

## ***Interactive comment 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” by P. Brophy and D. K. Farmer***

**Anonymous Referee #2**

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Overall Comment and Recommendation:

First, let me apologize directly to the authors for my delayed review. Sadly, I had a family member slowly passing away during this time and eventually left us. Under normal circumstances my review would not have taken so long to submit.

On a brighter note, I think this manuscript is an important and necessary contribution

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to the field of atmospheric chemistry! Chemical ionization mass spectrometers (CIMS) are being used more and more by our community due to the intense commercialization of this technology; specifically, Aerodyne/Tofwerk have teamed together to sell CIMS instruments that are capable of using whatever reagent ion chemistry the user prefers to use for their specific application. With this degree of flexibility, especially with newer users of this analytical technique, problems or pitfalls can arise. In my opinion, the authors of this manuscript have presented a "tour de force" in analytical chemistry. They have tried to carefully devise an approach that allows for the switching of acetate and iodide reagent ion chemistry in near real time. The choice of these ion chemistries is done appropriately and wisely, where both are suitable for negative ion mode operation, thus preventing the need or potential issues that likely arise when switching polarity in the instrument. Further, the zero air and calibration system developed for their CIMS is well characterized and demonstrated in this paper. This paper will certainly help many new users of this analytical technique properly operate their own as well as help users (but not operators) of CIMS data understand the limitations of this type of data. The latter could certainly apply to the modeling community. The paper is well-written and deserves publication in Atmospheric Measurement Techniques, especially after they address my minor specific and minor technical comments here as well as the other reviewer's comments. I agree with the suggestions made by the other reviewer.

Specific Comments:

1.) Formic Acid: I understand why the authors opted to only quantify formic acid from their field data since they had a calibration in place for it. However, since acetate CIMS is highly selective to organic acids, I wonder why not use its calibration factor to quantify the other organic acids? Have the authors tried exploring how different the response factors are between different organic acids in the lab? Many of the acids are commercially available that you detect from the field. I would think you could devise a way to see how different they really are in the lab. If you don't expect the response factors to vary that much (say less than a factor of 2-3), then maybe it is reasonable to

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quantify the other organic acids and apply the uncertainty to the value? I agree with the point made by the authors though that the time series of the unquantified data itself is useful to understanding potential reactions or sources of these compounds.

2.) Isoprene oxidation products: How did MAE's time series compare with isoprene and IEPOX/ISOPOOH data? Was there a correlation with these? Also, since NO<sub>x</sub> appears to play a role in which products are favored, would the authors consider using collocated data from their SOAS site to explore these connections further? I wonder if the authors have plans to further explore this in subsequent work. I know that this isn't the primary focus here.

3.) Monoterpene oxidation products: Similar to # 2 above, for the monoterpene products, was there any relation to monoterpenes or their products from PRTMS other methods at this site?

4.) RH effect on Iodide: I'm curious as to why the authors didn't more carefully examine RH effect with zero air and with some standard compounds with iodide CI in the lab? Could this provide insights into field operation with high purity zero air?

Minor Comments:

1.) In several places you have "isoprene hydroperoxide (ISOPOOH) and isoprene epoxide (IEPOX)." I would change to "isomeric isoprene hydroperoxides (ISOPOOH) and isoprene epoxydiols (IEPOX)." There is more than one isomer for both.

2.) In a few places you have "South Eastern." I would use instead "southeastern" right?

3.) I think the number of figures you have in the main text is too many, and not all are probably necessary. Would moving Figures 6 and 7 to SI make sense?

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Interactive comment on Atmos. Meas. Tech. Discuss., 8, 3199, 2015.