Comment on amt-2022-228
Anonymous Referee #1


Review of the manuscript “Chemical Ionization Mass Spectrometry Utilizing Ammonium Ions (NH4+ CIMS) for Measurements of Organic Compounds in the Atmosphere” by L. Xu et al. (https://doi.org/10.5194/amt-2022-228)

The manuscript presents a detailed overview of the operation and sensitivity of NH4+ chemical ionization applied in Vocus-type mass spectrometer that uses an improved ion-molecule reactor FIMR. The authors discuss operational constraints, sensitivity calibration as a function of cluster stability (inferred from dissociation voltage inside the instrument) and present detailed comparison of selected species with other CIMS types in the field. The paper is thorough in presenting limitations and advantages of this chemical ionization technique and therefore it will be very valuable for the community. Some comments and suggestions are outlined below.

General comments

While I appreciate how detailed the paper is, I found it quite long as it includes a lot of information: investigations into different instrumental parameters, sensitivity comparison to other instruments as well as CIMS intercomparison in the field. I found few repetitive parts of text that could be shortened to my mind, both between Methods and Results (section 4), and in Supplement. I suggest authors go through the text to try to make paragraphs shorter and focus clearer. I also found myself jumping between formulas in different parts of main text and Supplementary to get the full picture.
Specific comments

Line 36: Please include Lindinger et al. (1998) and Blake et al. (2006) as references to early NH$_4^+$ ionization works.

Lines 46 and 49: Maybe for comparison, report sensitivities in same unit as in your calibrations, cps/ppb?

Equation 10: would be nice to report the value of $\mu_0$ used.

Section 3.3. in relation to section 3.2: It would be useful to see the modelled reagent ion distribution for the conditions that were selected for sensitivity characterization? T = 314K, P = 3mbar was used in Section 3.3., was it the same for determining sensitivities in Table 1? It could be mentioned in Methods.

Line 253-254: Authors say that different compounds have maximum sensitivity at different ratios of reagent ions because they have different reactivities “towards NH$_4^+$.H$_2$O and other reagent ions”. What does this mean? Isn’t it so that sensitivity is calculated based only on A.NH$_4^+$ and the sensitivity is a function of the cluster stability?

Figure 3: Line colors are so that it is hard to see. Could the compounds be grouped somehow like in Fig. 5, if it is feasible and improves the visibility of lines. How is optimal range determined? By eye, even smaller ratios would be okay.

Lines 217-218: Authors say that E/N affects 3 things: reagent ion distribution, focusing effect and declustering. I think in FIMR E/N affects declustering and therefore this regulated reagent ion distribution, so one leads from another. The authors mention just this in the beginning of this paragraph.

Lines 343-346: This already is described in section 2.1. It could be more concise here. And also same text is again in Supplement, section 3.

Figure 5: Could authors specify somewhere why KE$_{cm,50}$ is different than in Zaytsev et al. 2019? I assume it is the geometry of the ion-molecule reactor?
Line 425: Could authors clarify what “anticorrelation” mean here? Orange data points and right axis on Figure 6 are absolute CIMS sensitivity and left axis (blue bars) is ratio, so if NOAA H$_3$O$^+$ would have constant sensitivity, I think we would observe similar trend in the ratio as now.

Lines 430-432: A statement that is not necessarily a conclusion from the data presented in this paper. I would suggest to include a reference or remove. Also lines 543-544.

Lines 440-441: Similar as above. Where is it shown in the paper how sensitivity in the presented instrument changes (or doesn’t) with RH? Maybe in Methods, line 104, it is mentioned. Would it be possible to add a figure to SI?

Line 455: Which H$_3$O$^+$ CIMS is this? NOAA?

Line 523: It seems to me that in Figure S13, pentenes peak in early morning.

Line 547: “strong relationship”- maybe worth mentioning exceptions here (like monoterpenes and other).

Equation S6: Are “E” in Eqn. S6 and “E” Eqn. 10 same variables?

Figure S7: If possible, it would be very useful if authors included a table with detected ion compositions in this figure.

Technical corrections

Line 66: Change "Tofwer" to "Tofwerk".

Line 146: Remove word “does” after H$_2$O.
Line 164: Authors use I+ in here probably with “I” standing for “ion”, so H$_3$O$^+$ and NH$_4^+$. It could be mentioned in the text, just like A is NH$_3$ and H$_2$O.

Figure 1: Somewhat difficult to separate solid and dashed lines in the legend.

Line 323: Here, f(NH$_4^+$.H$_2$O) is defined, but it is already used in previous section.

Line 333: Change “k have less uncertain” to “k is less uncertain”.

Line 476: Change “produces” to “produce”.

Line 489: Change “absent” to “absence”.

Line 506: Suggestion to change “as adduct ions” to “as adducts with reagent ions”.

Line 516: Change “a day” to “the day”.

Supplementary line 58: Change “dipoment” to “dipole moment”.

References
