Interactive comment on "An in situ gas chromatograph with automatic detector switching between Vocus PTR-TOF-MS and EI-TOF-MS: Isomer resolved measurements of indoor air" by Megan S. Claflin et al.
Anonymous Referee #1
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This paper presents a new instrument taking advances of both chromatographic and direct MS methods and two different ionization systems having therefore high potential for producing new kind data future air chemistry studies. Manuscript is clearly suitable for AMT. The method is well-described. Detection limits are low enough not just for indoor/urban air, but also for measurements of ambient air at more remote sites. Here results from indoor air measurements were presented showing the great potential of the instrument. I recommend publishing with minor changes.

Specific comments:
Line 109: The range of compounds is not this large if you use the trap at 20C. For very light VOCs, like ethane and ethane, breakthrough volume even at -30C is quite low. Please, correct this.

Authors' response: The reviewer is correct that the range quoted here is mis-leading as it is the maximum range of the trap itself and not for the entire TDPC-GC system. We have updated the text to clarify, the text now reads:

"The combination of adsorbents in the TO-15/TO-17 trap allows for the analysis of a wide range of VOCs (including oxygenates) in the C_2 – C_{32} n-alkane volatility range. However, for the system deployed for this work the instrument was operated in a way that was optimized for VOCs in the C_5 – C_{12} volatility range. Details of operational parameters (e.g. temperatures, flows) are described in Section 2.8."

Line 199-200: Did you flush whole 5 ml/min into the column or did you have some split? What was your desorption efficiency?

Authors' response: We did not use a split flow for our injection, so the entire 5 sccm was sent to the column. To gauge our desorption efficiency, we would run a sample and then an instrument blank and measure the residual sample. The result of the instrument blank was < 1% of the signal measured in the sample. We have added the following text to Section 2.8 to address this:

"To gauge our desorption efficiency, we would run a sample and then an instrument blank, with no sample flow through the trap during the collection period, to measure the residual sample remaining in the trap. The result of the instrument blank was < 1 % of the signal measured in the sample indicating highly efficient transfer of sample, and this was deemed acceptable."

Line 245: You calibrated your system with 2 ppb standard and sampling of time of 1 to 6 min.. Lowest calibration corresponds the ambient air concentration of 333 pptv, which is clearly higher than your detection limit. Did you test the linearity of your calibration curve with lower concentrations? Sometimes with TD systems curve is not linear with lower concentration for all

compounds (due to the incomplete desorption or other losses in the system). At least camphene results in Fig. S1 give some indication on this.

Authors' response: The reviewer presents an excellent point, and for this study we did not calibrate to lower concentrations. The authors acknowledge the reviewers point about incomplete desorption and other losses impacting the lower end of the calibration curve. Since this study, we have transitioned to multi-stage trapping which has many benefits, making the single-stage TD configuration described in this paper obsolete. With our multi-stage trapping configuration, we have increased the dynamic range of our calibrations to over 2 orders of magnitude (down to 0.2 ppb). We are continuing to expand this range to lower concentrations. But until we can calibrate to lower concentrations, we acknowledge larger uncertainties at the lower mixing ratios.

Section 2.7: You have quite long inlet line (3.4m) for this low flow (30 ml/min). Maybe for future prototypes you will increase the flow to enable the quantitative measurement of more sticky compounds as well.

Authors' response: We agree with the reviewer. For campaigns since this work we have implemented a "fast inlet" which uses ¼" OD PFA tubing with an external pump, with a short 1/8" PFA line via tee to the GC inlet; this new inlet typically has a total residence time of <1s from the inlet tip to GC port. The GC system has also improved, and we now sample at much faster flows (100-150 sccm typical).

Section 2.8: Could you add a chromatogram (calibration and indoor air) maybe as a supplement? It is very nice if with this short chromatogram, you are able to separate so many different compounds.

Authors' response: We have added an example calibration and indoor air chromatogram from the GC-Vocus to demonstrate the separation of monoterpenes and C_7 and C_8 aromatics during this project. This new figure is in the supporting information, Figure S2. However, the instrument has progressed significantly since this study and now use multi-stage trapping and focusing which has greatly improved the chromatographic separation and thus rendered obsolete the performance shown here. However, we are happy to include this figure for the sake of completeness. Along with the new figure, we have added the following sentence to the main text:

"GC-Vocus chromatograms of both calibration and ambient indoor air are shown in Figure S2 to demonstrate the chromatographic separation of this system."

Section 2.8.: Did you detect any blank/background for any of the measured compounds? Degradation of Tenax TA results often to some blank (e.g benzene).

Authors' response: To check for residual backgrounds of these compounds, we ran instrument zeros (where the traps were filled with zero air during the sample collection period) and instrument blanks. In these samples, remaining peaks that were above the baseline were < 1% of the signal measured during a typical ambient sample. We appreciate this comment from the reviewer, as we have also noticed elevated signal as the trap degrades over time (e.g. benzaldehyde) and contaminations from our gases.

