

## Responses to Reviewer #2

The authors presented a very nice characterization and application study of chemical ionization mass spectrometry (CIMS) using both ammonium and hydronium ions as reagent ions in the Vocus time-of-flight (ToF) CIMS. Automatic switching between these two reagents was realized and applied in a field campaign at a forested site. The results showed that although these two methods can detect most of VOCs studied (in total 23), hydronium ion (as in PTR-ToF-MS) is more suitable for reduced VOCs, while ammonium ion is more suitable for functionalized VOCs (S/IVOCs). A method was proposed to filter the periods with hysteresis during reagent ion switching, and field data were used to evaluate the performance of this method with auto-switching of reagent ions. The study is well designed and conducted, and the manuscript is clearly written. The findings are valuable in atmospheric chemistry research community in that it provides a method that can efficiently measure a wide range of VOCs and S/IVOCs in the atmosphere. I therefore recommend publication after Minor Revision, with some comments as follows.

### Main:

The only concern I have is on the criteria of setting the time periods of data to filter out during the hysteresis due to reagent ion switching (section 3.4). In addition to the reagent ion (ammonium-water adduct), the author also chose the C<sub>3</sub>H<sub>6</sub>O-ammonium adduct to get the decreasing/increasing rates by taking the derivatives. And it seems that the authors preferred to use the results from the C<sub>3</sub>H<sub>6</sub>O-ammonium adduct to determine the time periods of data for filtering (comparing Figure 5 and L325). I have reservation on this for two reasons. First, it is indeed okay to assume that the constituents leading to the signal of C<sub>3</sub>H<sub>6</sub>O-ammonium adduct do not change within the 15 min of reagent ion switching. But one might not have good reasons to assume that the proportions of the C<sub>3</sub>H<sub>6</sub>O species in the air sampled (presumably acetone and propionaldehyde?) remain the same in the 550+ hours of data (2000+ decreasing/increasing curves used in Figure 5b and 5d). I assume that the ionization efficiency (or sensitivity) of acetone and propionaldehyde might differ with ammonium CIMS, or the authors can convince me otherwise. If so, and if their proportions in the C<sub>3</sub>H<sub>6</sub>O species changes, the shape of the exponential curves in Figure 5b and 5d) will be substantially distorted after averaging, thereby resulting in a high uncertainty in the estimation of the time for data filtering. The second reason is that by looking at Figure 5, the ammonium-water ion has both obvious exponential shape and its normalized signal intensity can restore to 1 in the switching from hydronium ion to ammonium ion (Figure 5c); the C<sub>3</sub>H<sub>6</sub>O-ammonium adduct ion, however, cannot restore even after 300 s (Figure 5d). Therefore, a better justification and clarification of choosing the data C<sub>3</sub>H<sub>6</sub>O-ammonium adduct ion instead of ammonium-water adduct ion to determine the time for data filtering are needed.

We agree with the reviewers concerns in utilizing C<sub>3</sub>H<sub>6</sub>O-ammonium adduct for monitoring switching due to changes in the isomer composition of ambient air sampled. The ammonium-water cluster does have a clear double exponential shape; however, the impacts of the BSQ on this signal make it so that the decay is dominated by the changing instrument voltages and it thus provides much less information about the ion chemistry taking place in the FIMR. Because the ammonium-water clusters are the reagent ions and we want to avoid hysteresis in ion chemistry, we argue that using an analyte ion is a more direct measure of ion chemistry relevant to analyte ion detection. However, as the reviewer points out, these reasons may not justify the assumptions required to use a persistent ambient ion. To address this shortcoming in our analysis, we provide additional data and associated analysis from another deployment (ARTofMELT) where we were able to deploy a deuterated internal standard constantly infused into our sampling inlet (Fig. 6 in the revised manuscript; see also our response to reviewer 1 comment related to Line 318 of the original manuscript). We monitor 2-hexanone-d<sub>4</sub> as a ammonium adduct and a proton-transfer product, and find that the average timescale for reagent-ion hysteresis is lower than that obtained with C<sub>3</sub>H<sub>6</sub>O-ammonium adduct at MEFO. While the C<sub>3</sub>H<sub>6</sub>O-ammonium adduct observed during ARTofMELT was too variable in time to allow a hysteresis analysis (shown in Fig. S7 of the revised manuscript), and so we cannot perform a perfectly direct comparison between the two deployments, our analysis does suggest that the hysteresis timescales obtained with C<sub>3</sub>H<sub>6</sub>O-ammonium adduct at MEFO are reasonable (i.e., a 75 s cutoff for NH<sub>4</sub><sup>+</sup>, and a 175 s cutoff for H<sub>3</sub>O<sup>+</sup>).

For the field data, the authors only used the average mass spectra to compare the signal-to-noise ratios of

ammonium and hydronium ionization results. It would be good to show some comparison of selected species for both ionization methods to demonstrate the applicability of this method. That is, it is good to show that sensitivity of certain compound classes might differ with different reagent ion, but the quantification results are still comparable. In addition, Figure 6 is a bit too difficult to distinguish the differences for those with small signal-to-noise ratios. It would be better to show results in bar charts for those series of compounds with different oxygen atoms that are generally in accordance with the discussion in the text (L346 onward).

We have added three figures to the supplement to address the reviewers' suggestions. Fig. S9 shows bar charts for the species we discuss in Sect. 3.5 to help the reader visualize our discussion. Fig. S12 and Fig. S13 have been added to demonstrate what a time series and diurnal cycling looks like when using this reagent-ion switching method.

**Minor:**

L70: "A" should be no charge on it as a neutral analyte?

The reviewer is correct. This has been changed in the revised document.

L172-173: this looks like two sentences.

We agree the punctuation in this sentence was unclear. This now reads "*A change between ionization modes results in hysteresis where the ion chemistry is impure. The filtering of hysteretic periods is discussed in Sect. 3.4.*"

L195: "evident from" or "different from"?

We used "evident from" here to suggest that the reduction in benzene sensitivity at lower  $E/N$  was evidence of the production of protonated water clusters. We have adjusted the wording to make this distinction more clear for the reader. It now reads as follows: "*Second, at low  $E/N$  protonated water clusters contribute to the ionization of  $\alpha$ -pinene. The production of protonated water clusters is evident from the reduced benzene sensitivity at lower  $E/N$  (Fig. A1) (Gouw and Warneke, 2007).*"

L282: "Reagent-ion chemistry"?

This typo has been corrected.

Subsection title of 3.5: "Reagent-ion comparison"?

This typo has been corrected.

## References

- J. D. Gouw and C. Warneke. Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrometry Reviews*, 26:223–257, 2007. ISSN 0277-7037. doi: 10.1002/mas.20119. URL <http://10.0.3.234/mas.20119> <https://dx.doi.org/10.1002/mas.20119>.