

Responses to Reviewer #3

General Comments:

In this manuscript, Zang and Willis present the development and evaluation of a method for switching between the reagent ions, NH_4^+ and H_3O^+ , in a Vocus-CI-ToFMS to detect reduced and oxygenated gas-phase reactive organic compounds (ROC). They detailed the optimization of ion-molecule reactor conditions for both reagent ions, compared their ability to detect a variety of ROC species, and applied the $\text{NH}_4^+/\text{H}_3\text{O}^+$ reagent-ion switching to the ambient measurements in a rural pine forest. Compared to CIMS measurements that employ complementary reagent ions either with repeated experiments or using different instruments, switching reagent ions in a single instrument as described in this study avoids the interferences from the changing inlets and instruments and enables a better evaluation of the capabilities of different reagent ions in detecting ROC species. Overall, this work is solid and well designed, and the manuscript is nicely written. I recommend the publication of it in AMT after the following minor comments are addressed.

Specific Comments:

Line 127: Please also specify the default settings of fIMR pressure and front voltage here.

This information has been added as follows: *“With NH_4^+ , we characterized from 2.5 to 3.5 mbar and from 45 to 65 V cm^{-1} (60-120 Townsends (Td)). For H_3O^+ , we characterized from 1.5 to 2.5 mbar and from 45 to 65 V cm^{-1} (80-200 Td).”*

Line 140: Please provide the RH range evaluated here.

This information has been added.

Line 152: The ambient air was sampled using a 4-m long PFA tubing. Was the wall loss of ROC compounds significant in the sample inlet, especially for the oxygenated ROC?

We did not quantify the wall loss of ROC in the sampling inlet. We have added the following sentence to address this: *“The inlet likely produced wall loss of oxygenated ROC and while the extent was not quantified, minimizing the inlet inner diameter and maximizing the flow rate, while maintaining laminar flow, serve to minimize inlet losses and tubing delays (Pagonis et al., 2017).”*

Line 244: “Comparable” is not appropriate word here, as for many oxygenated ROC species shown in Figure 2, H_3O^+ exhibits significantly higher sensitivity than NH_4^+ .

We have modified this statement to more accurately communicate what we intended with the word “comparable” here: *“For the compounds detected with both ionization modes, sensitivities and detection limits for H_3O^+ and NH_4^+ are in the same order of magnitude (Fig. 2 & A3).”*

Line 263: Not only 2-octanone, but also acetone. In Figure 3, only the molecular ion fraction of 2-hexanone is displayed for ketones. Suggest adding other ketones such as hydroxyacetone, methyl ethyl ketone, and methyl vinyl ketone to the figure, which also have a lower detection limit in NH_4^+ mode than in H_3O^+ mode.

We have noted the additional exception of acetone to this statement: *“This is consistent with the lower NH_4^+ detection limit for the majority of ketones we examined (with the exceptions of acetone and 2-octanone) and the aldehyde trans-2-hexenal (Fig. 2).”* Our intention with Fig. 3 is to display compounds that are complementary to those displayed in Fig. 2 while providing insight into the general fragmentation patterns with NH_4^+ and H_3O^+ ionization for a range of compound classes and functional groups. Including the fragmentation patterns of smaller ketone species will therefore not add unique information to Fig. 3.

Line 264-265: The authors stated that “reduced fragmentation has a larger impact on sensitivity between the two reagent-ions for more highly oxidized compounds with multiple functional groups.” However, the H_3O^+ ionization induces stronger fragmentation while having higher sensitivities to all ketone species, compared to the NH_4^+ ionization. Please modify this statement.

This statement was intended to apply to larger oxygenates that we discuss later in Sect. 3.5, but we acknowledge this was not clear. We have amended the sentence so that it clarifies that we are not referring to the ketone species in Fig. 2 and 3 as “highly oxidized compounds.” The sentence now reads as: *“Our observations suggest that reduced fragmentation has a larger impact on detection capability of the two reagent-ions*

for more highly oxidized compounds with multiple functional groups. This is observed for propane-1,2-diol which is readily detected with NH_4^+ but not with H_3O^+ ; the detection of oxidized ROC is discussed further in Sect. 3.5.”

Line 270: As shown in Figure 4, ion signals of several species show a small but noticeable positive dependence on the RH for both reagent ions. This phenomenon should be mentioned and the reason should be discussed. We appreciate this suggestion and have now added the following sentences discussing the mild humidity dependencies with both reagent ions: *“Varying sample humidity with constant analyte concentration demonstrates low humidity dependence with both NH_4^+ and H_3O^+ ionization across a range of reduced and oxygenated ROC (Fig. 4). We note an approximately 10 % increase in the NH_4^+ sensitivity to nitriles and oxygenates while alkene sensitivities remain unchanged up to 85 % RH. We also observe a slight (5-10%) increase in sensitivity with humidity for oxygenated species with H_3O^+ , while alkene sensitivities are less affected. The low humidity dependence of the Vocus-CI-ToFMS has been demonstrated previously for H_3O^+ for a variety of analytes (Krechmer et al., 2018; Kilgour et al., 2022; Li et al., 2024) and for a select number of small oxygenates, alkenes, and acetonitrile with NH_4^+ (Khare et al., 2022; Xu et al., 2022).”*

Line 281 and Figure 5: Although the authors mentioned in the text that the influence of H_3O^+ reagent ions were not observed in NH_4^+ mode, it would be good to also plot the signal profiles of an example protonated ROC species in Figure a-e or in a separate figure.

A figure demonstrating this has been added to the supplement as Fig. S3.

Line 331: This comment is also related to Figure 5. As shown in Figure 5a, there remains a non-negligible fraction of $\text{NH}_4\text{H}_2\text{O}^+$ ion signals after switching the reagent ion to H_3O^+ for 300 s. Do the residual $\text{NH}_4\text{H}_2\text{O}^+$ ions in H_3O^+ mode contribute to the ionization and detection of the highly oxygenated ROC species that are undetectable with H_3O^+ in ambient measurements?

We do not observe the ionization of highly oxygenated ROC species by ammonium adduct ionization during H_3O^+ ionization periods. While it may appear to be a non-negligible fraction, there is a delay in data acquisition of approximately 10-30 seconds between each ionization mode, and as a result some instrument settings have already changed before data collection begins and some $\text{NH}_4^+\cdot\text{H}_2\text{O}$ is already depleted. As a result, 100% signal intensity in H_3O^+ ionization mode is not equivalent to 100% signal intensity in NH_4^+ ionization mode in Figure 5.

References

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