Response to Referee #1's Comments for: "Measurements of VOCs in ambient air by Vocus PTR-TOF-MS: calibrations, instrument background corrections, and introducing a PTR Data Toolkit"

We thank the Editor and Referees for their time and constructive feedback on the manuscript. We have addressed all referee comments and updated our manuscript accordingly. Please find our summarized responses below. Referee comments are printed in **bold black**, our specific replies are in this blue color, quotes from the submitted manuscript are *in this blue color and italics* and quotes from the revised manuscript are provided in this *green color and italics*.

In addition to corrections made in response to Referee comments, we have made additional corrections for clarity and grammar.

We have corrected methanol's "Quantitative Ion" entry in Table S1 to reflect that the sensitivities and LODs correspond to protonated methanol summed with its water cluster (as already stated in the text, line 167).

Following discussions and troubleshooting with members of the community, we have fixed a bug in the PTR-DT which prevented it from compiling in Igor Pro 8. We have clarified which versions of Igor Pro are known to work with the PTR-DT.

- (line 200) *"Currently, version 1.1 is known to function in Igor Pro 8 and 9."*

We identified minor mistakes in Figure 6 where traces were misnamed. The scientific conclusions have not changed aside from the minor observation that *acetonitrile* experienced reduced fragmentation due to increased water clustering as opposed to *acetone* (line 600).

Anonymous Referee #1 Responses:

Jensen et al provide a comprehensive and useful analysis of best practices for interpretation of high-resolution PTR data. The manuscript provides a detailed discussion of factors contributing to PTR sensitivity and its variability in the field. The manuscript will be a helpful asset to the community and should be published following the authors attention to the following comments:

We thank Referee #1 for the time to evaluate this work and for their detailed feedback to help improve this manuscript.

General Comment:

The authors do an excellent job discussing how fragmentation of a parent ion impacts its sensitivity. That is, fragmentation reduces the expected signal at MH+ as some fraction of the molecules fragment to smaller ions. This impacts the retrieved sensitivity and the comparison of the measured and expected sensitivity. The value of f for a molecule can be determined from the GC. There is less discussion about the positive bias that fragmentation can invoke. For example, at 69 m/Q (or the exact mass of C5H9+), some fraction of the ions detected here are protonated isoprene (you know this fraction from your C5H9+ chromatogram) and some fraction is fragmented larger molecules. This can be significant. From what I can tell the toolbox here does not address this issue of fragmentation. I appreciate that this is tricky. If the authors do not want to tackle this, I think that is fine, but it would be helpful to provide a short statement about how this could impact this analysis.

We agree that contributions to target ion signals from the fragmentation of larger ions are a significant issue worthy of discussion. Referee #1 is correct that the toolkit does not address this issue; that is, the sensitivities calculated by the toolkit apply to the signals of the target analyte alone. Corrections for such biases have been used in literature, e.g., Vermeuel et al. (2023) corrected for aldehyde fragmentation contributions to isoprene. However, in our own experience, we have found that methods to apply these corrections will vary significantly between analytes. Regardless, we have added a brief discussion to Section 4.1.6:

- (line 471) *"Additionally, the PTR-DT does not account for spectral interference. That is, the fragmentation or adduct formation of other species increase the measured signals of a target analyte. Sensitivities from the PTR-DT, which correspond to the target analyte alone, will yield overestimated concentrations. Values of k_{PTR} used in the PTR-DT will also only correspond to the target analyte and have no relation to interfering fragment ions. However, these limitations are not unique to the PTR-DT and also apply to the use of standards to measure sensitivities. To account for these interferences, analyte- and interference-specific corrections could possibly be applied to the estimated sensitivities, but these interferences may be on shorter timescales than routine calibrations. Instead, corrections informed by GC may be applied to the real-time measurements as demonstrated by Vermeuel et al. (2023) for aldehyde fragmentation contributions to isoprene's quantitative ion. Briefly, they used GC to characterize the relative abundance of $C_5H_9^+$ (the quantitative ion used for isoprene) compared to the parent ions for n-aldehydes. Then, they scaled the real-time signal for those aldehydes by that relative abundance*

and subtracted those contributions from the real-time signal for $C_5H_9^+$. The remaining signal uniquely corresponded to isoprene and was calibrated using the isoprene sensitivity."

