The black color of the text in this document shows the reviewer's comments, while the green color shows the authors' responses, and the revised text is shown in italics.

In this manuscript, Riva et al. introduced a newly developed medium-pressure chemical ionization reactor, Vocus AIM, utilizing adduct ionization for the detection of gaseous inorganic and organic compounds. The performance of the Vocus AIM reactor in terms of time response, sensitivity, and selectivity under different ionization schemes was characterized using selected inorganic and organic species, as well as experiments of alpha-pinene ozonolysis. The novel design of Vocus AIM significantly improves the time response of instrument, enables sensitive detection of a range of inorganic and organic species in sub-ppt level, and effectively eliminates the water vapor dependencies of the sensitivity by introducing an appropriate dopant. In addition, by combining multiple ionization schemes with different selectivity, the Vocus AIM is able to measure organic compounds spanning a wide range of volatility and oxygenation level. This work is scientifically sound and the manuscript is nicely written. I recommend its publication in AMT after the following comments are addressed.

We thank the reviewer for his/her careful consideration of our article. We have attached a revised version of the manuscript in which we considered all the comments raised by the reviewer.

L186-188: I would expect that the reagent ion current is affected by the mixing ratio of benzene with other reagent ion precursors. Do the authors have any recommendations for those mixing ratios?
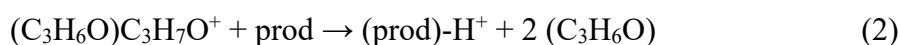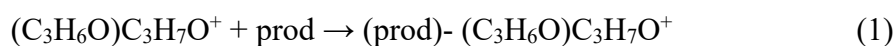
The choice of the reagent ions should be made to avoid any interference. In the case of the example mentioned by the reviewer, methyl iodide or bromo ethane are not detected by benzene chemistry even at mixing ratios ranging from 0.1-10 ppm. Some other cases would be more problematic, e.g., running the Vocus AIM reactor using benzene and acetone-NH_4+ chemistries. Indeed, the large quantity of NH_3 injected within the AIM reactor will be detected by benzene cations and will ultimately impact the TIC. Overall, the compatibility of ion chemistry in the AIM system is determined by whether a generated reagent ion can detect the neutral precursors from any other attached ion source. Therefore, reagent ions should be chosen to avoid any interference. For instance, the combination of Iodide, Benzene, and acetone ion chemistry works effectively even at gas mixing ratios of 1 ppm for benzene and 3 ppm for acetone. This demonstrates that these chemistries can coexist without significant interference, allowing for accurate detection and measurement.

We have added the following sentence.

Lines 189-191: *"The compatibility between multiple ion chemistries in the AIM system is determined by whether a generated reagent ion can detect the neutral precursors from any other attached ion source."*

L212: In the protonated acetone dimer ionization chemistry, are the species mainly ionized by adduct formation or proton transfer? How does the relative contribution of these two ionization pathways depend on the molecular properties of analytes?

In the case of protonated acetone, both mechanisms i.e., adduct formation and proton transfer occurred. This depends on multiple aspects, including the proton affinity of the analytes, the stability of the adduct, and the energy the ions might experience when traveling through the ion optics. Hence the ionization mechanism proceeds according to the following equations:

$$(C_3H_6O)C_3H_7O^+ + prod \rightarrow (prod)\text{-} (C_3H_6O)C_3H_7O^+ \qquad (1)$$

$$(C_3H_6O)C_3H_7O^+ + prod \rightarrow (prod)\text{-}H^+ + 2\ (C_3H_6O) \qquad (2)$$

The stability of the adduct is governed by the polarizability of the analytes (i.e., functional groups). In general, the more the molecule is functionalized the more likely adduct formation will be the prevalent ionization process. This mechanism is not only valid for acetone dimers but general to positive ion chemistry involving protonated reagent ions.

L261-263: Was the sensitivity of protonated acetone dimers to levoglucosan also measured? If so, the relevant results should be presented and discussed in the manuscript.

