

Atmos. Meas. Tech. Discuss., referee comment RC2  
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## Comment on amt-2021-125

Demetrios Pagonis (Referee)

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Referee comment on "Constraining the response factors of an extractive electrospray ionization mass spectrometer for near-molecular aerosol speciation" by Dongyu S. Wang et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-125-RC2>, 2021

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This manuscript describes the use of PTR-MS and AMS to constrain the response factors of EESI-TOF. The authors oxidized VOCs in a flow tube, varied the seed aerosol concentrations (and thereby the condensational sink), and compared the reduction in gas-phase concentrations of organic compounds measured by Vocus PTR-MS to the increase in aerosol-phase signal measured by EESI-TOF. This dataset provides the most comprehensive attempt to constrain EESI-TOF response factors to date and will be valuable to the continued development of EESI-TOF as a technique for studying atmospheric aerosol. I recommend that this manuscript be published in AMT after the following comments are addressed:

1) I agree completely with Referee #1's comment that the authors must expand discussion of how the uncertainty in the Sekimoto et al. 2017 parameterization propagates through to the calculated  $RF \cdot x$  in this work. The error bars from the fit uncertainty shown in Fig. 3 suggest to me that the authors' methods produced good fits between the EESI-TOF and Vocus signals, and so the 50% uncertainty from the PTR parameterization is going to be a major contributor to the overall uncertainty.

2) The authors' assumption that there is no fragmentation in the Vocus PTR-MS does not seem consistent with the literature on PTR fragmentation, especially for monoterpenes. See for example the recent GC-Vocus work from Clafin et al. 2021 AMT which documents limonene fragmentation of 50% (Table 3). While the extent of fragmentation will vary significantly with drift tube conditions, the oxidation products of limonene (e.g. alcohols, peroxides) typically show fragmentation of 70% or more (Pagonis et al. 2019). I am a coauthor on both of these papers and so I don't insist that the authors cite either one. In my opinion, fully constraining the fragmentation patterns of the compounds in these oxidation systems is far beyond the scope of this work, so my suggestion for the manuscript is to move Fig. S7 into the main text. This analysis nicely shows the extent to which fragmentation could impact the results, and should be featured prominently since the true relationship is likely somewhere between Fig. 3 and Fig. S7.

3) The difference in predictive capability within a VOC system (Fig. 3a: TMB-only) and across the three VOCs studied (Fig S10b: all precursors, no label) gives the best chemical insight into the chemistry underlying EESI-TOF response factors. The authors have some discussion about this, but I think that this result supports further discussion. Molecular formula becomes a more useful parameterization when the carbon backbone and positions of functionalization of the analytes are consistent (a constraint brought on by using a single VOC precursor). To me, this indicates that a structure-activity relationship could be a very promising approach as e.g. EESI-MS-MS techniques are able to give information about the identity and position of functional groups.

4) The EESI-TOF ion transmission as a function of  $m/z$  is left unconstrained in this work. This is a gap that I would like to see addressed more in the text, especially since it gets a full treatment on the Vocus half of the analysis.

Line 89: "Milliliters" is missing a number

Line 104: L-ToF is not informative for readers who do not use ToFwerk instruments, please replace with a description of the mass resolution for the Vocus during this study.

Line 108: Please confirm for the reader that the  $H_3O^+$  depletion was negligible in this study.

Line 232: Equation 7 is not for  $NI_{CO}$

Line 275: I do not follow the reasoning behind why the  $H_{12}$  products should favor the particle phase to a greater extent than the  $H_{14}$  products. I'm assuming that you're comparing SIMPOL coefficients of (hydroperoxide) against (aromatic ring + alcohol + ketone), but this is certainly not going to be clear to many readers. More broadly, I think this is overstating the precision of SIMPOL, and that it would be sufficient to rely on the signal ratios and the identical numbers of oxygen and carbon atoms to rule out differences in partitioning.

Line 445: Do the authors have any levoglucosan calibrations from the same time period as these experiments to help connect these bulk sensitivities to those already published? If so, I strongly encourage the authors to include that value