Table 1: Could you also give precision and uncertainty of these systems in this table or in some other part of the paper?

Authors' response: We have added 1-σ uncertainties and precisions as requested by the reviewer. As an example, the uncertainty of the sensitivity calculated from the calibration curve for α-pinene measured by the GC-Vocus was 4.9% and the accuracy of the calibration preparation was 3.0%, resulting in a total uncertainty of 5.7%. This is an explicit explanation for α-pinene; the uncertainties for the other compounds can be found in the newly added Table S1. We have also updated the text in the main paper to mention the uncertainties and precisions. The text now reads:

"From our calibration data, we estimate typical 1-σ uncertainties to be 12 % and 5 % for the GC-EI-TOF and GC-Vocus configurations, respectively, with typical precisions of 5 % and 1 %. The individual uncertainties for each calibrated compound reported from the GC are listed in Table S1."

Table 2: Even though you are able to detect some compounds (e.g. methanol, acetaldehyde etc.) I doubt their measurements are not quantitative. I would expect high breakthrough of them from the cold trap. Also some other molecules may have high losses in TD. If you have some results that show they are quantitative, please present it. If not, maybe you could mention more clearly that GC can also be used just for identification of these compounds and maybe RT-Vocus can be used for quantification of some of them?

Authors' response: The authors appreciate this comment from the reviewer, and agree that clarification in the text was needed. We have added an explanation to section 3.2 about Table 2. The text now reads:

"Table 2 reports the EI characteristic ion and the ion(s) detected by the Vocus (typically a combination of the molecular ion [MH+] along with water clusters and/or fragments) for a subset of the chromatographic peaks that were identified through the GC analysis. These identified species include alcohols, aldehydes, ketones, ethers, nitrogen containing compounds, halocarbons, siloxanes, alkanes, alkenes, and aromatics. It should be noted that not every compound listed in Table 2 can be reported quantitively from the GC system due to breakthrough in the thermal desorption trap or other losses in the system. However, even for these species that are difficult to quantify, the GC is an excellent tool for compound identification."

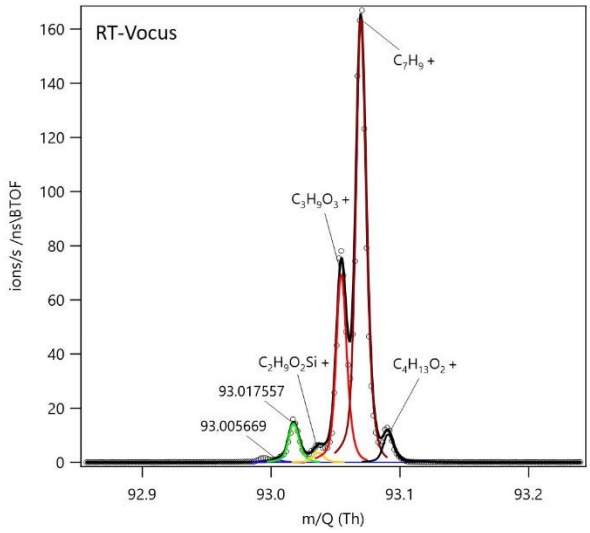
Line 342: Benzaldehyde has often quite high background in TD-GC runs (possibly due to degradation of Tenax TA). Even though it does not matter here, it could be more appropriate to use some other compounds as an example.

Authors' response: We agree with the reviewer that benzaldehyde can be an artifact of Tenax TA used in thermal desorption traps. However, benzaldehyde was used here as a model example of how to use the PTR mass spectrum, EI mass spectrum, and GC retention time to identify a compound. This example does not attribute the source or characterize the benzaldehyde time

profile, and so we feel it is appropriate to keep this section as is to demonstrate a "work flow" for how to use all of the information given from this system.

Section 3.4: Did you detect this compound with RT-Vocus? If so, please, show the results. This would prove that this is not coming from the TD system. Is DMSD known to have some health effects?

Authors' response: Unfortunately, in the RT-Vocus spectrum, the DMSD protonated molecular ion ($C_2H_9O_2Si^+$, *m/z* 93.0366) appears at a mass where there are large signals for species like toluene (*m/z* 93.099), and the water clusters of $C_4H_{10}O$ (*m/z* 93.0910) and $C_3H_6O_2$ (*m/z* 93.0546), among others. These other species are present in the spectrum in larger amounts, causing the DMSD signal to be a minor peak on the shoulder of these others, making it difficult to quantitate.



With the added dimension of the GC, we are able to separate the DMSD from these other species. As noted in the text, we were concerned that the DMSD could be an artifact of the TD system so we ran humidified system zeros to check. From these experiments we found no generation of DMSD and thus ruled out its formation from the TD system itself.

The authors are not aware of DMSD health effects. However, currently very little is known about this compound.