Levoglucosan was not measured in this ion chemistry due to its known reaction at the collision limit with iodide (Lee et al., 2014), which we utilized for calibration purposes. Therefore, we did not explore alternative ion chemistries for this molecule.

L385: Please provide the sensitivity deviation value for formic acid and nitric acid.

This has been updated within the new version of the manuscript:

Lines 387-389: *"With acetonitrile as the dopant, the change in sensitivity across the humidity range is reduced to a deviation of <20% relative to dry conditions for all model compounds, more for formic acid and nitric acid (<10 %)."*

L402: What are the typical reagent ion currents for chloride and ammonium ionization schemes? Also, what are their sensitivities and LoDs toward the calibration standards used in this study?

The typical total ion currents for Chloride and Ammonium reagent ion chemistries are generally 1-2 and 3-6 x 10^6 ions/second. The lower reagent ion current of Cl chemistry is explained by the BSQ settings that greatly reduce the transfer efficiency of ions below m/Q 50 th. In our study, we did not perform calibration using the Chloride reagent ion chemistry. Acetone-NH$_4$+ ion chemistry does not exhibit sufficient sensitivity to detect the specific species chosen as calibrants in this manuscript. Instead, we routinely calibrate Vocus AIM for this mode using methyl ethyl ketone (MEK) via cylinder, achieving normalized sensitivities of 5 ncps/ppt, with a corresponding LoD of 4.8 ppt (60 s). Values have been added to Table 1

L410: How the limit of the detection is determined should be described in the manuscript.

The following sentences have been added to mention how LoDs were determined:

Lines 415-418: "*LoD measurements were performed by introducing 2 SLPM of dry UHP N2 (i.e., background measurement) for 10-15 minutes. The LoD was estimated by using Tofware and calculating the Allan variance (i.e., the stability of the signal over time). Finally, the LoD corresponds to 3-standard deviations (sigma) of the Allen variance and is determined as a function of integration time estimation.*"

L455: In the ammonium ionization scheme, protonated acetone dimers are also present. Were any organic compounds ionized by protonated acetone dimers, via adduct formation or proton transfer?

