Final Author Comments on "A switchable reagent ion high resolution time-of-flight chemical ionization mass spectrometer for real-time measurement of gas phase oxidized species: characterization from the 2013 Southern Oxidant and Aerosol Study"

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We would like to thank both anonymous referees for their comments and their time spent in reviewing this manuscript. Some of our own concerns were reinforced by referee comments and other new ideas have given us additional direction/reinforcement of the importance in analytical evaluation of these complex measurement systems. We have plans of writing a future manuscript to address various science questions relevant to oxidation chemistry in the Southeastern United States within the scope of the numerous CIMS measurements conducted during SOAS.

Response to Anonymous Referee #1: Substantial Comments

1. Figure 9: Reported correlation coefficients of un-calibrated, normalized, and background subtracted data with calibrated, normalized, and background subtracted formic acid

Referee Comment:

> *As part of this work the authors carefully analyze the change in instrument sensitivity to formic acid. Here they compare the (calibrated, I think) concentrations of formic acid to (uncalibrated) signals of other ions and report correlation coefficients with formic acid. Would the instrument sensitivity to these other acids be expected to change similarly as the sensitivity to formic acid? If that is the case would that not affect the correlation coefficient, and is it surprising that the correlation coefficients are this high? What would be the correlation coefficient if the concentrations of the other acids are adjusted by the observed percent change in sensitivity to formic acid?*

We currently have no direct evidence to support or deny that the sensitivity to each species will track the changes in sensitivity of formic acid. It does not seem appropriate to introduce to the literature the idea that changes in sensitivity for one compound can be extrapolated to all compounds given the complexity of the reagent ion chemistry and a lack of additional online calibrations. More importantly, background fluctuations are the main source of instability. While the sensitivity does change throughout the campaign, the most important constraint is the background count rate at each mass.

The high degree of correlation for the reported species with formic acid is likely indicative of the strong photochemical cycle observed during the SOAS campaign. The current understanding of formic acid suggests that formic acid, like nitric acid, is photochemically produced. What is surprising about the formic acid time series is that when the sun sets and photochemical

production stops, the concentrations rapidly decreases below our instrument's LOQ. This appears to be the case with all the acids reported as time series in this manuscript. Thus, the high degree of correlation is consistent with rapid photochemical production and large sinks for these species.

2. Section 4.3 (mass defect plots)

Referee Comment:

> *At the beginning of the section the authors present the mass defect plots as one way to "examine complex, high resolution time-of-flight mass spectral data" and at the end of the section state that "additional dimensions of data can aid in the interpretation of these enhancement mass defect plots." It would be useful if the authors could describe what these plots show for this particular data set and how the data could be interpreted (rather than just state that the plots could be used to interpret the data). I understand that the focus of this paper is on techniques, but at the moment the purpose of the technique (e.g. plotting the data int his way) is unclear to me. Also, what is the purpose of focusing on species which change by more than 5% from morning to evening? This seems to imply that species which do not change much over the course of the day are not interesting, which is not necessarily the case.*

Supplemental information figure S4 shows a mass defect enhancement plot colored by the correlation coefficient (r) for each species with formic acid. Other chemical spaces can certainly be used to help with the interpretation of these data. The reality of these HR-TOFs is that more data are produced than one can possibly deal with if the goal is to extract as much information as possible. Thus, we report one species that we calibrated and a set of other time series that we have high confidence in molecular identification. The real question the HR-TOF-CIMS world faces is how to draw ones attention to the most interesting subset of the data set. During SOAS we observed that formic acid had an extremely strong diel profile. Thus, S4 helps to draw attention to the species that correlate with formic acid, which essentially acts as a marker for rapid photochemical production and rapid deposition.

The idea that one can look at species that change by more than 5% from morning to evening is essentially a filter for photochemically produced species. The importance of morning to evening is really not the point. One can apply this type of cutoff at any point in the day or from one day to another depending on the question asked. The main motivation of this approach applies to the way in which we were operating iodide. We observed large discrepancies in formic acid concentrations when calibrating the iodide source in zero air and ambient air. Our zeros were dry (~0% RH) and thus not representative of the true background. This 5% cut from morning to evening was an attempt to find the compounds that have been enhanced throughout the day due to photochemistry. This neglects the species that remain at constant concentration, but it is the best we can do given the data available; this is an important point.

Currently lines 24-26 on page 3214 read: “Thus, the diel approach to mass defect plots quantifies the enhancement in signal in daytime over nighttime” will be changed to read: “Thus, the diel approach to mass defect plots quantifies the enhancement in signal in daytime over nighttime. One must recognize that this approach neglects species that do not change over time, but these may be of importance.”

3. Page 3217 Cross Talk

Referee Comment:

> *The authors state that “while not the focus of this study, detection of acetic acid and hydroiodic acid using iodide CIMS and acetate CIMS, respectively, in a reagent switching setup may suffer a larger cross talk problem because the detected species are the reagent ions in the complementary mode. The use of hourly zeros, or zeros immediately after switching reagents, may counteract these effects but would require investigation.” The issue of cross talk in this set up (esp. for acetic acid and hydroiodic acid) is of interest to the research community, and I would suggest/request that the authors investigate and analyze this issue and present it in a revised version of the manuscript, esp. considering that they have the data to investigate this.*

This suggestion is something we are currently thinking about for future work. To address this correctly, online calibrations of both acetic acid and hydroiodic are needed and were not conducted during SOAS. The larger problem is that the backgrounds during iodide CIMS operation are not representative due to the use of dry zero air. Iodide has a strong humidity dependence, and thus, half of this problem is completely not addressable given the data set. Our initial thoughts on this were that sacrificing two compounds out of the hundreds detected was an acceptable tradeoff.

4. Section 5.2

Referee Comment:

> *The authors mention twice in this section that changes in instrument sensitivity could be associated with variability of environmental factors such as the trailer temperature. Considering this it seems appropriate for the authors to present and discuss correlations of trailer temperature with e.g. the sensitivity to formic acid.*

Trailer temperature data are, unfortunately, not available for this data set due to communication issues that were present during the SOAS campaign. These have since been resolved. Ambient temperature data are available, but this will give the wrong correlation.

Response to Anonymous Referee #1: Editorial Comments

1. Page 3201 lines 10-15 reads:

“Multiple reagent analysis in CIMS provides a wealth of information and allows investigators to observe the system of interest using different ionization schemes; each reagent ion softly, little to no fragmentation of neutral species upon ionization, ionizes different species to a different degree providing the analyst with different sets of information”

This will be changed to read:

“The use of multiple reagent ions provides a wealth of information and allows investigators to observe the system of interest using different ionization schemes; each reagent ion softly, little to no fragmentation of neutral species upon ionization, ionizes different species to a different degree providing the analyst with different sets of detectible species”

2. Page 3222 section 5.5

“Aljawhary et al. (2013) use a similar method where direct subtraction of mass defect plots is applied and referred to as the “difference mass defect plot.””

This sentence will be removed from Section 5.5 and moved to section 4.3 on page 3213 after the first sentence of section 4.3