

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

In the revision, the authors have addressed most of my prior comments. But there are a few remaining ones:

-We thank the reviewer for his/her careful consideration of our article. We attached a revised version of the manuscript in which we considered all the comments raised by the reviewer. Below, you will find our point-by-point reply.

1. My initial comment #6. The first question to suggest adding uncertainty discussion was not replied or addressed. The method assumes all the $C_{10}H_{14,16}O_x$ formulas measured by the three instruments are the species. Is this valid?

Response: We added an uncertainty discussion in the revised text, and further revise the manuscript to clarify our statements in this version. Instead of all the $C_{10}H_{14,16}O_x$ formulas, we only assumed those with Pearson correlation coefficients (R^2) of time series greater than 0.9 between NH_4^+ -Orbitrap and another instrument (18 species for NO_3^- -LTOF and 32 species for PTR3-TOF) were produced from the same chemical process and yielding likely the same species. The correlation factor was derived based on the average sensitivities of these species. For other compounds, we believe they could represent different isomers or arise from decomposition/fragmentation of larger species.

Line 154-172: Correlation analysis were performed between the NH_4^+ -Orbitrap and the two reference instruments including NO_3^- -LTOF and PTR3-TOF (referred to as REF). The Pearson correlation coefficients (R^2) were determined using the timeseries during two runs (run 2211 and 2213). This included AP injection, steady state stage, NO_x or CO injections, and RH variation. As a result, for one compound, 755 data points were recorded and used for the correlation analysis. Although product ions with same molecular formulas might lead to low correlation (See details in section 3.3) and would suggest different species (i.e., isomers, fragment ions,...), a few molecules with R^2 greater than 0.9 (18 for NO_3^- -LTOF, 32 for PTR-TOF, and 5 for F-CIMS) were selected and be likely attributed to the same species.

Although no direct calibration has been performed for the NH_4^+ -Orbitrap, the OOM concentrations were estimated based on comparisons between NH_4^+ -Orbitrap and the two reference instruments which has developed reliable quantification methods. For the OOMs whose timeseries had R^2 greater than 0.9 between NH_4^+ -Orbitrap and REF, linear regression was conducted for normalized intensities in NH_4^+ -Orbitrap (dimensionless) and concentrations in REF (molecules cm^{-3}), and the slopes were recorded as their relative sensitivity. The calibration factor $c_{Orbi-REF}$ was derived from the averaged relative sensitivity of these species ($\sim 2.62 \times 10^8$ molecules cm^{-3} for NO_3^- -LTOF and $\sim 4.83 \times 10^8$ molecules cm^{-3} for PTR3-TOF). Applying the calibration factors to all the OOMs, their concentrations detected by NH_4^+ -Orbitrap could be calculated as shown in equation (4). Additionally, a temperature-dependent sampling-line loss correction factor was applied (Simon et al., 2020).

$$[OOM]_{Orbi-REF} = c_{Orbi-REF} \times [OOM]_{nor} \quad (4)$$

Lines 343-357: *The reason why the correlations of certain molecules are lower than 0.9 might be due to the molecules' composition or potential ionization artifacts. RH dependence is an important property leading to the low correlations as the experiment includes RH variation from 20% to 80%. Although NO₃⁻ ion chemistry had been reported to be less dependent on RH (Viggiano et al., 1997), the sensitivities of PTR3-TOF (Breitenlechner et al., 2017) and I-CIMS (Lee et al., 2014) both showed high dependence on RH. In addition, the relative sensitivity of NH₄⁺-Orbitrap was also influenced by the varying RH (See details in Section 3.6). Fragmentation, such as decomposition of dimers, would also lead to low correlations. However, less fragmentation is expected to occur in the NH₄⁺-Orbitrap using similar settings as our earlier studies (Riva et al., 2019a; Riva et al., 2020). In comparison, decomposition of peroxides (i.e., ROOR and ROOH) can be expected within the PTR3-TOF. While fragmentation of dimeric compounds can contribute to the overall signal of the monomers, the concentration of such species remains minor (Li et al., 2022). As a result, no large enhancement of the monomers signal intensity is expected. There are also other artifacts which cannot be excluded based on current dataset, including potential isomers and differences in response time between instruments, would also lead to the low correlations.*

NO₃-CIMS and PTR-MS are both more selective than NH₄⁺-CIMS.

In this study, the PTR3-TOF had been optimized for amine detection, while in a previous study, PTR3-TOF has been shown to measure molecules with oxygen number ranging from 0 to 18 (Breitenlechner et al., 2017). As result, we do not want to conclude on the selective of the different ionization techniques used in this work. Overall, we believe that the NH₄⁺-Orbitrap has a lower selectivity compared to current NO₃⁻-CIMS (sensitive to highly oxidized molecules) and traditional PTR-MS (sensitive to molecules with lower oxygen numbers), according to our previous study (Riva et al., 2019b).

2. In several occasions, the authors responded to my questions (e.g., #10 and a couple of others), but the clarification was not added to the revised manuscript.

We added revisions for comments #10 in this version. But for other questions (i.e., #5 and #13), we think there is no proper position to add the clarification in the paper, thus we only replied to the reviewer without revising the manuscript or SI. We would like to point out that the discussion will be part of the article and will remain available.

For #10, the meaning of values following “±” are clarified in the revised manuscript.

For #5, as we have no concrete evidence from Vocus-NH₄⁺ or other NH₄⁺-CIMS to make a comparison, we did not mention it within the manuscript for the discussion.

For #13, we have added some discussions regarding the uncertainty i.e., Lines 342-355. As we have explained, there are multiple factors which might affect the correlation. Showing the elemental characteristics of one or several species to the readers would not summarize the real situations and might lead to unnecessary misunderstanding.

Lines 311-314: *The number of O atoms in OOMs varied from 1 to 11 in monomers (C₂₋₁₀) and from 2 to 16 for dimeric products (C₁₄₋₂₀), with an average elemental oxygen-to-carbon ratio (O:C) of 0.4 ± 0.2 (the value following “±” herein and after refers to the standard deviation of O:C during the experiment).*

3. Without the calibration or estimation of sensitivity in any way, I suggest not use the terminology "semi-quantitative". At best, this is intensity-based relative comparison among different instruments.

We have revised the terminology in the different parts of the manuscript.

Lines 42-44: *OOMs concentrations measured by NH₄⁺-Orbitrap were estimated using calibration factors derived from the OOMs with high timeseries correlations during the side-by-side measurements.*

Lines 361-362: *The sensitivity of NH₄⁺-Orbitrap was constrained based on the intensity comparison between NH₄⁺-Orbitrap and the other two instruments.*

Lines 369-371: *Taking into consideration that such ranges are also the oxygen number ranges with high sensitivities respectively, this proves the robustness of the NH₄⁺-Orbitrap and the intensity-based relative comparison between NH₄⁺-Orbitrap and two reference instruments.*

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