In the ionization scheme, acetone dimer formation is hampered by the large presence of ammonia (NH_3). It should be noted that, if the NH_3 concentration is below ~ 100 ppm, multiple ionization processes might occur, including mechanisms involving protonated acetone dimers. A sentence has been added to clarify this aspect.
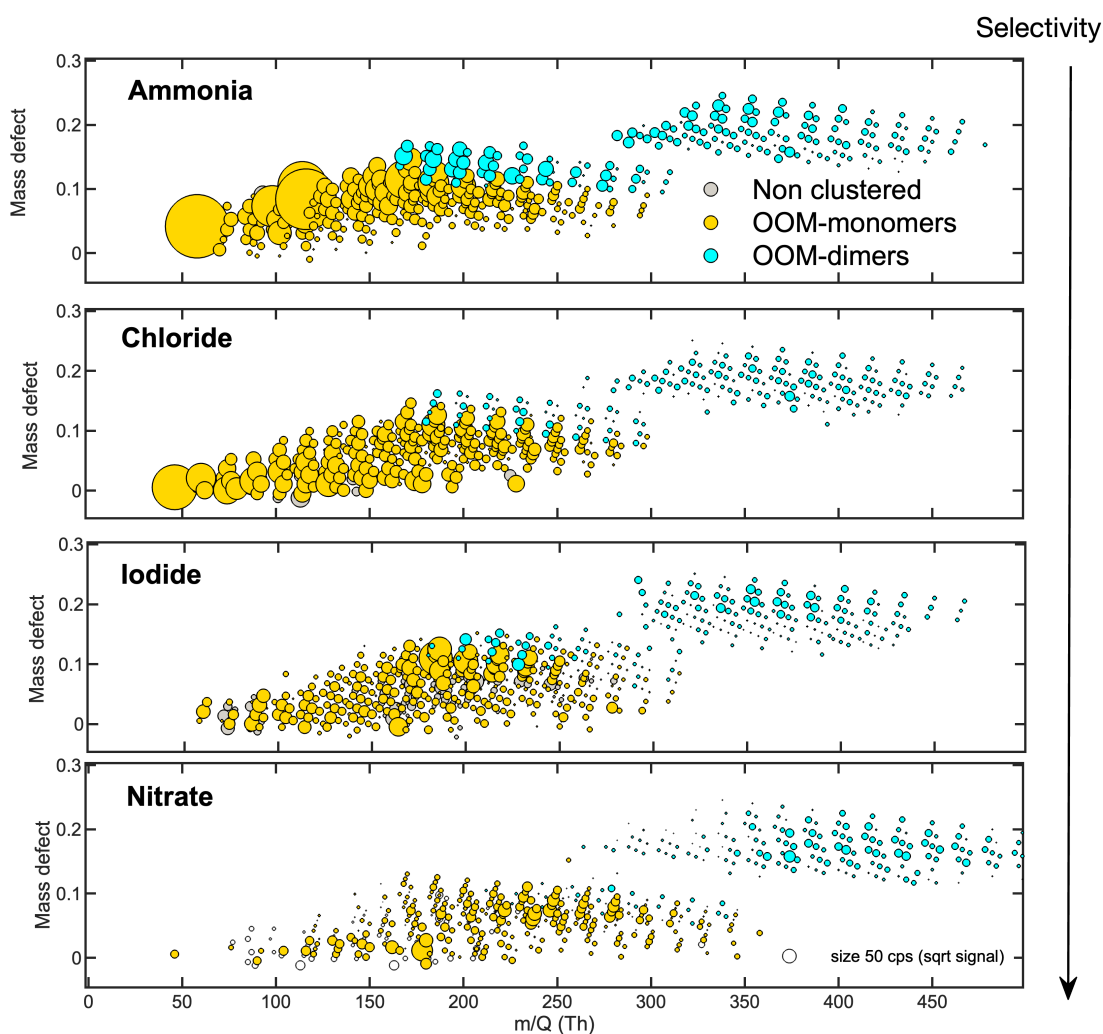
Lines 209-211: *"If the concentration of NH_3 is lower than 100 ppm, multiple ionization processes might occur (e.g., acetone dimers, charge transfer,…) which would complicate the mass spectrum analyses."*

L476: Eq. 10 is wrongly inserted into line 481. Please modify it.

This has been corrected in the new version of the manuscript

L733, Figure 5: The measured compounds were labelled as HOM-monomers or HOM-dimers. As substantial amounts of less oxygenated organic species were detected, particularly with ammonium, chloride, and iodide ions, I suggest labelling the compounds with OOM-monomers or dimers.

We agree with the reviewer, and we have revised the labels as suggested.

We thank the reviewer for his/her careful consideration of our article. We have attached a revised version of the manuscript in which we considered all the comments raised by the reviewer.

-line 230, "reagent ions and analyte ions that are very weakly bound to the reagent ions (e.g., water cluster with a binding energy of 42 kcal/mol)". 42 kcal/mol is not a weak binding energy - even the most strongly bound ELVOC*NO3- clusters are typically bound by less than this. And certainly iodine-formic acids (mentioned as an example of moderate binding a few lines below) is bound by less than this. Perhaps the 42 kcal/mol value refers to the total binding energy of multiple water molecules? Or is there a unit conversion error somewhere? Please explain/elaborate.

The units are indeed incorrect and we apologize for this error. Caldwell et al., 1989 reported value in kJ/mol and not kcal/mol. This is now corrected in the new version of the manuscript.

Lines 233-237: *"In general, reagent ions and analyte ions that are very weakly bound to the reagent ions (e.g., water cluster with a binding energy of 10 kcal/mol) (Caldwell et al., 1989) are often observed to deviate from the thermodynamic distribution with RF amplitudes >50 Vp-p. This is not entirely problematic, as the binding energy of these complexes is usually too weak for sensitive detection even at the weakest transfer conditions."*

-line 385: "(XX%)", please update the actual number here (or explain the notation) - this looks like something that a co-author forgot to fill in during finalising of the manuscript.