The above edit to the manuscript is also meant to address some specific comments related to this general comment.

Specific Comments:

Line 115: Please confirm whether the entire inlet or just the Vocus subsampling inlet was overflowed for calibration and zero.

We clarified the sample flow path to help address this point and also modified our inlet schematic (now Fig. S1) to include the flow path used in this study:

- (line 94) *"Air was drawn via an external pump connected to the Vocus inlet such that the sample line led directly into the Vocus inlet for subsampling and the excess flow was removed from a perpendicular line."* Has been updated to:
- (line 110) *"Air was drawn via an external pump connected to the Vocus inlet such that the sample line led directly into the Vocus inlet (sample flow directed toward the IMR) for subsampling and the excess flow was removed toward the external pump via a perpendicular line also attached to the Vocus inlet (Fig. S1a)."*

Only the subsampling line was overflowed:

- (line 138) *"Excess flow was drawn downstream to the external pump (Fig. S1a) and the main sample line upstream of the Vocus inlet was unaffected aside from reduced flow rates of ambient air (at most, a reduction of ~0.3 L min^{-1} at STP)."*
- (line 156) *"Fast calibrations were performed every 2 h by overflowing the Vocus inlet (as described for instrument background measurements)"*

Section 2.3: Please confirm if the inlet for the HC trap and the catalytic zero source were drawn from room air or from ambient air.

We have included this information:

- (line 145) "*The inlets for both the HC trap and catalyst drew from room air."*

Line 175: This equation (E3) holds, so long as another (larger) molecule does not fragment into the detected ion [RH+]. I agree that E3 is correct in isolation, but in the atmosphere if a large fraction of the measured signal at RH+ is not from R but from a larger molecule that fragments, the sensitivity could not be applied to [RH+] to deduce [R] without knowing the fraction of the signal at [RH+] that is from R. Take for example isoprene, only 40% of isoprene is retrieved at RH+ (per your table S1), but the signal at RH+ is comprised on many other molecules beyond isoprene. This could be extracted from the chromatogram as well for the ambient data. Perhaps I missed it, but how is this side of fragmentation being accounted for?

We agree that Eqn. 3 is a simplification which does not necessarily hold when measuring the complex atmosphere. Our responses to Referee #1's general comment and their later comment on "spectral interference" apply here. We do not account for such contributions from fragmentation. The sensitivity estimates could possibly be modified to account for these issues, but the dependence would likely be on shorter timescale than calibrations (temporary plumes). Instead, we recommend correcting the measured signal to approximate the isolated analyte, then apply the estimated sensitivity.

We attempted to explain that Eqn. (3) makes assumptions by:

- (line 177) "*Assuming no additional, outside factors, e.g., passivation effects and spectral interference, then S_{inst} is expected to equal the measured sensitivity, S_{meas}.*"

However, we believe the clarification of "spectral interference" as suggested by Referee #1 improved this point. Additionally, we have included:

- (line 221) "*Equation (3) is a simplification since atmospheric measurements are complex and interferences are common. The PTR-DT does not account for spectral interference as discussed in Section 4.1.6.*"

Line 200: These are Tables S1 and S2, not Tables 1 and 2 (took me a while to find them).

Thank you for identifying this mistake (and apologies for the confusion). We have updated them to Tables S1 and S2 (same for Fig. 7's caption).

Line 205: I'm a bit confused by this sentence. Why does it matter if the transmission function is different for the fragments. Is this because you need to know T(m/Q) to accurately determine f (i.e. if the transmission of the fragment is not accounted for and it is smaller, you would overpredict the actual value of f?) Otherwise, isn't the value of T(m/Q) in equation 3 specific to RH+? Sorry, if I'm turned around on this a reader may be as well, so it wouldn't hurt adding a sentence or two here to more fully describe this.

In calculating *f*, we hope to account for all ions produced in the IMR (in the absence of T(*m/Q*)) from some parent ion, RH+. The fragments once belonged to RH+ and represent some of the analyte that has undergone ionization, but the BSQ influences the measurement after fragmentation. A lower transmission efficiency causes undercounting of those fragments and overestimates the relative abundance of the quantitative ion. We have attempted to add clarification:

- (line 255) "*Values of f should reflect the product ion distribution in the IMR rather than the measured distribution. Without accounting for transmission efficiency for these fragments, the sum of all ions produced by a standard's ionization would be underestimated and f as well as the calculated sensitivity would be overestimated*."

