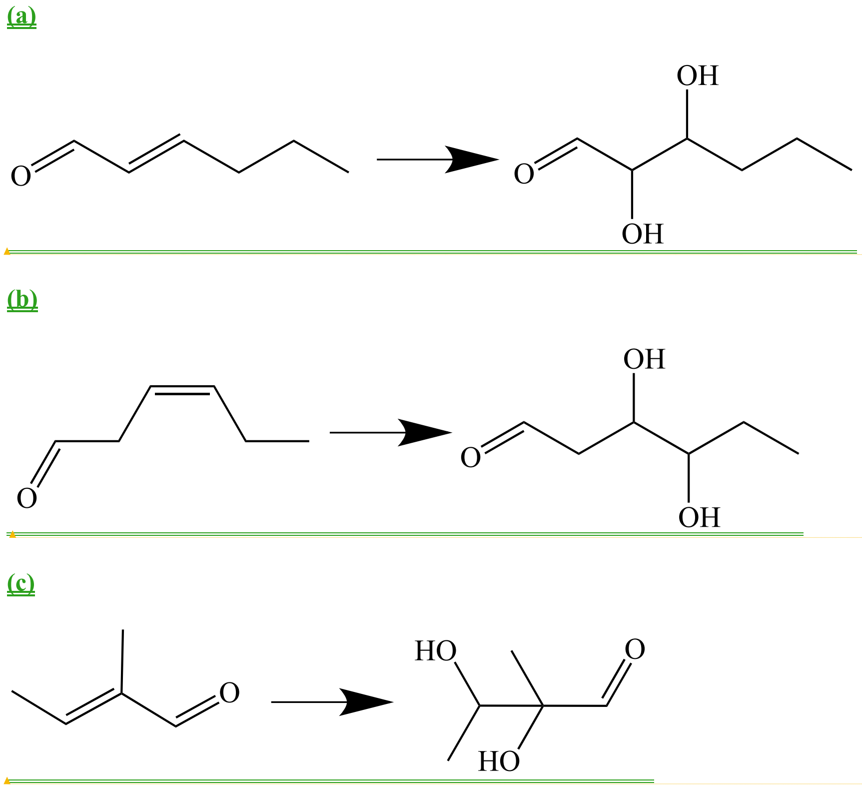

Figure 4: Gas-phase oxidation of (a) *E*-2-hexenal and (b) *Z*-3-hexenal and (c) (*E*)-2-methyl-2-butenal.

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Deleted: Figure 3: Gas-phase oxidation of (a) *E*-2-hexenal and (b) *Z*-3-hexenal and (c) (*E*)-2-methyl-2-butenal.

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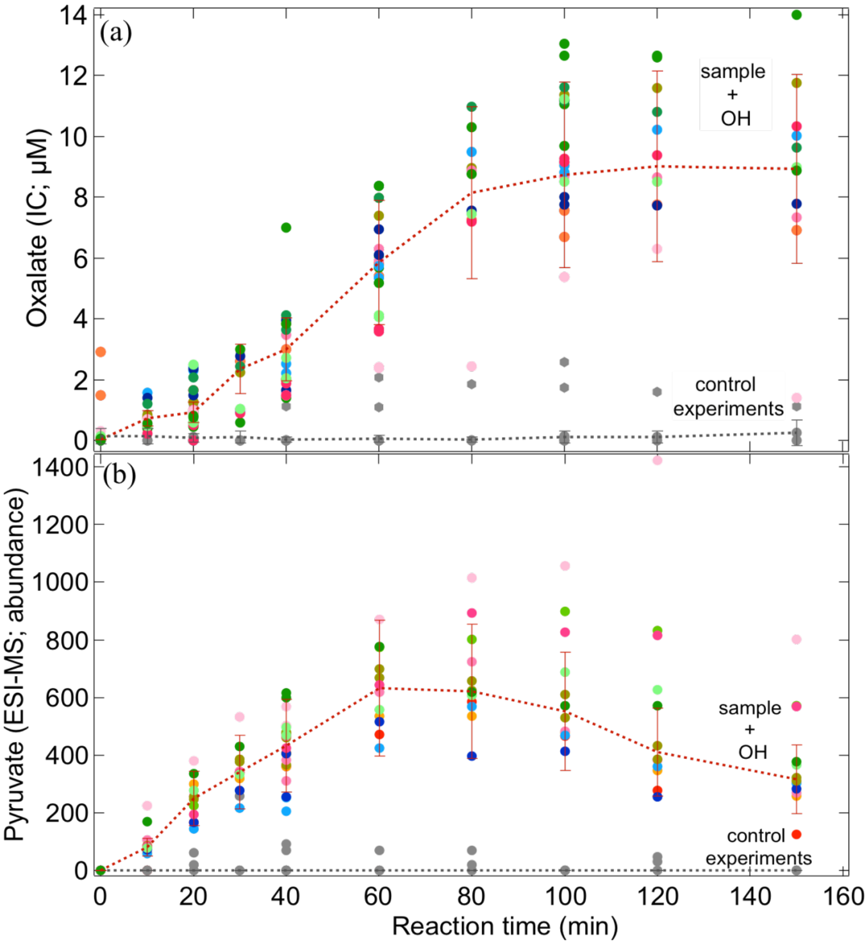

Figure 5. (a) Oxalate (by IC) for all OH radical oxidation experiments conducted with ambient samples (Table 1). (b) Abundance of the negative ion at *m/z* 87 (pyruvate) as observed in the ESI-MS when the ambient SOAS samples are exposed to OH. Error bars represent the pooled coefficient of variation calculated across experimental days. Note that oxalate and pyruvate are formed in all samples in the presence, but not the absence,

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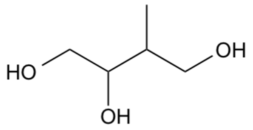
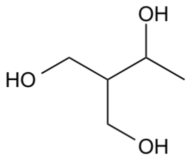
m/z+ 143

$C_5H_{12}O_3$





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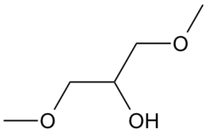

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of OH. Gray points represent control experiments (June 11 sample + UV, June 11 sample + H_2O_2, June 30 field water blank + OH).