This has been updated within the new version of the manuscript:

Lines 387-389: *"With acetonitrile as the dopant, the change in sensitivity across the humidity range is reduced to a deviation of <20% relative to dry conditions for all model compounds, more for formic acid and nitric acid (<10 %)."*

-Line 448: something is grammatically wrong with the formulation of this sentence: "the formation of"… "can react". Maybe reformulate to "The RO2 radicals generated"… "can further react"?

The sentence has been modified as follows:

Lines 457-458: *"RO$_2$ radicals generated from the combined ozonolysis and OH radical reaction of α-pinene can further react yielding mixed oxidation products during the reaction time in the flow tube."*

-Line 511: "Differences in the contribution of these compound groups with previous work could be due to different sensitivities of the instruments…". While certainly true, isn't it also the case that especially the formation of ELVOC and ULVOC compounds (by a combination of

We agree with the reviewer that product distribution can be greatly impacted by the experimental conditions. A sentence has been added to underline that experimental conditions and systems can alter the OOM distribution.

Lines 519-523: *"Differences in the contribution of these compound groups (i.e., relative signal contribution to total OOMs) with previous work could be due to different sensitivities of the instruments towards organic compounds with varying oxidation extents (Riva et al., 2019). In addition, experimental conditions (e.g., RH, temperature, precursor concentration) and setup (flow tube reactor, atmospheric simulation chambers) can greatly impact the distribution of OOMs retrieved by MS techniques."*

Figure S4 has been modified as suggested
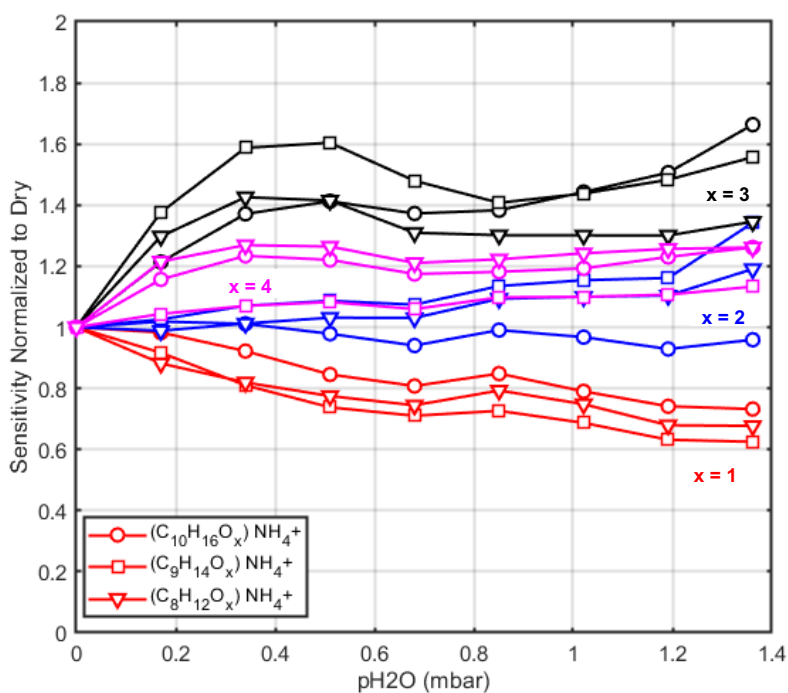
The authors present results from a newly designed VOCUS AIM reactor. They evaluate the instrument's performance by examining its time response (focusing on sticky molecules), sensitivity, limits of detection, and selectivity. Additionally, they use dopants to mitigate the influence of humidity on the sensitivity of different molecules, with acetonitrile being the most effective dopant. The authors highlight the strength of the AIM, which can switch within 2Hz between multiple reagent ions to access compounds of varying volatility. The instrument is tested in the oxidation of α-pinene to assess the selectivity of different reagent ions and the broad access to all products of such oxidation with high sensitivity. This paper is well-written and suitable for publication. Only minor comments from my side.