Line 215: It would be interesting to add how many k(PTR) values are known, calculated, vs estimated based on parameterization.

In this analysis, all values of k_{PTR} were estimated based on parameterization:

- (line 226) *"In this study, all values of k_{PTR} were calculated based on the reactor conditions as well as molecular polarizability and permanent dipole moments from the literature, if available, or otherwise estimated based on Sekimoto et al. 's (2017) parameterizations."*

We relied on this parameterization due to a lack of experimental and calculated values k_{PTR}, particularly for our operating conditions. We have updated this paragraph to be more explicit:

- (line 235) "*Experimental values of k_{PTR} are typically scarce, particularly for exact instrument operating conditions of a given set of measurements (for example, E/N of 160 Td). Instead, they can be estimated given molecular properties.*"

Line 215: I can understand how this procedure is applied to ions that are the protonated parent molecule (RH+), but how/when do we know that is true and how is this applied to a measured ion that could be a combination RH+ and fragments? (related to the question above). For example, at 69 m/Q, some fraction of this is protonated isoprene (you know this from your chromatogram) and some fraction is fragmented larger molecules. It might help the reader to walk through your procedure for an example like this on how you would extract [isoprene].

We believe GC is truly necessary to fully understand and properly quantify the measurements. As with fragmentation (which has been discussed in previous comments), the rate constant and estimated sensitivity may not be the best aspect to modify, but rather the measured signals should be corrected where appropriate. Our response and edits in response to Referee #1's general comment address this comment as well, including an example processing procedure for isoprene from Vermeuel et al. (2023).

Line 248: There is some strange formatting here with the inserted symbols.

Thank you for identifying that issue, we have removed the erroneous strikethroughs.

Line 265: What is the physical reason for transmission to decline at high mass? I would have expected this to be operating as a high (mass) pass filter?

Our use of "transmission" in the high mass regime is not wholly correct and should include "detection efficiency". We have made this correction throughout the manuscript (lines 336, 447, 452, 664).

The fields within a quadrupole ion guide are imperfect, especially at the entrance and exit. Slower high *m/Q* ions experience more RF cycles in these fringe fields, leading to greater losses and reduced transmission relative to lower *m/Q* ions.

Detection efficiency requires that electrons be produced by the impact of the ion with the multichannel plate detector. The number of electrons produced depends on, among other things, the velocity of the ion (until that velocity is much greater than the threshold velocity, and it is no longer *m/Q* dependent). We have included additional information and references with this discussion:

- (line 330) *"A high m/Q mass discrimination is introduced by the quadrupole ion guides due to slower velocities and non-uniform fields near the entrance and exit of the quadrupoles ((Antony Joseph et al., 2018; Dawson, 1975; Fite, 1976; Ehlert, 1970). Additionally, aging or poor tuning of a multichannel plate detector may reduce the relative detection efficiency at higher m/Q, resulting in mass discrimination (Müller et al., 2014). Absolute detection efficiencies are negatively correlated with m/Q when not operating the detector in saturation mode (that is, the electron cascade is in saturation regardless of the ion's m/Q) (Oberheide et al., 1997). Typically, PTR-TOF-MS users do not operate in saturation mode due to artefacts such as ion feedback (Pan et al., 2010). To account for reduced detection efficiency in the high m/Q regime, a second, optional sigmoid function is available in the toolkit."*

Line 380: You have used the term "spectral interference" a few times. I did not see it defined. Since there could be a few different interpretations of this, it would be helpful to clarify this at first use. My apologies if I didn't catch it.

We have added a definition of spectral interference as it is used in this manuscript:

- (line 219) "*Here, spectral interferences refer to contributions to an analyte's quantitative ion from the fragmentation and/or adducts of other ions (for example, ethylbenzene commonly fragments to form $C_6H_7^+$, contributing additional signal to that of protonated benzene)."*

Line 410: What is the y-intercept in the slope that is not constrained by the zero. It looks quite large. Were lower concentration calibration points done to fill in the gap between the 1-3 ppb region to assess this further?