We thank the reviewer for his/her careful consideration of our article. We have attached a revised version of the manuscript in which we considered all the comments raised by the reviewer.

Comments:

Line 399-403: The straightforward normalization using the recorded reagent ions measured at the detector is great. It would be helpful if the authors could clarify the differences in the AIM-VOCUS that make this possible compared to the traditional VOCUS, where such normalization can be challenging.

Unlike the Vocus AIM, the reagent ions (i.e., hydronium ions) are not detected when operating the Vocus PTR. Indeed, only the water clusters are measured with a distribution that is greatly impacted by the conditions within the reactor (i.e., temperature, DC gradient, RF amplitude). As a result, the normalization procedure cannot be compared and the direct measurement of the reagent ions with the Vocus AIM makes the normalization of the data straightforward

Line 432-436: Switching chemistries at up to 2 Hz is impressive. However, could there be any interferences from one ion chemistry to the next that were observed? Are the 2Hz switching timescales recommended to ensure no interferences? Considering that the authors have already demonstrated the impact of tailing for sticky molecules, which may take several seconds to stabilize when fluctuations occur, I wonder if such frequent switching is ideal. Discussing potential limitations in this regard would be beneficial, as it could save the community considerable time in determining the optimum operating conditions of the AIM. Additionally, it would be interesting to note how these datasets are handled from a software perspective.

The fundamental time limitation is the residence time of the ions within the AIM reactor which is 10 ms. As long as the different reagent ion precursors do not interfere with each other, their stickiness is not a critical parameter. In addition, the flow profile within the AIM reactor remains constant and no fluctuation will occur when solely turning ON/OFF the VUV lamps. Hence, the future user will need to evaluate the necessity to use high frequency based on the scope of their measurements as well as the desired sensitivity/LoD. All the data will be recorded within the same data file and will be handled in the same manner by the software.

Line 462-464: What are the expected concentrations though? The introduced a-pinene is at high concentrations and I wonder whether these compounds could be observed at such high intensity in ambient air.

Within the conditions tested in the flow tube up to ~ 4.5 ppb of AP reacted (from OH radical and O_3 oxidation) within the 70 s. Assuming a total HOM yield of 4% (Bianchi et al., 2019),

the total HOM concentration should have been in an order of 180 ppt. As a result, we do expect to be able to measure HOMs under typical atmospheric conditions (~10-20 times lower compared to the flow tube experiments). Finally, the flow tube experiments were analyzed using a 1 s time resolution while ambient measurements are often analyzed using a much lower time resolution (1-15 min), which would help the detection of compounds at sub-ppt levels.

Figure 1: It would be nice if the authors could indicate the pressures in the different sections of the IMR in A or B. Is the dopant flow included in the CFD calculations? I am sure the effect should be minor but still something to mention.

The pressures in the AIM reactor and the SSQ have been added in Figure 1. The CFD calculations did not consider the dopant flow, which is now mentioned in the caption in Figure 1.

Figure 3: I would recommend that the authors change the acronym of the color bar caption from "ACN" to "dopant flow".

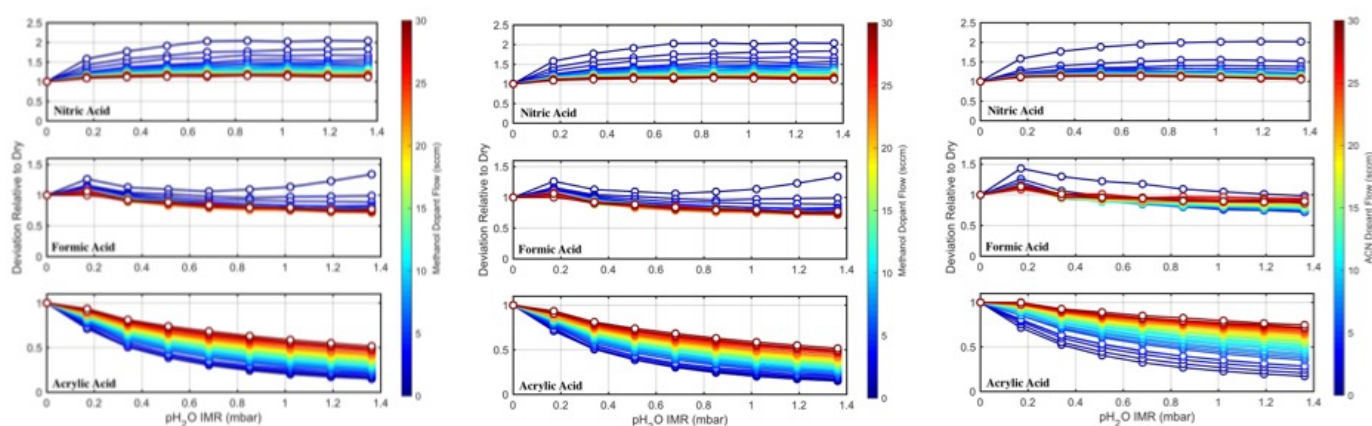The Figure has been modified as suggested.

Table 1: It would be great if the authors could provide the contribution of any interfering clusters to these calibrations that could complicate the spectra. How clean are the spectra for these calibrants and what is the expected % interference of clustering? Also, more AIM reagent ion chemistries are presented including NH4+, Cl– , and NO3-. Are there separate sensitivity results for these ionization modes?

We expect that analytes for any of these ion chemistries will be detected primarily as cluster adducts, except acid compounds (e.g., sulfuric acid, polyacids,…), which are detected as deprotonated ions in negative mode such as nitrate and bromide. For detailed sensitivity results, please refer to our response to reviewer 1. However, calibrations for ion chemistries beyond those commonly used in the community were not extensively performed in this study, as they go beyond the scope of our current work.

Additionally, nitrate ion chemistry historically presents challenges in calibration, particularly because it targets very low volatile compounds that are difficult to handle and transfer

quantitatively into the gas phase. We successfully calibrated the nitrate mode specifically for PFAS molecules and pesticides, achieving calibration factors ranging from 0.2 to 5 ncps/ppt, more information can be found here: https://www.tofwerk.com/pfas-detection-air-vocus-aim/

Figure 5: The yellow color is not consistent in all graphs. There is no indication of what the size is. If it is selectivity, it would be great if the authors define how it is determined in the caption.

We appreciate the reviewer's observation regarding the inconsistency of the yellow color in the graphs. We have revised the color scheme to ensure consistency across all graphs. Additionally, we have included a legend to explain the size of the points. The size of the circle is determined by the square root of the signal intensity. The caption has been revised as follows:

Lines 743-747: *"Figure 5. Mass defect plots of organic compounds measured by the Vocus AIM reactor using Ammonia, Chloride, Iodide, and Nitrate ion chemistries generated via the O3/OH initiated oxidation of α-pinene. The x-axis represents the mass-to-charge ratio of the neutral analyte, the y-axis represents the corresponding mass defect, which is the difference between their exact mass and nominal mass, and the size of the circle represents the square root of the signal intensity measured for each ion."*

The caption of Figure 6 has been also revised as follows:

Lines 758-754: *"Volatility distribution comparison for organic compounds detected by the Vocus AIM using nitrate, iodide, chloride, and ammonia ion chemistries. Ion intensity represents the cumulative signal recorded for each ion chemistry. The background colors represent the saturation concentration (C_{sat}) in the range of ultra-low volatility (ULVOCs), extremely low volatility (ELVOCs), low volatility (LVOCs), semi-volatile (SVOCs), intermediate volatility (IVOCs), and volatile organic compounds (VOCs, pink). The pie charts represent the corresponding contributions of VOC, IVOC, SVOC, LVOC, ELVOC, and ULVOC classes from the O3/OH initiated oxidation of α-pinene.*

Typos:

Line 266: Replace "slpm" with "sccm."

This has been corrected.

Line 385: Correct to "xx%."

This has been corrected.