We have included the y-intercept:

- (line 519) "…had a negative y-intercept of -1700±400 cps (Fig. S3; error reflects uncertainty in the linear fit)."

We were unable to do additional calibrations at lower concentrations due to limitations in diluting our standard. We have added this detail to the methods:

- (line 161) *"This range of concentrations was limited by the possible dilution flow rates.."*

Line 416: If diffusion is important, do the residuals scale with the diffusion constants as expected?

We see a minor correlation between the residuals and the diffusion coefficients and included a supplementary figure:

- (line 526) "*Figure S9 shows a minor correlation between standards' average residuals and their diffusion coefficients in air (Yaws, 2008), although there are likely other factors as well."*

We do not think this is the only factor affecting the calibrations. However, we did find a change in sensitivity (~5%) when simply changing the mixing geometry of the calibration tee (cal, zero, Vocus inlet vs zero, cal, Vocus inlet). This experiment and prior experiences with mixing issues have led us to attribute part of the discrepancy to mixing. This issue was not rigorously explored, so we do not attempt to discuss it much further.

Section 4.5: It would be helpful to include in Table S1 (or elsewhere) the average zero values for these ions. I appreciate that it could be back calculated from the LOD, but I think it would be helpful for Vocus users to be familiar with what zero (cps) can be achieved with these sources. Or perhaps add a panel to Figure 6 that has a characteristic zero spectra for the catalyst that everything is referenced to.

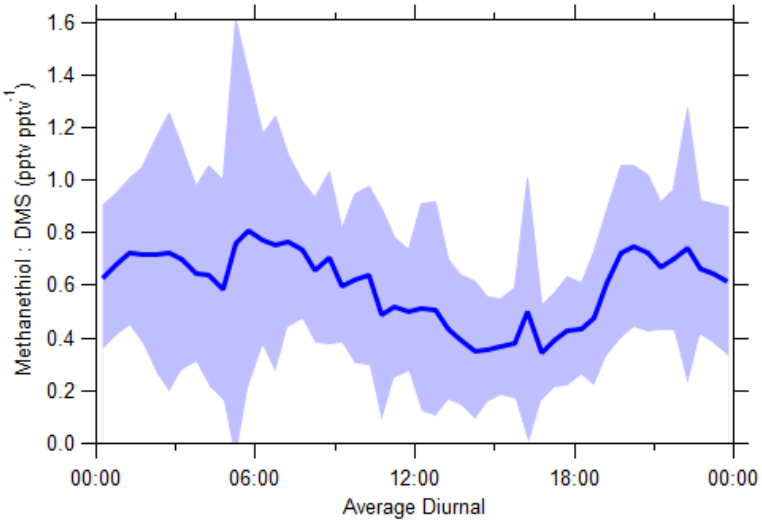
We have added Table S3 which shows standards' average signals for all three clean air sources during the latter half of the field measurements (when instrument response was stable and the inlet was not becoming clogged):

- (line 625) *"Table S3 summarizes the average signals for each of these three clean air sources during the latter half of the measurement period for the standards presented in Tables S1 and S2."*

Line 610: MeSH/DMS should show a strong diel profile due to the large difference in DMS+OH vs MeSH+OH. I'd expect if you look at the nighttime correlation it will be even stronger.

We have attached the diurnal average of the MeSH : DMS ratio. We certainly see the effect of OH chemistry during the day. We did also investigate the nighttime (22:00 – 6:00 MDT) correlation, but found the same correlation coefficient of 0.79. We do not believe this topic requires further investigation for the present manuscript, but we thank Reviewer #1 for the suggestion for future work. We have also noted the role of chemistry in these observations:

- (line 742) "*Some of the variability in their correlation may be attributed to chemistry as methanethiol reacts ~8 times faster than DMS with hydroxyl radicals during the day (Wine et al., 1981).*"



References:

Vermeuel, M. P., Novak, G. A., Kilgour, D. B., Claflin, M. S., Lerner, B. M., Trowbridge, A. M., Thom, J., Cleary, P. A., Desai, A. R., and Bertram, T. H.: Observations of biogenic volatile organic compounds over a mixed temperate forest during the summer to autumn transition, Atmospheric Chemistry and Physics, 23, 4123–4148, https://doi.org/10.5194/acp-23-4123-2023, 2023.