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Comment on amt-2022-246

Anonymous Referee #3

Referee comment on "Quantitative chemical assay of nanogram-level particulate matter using aerosol mass spectrometry: characterization of particles collected from uncrewed atmospheric measurement platforms" by Christopher R. Niedeck et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2022-246-RC3>, 2022

This paper describes a micro-nebulization plus HR-AMS technique to analyze very small aerosol samples collected with the type of collectors used on unmanned aerial systems (UAS). This is a welcome addition to the use of the HR-AMS for offline analysis and makes in situ sampling with UAS systems a real possibility. The paper is fairly well written and should be accepted for publication after the authors address the following points.

Line 16 and Table S3: This data does not justify 3 significant digits, especially in the detection limit. I would use at most 2.

Line 25: I'm not sure what you mean by "with temporal and spatial resolution." The UAS sampling time in Table S1 is 15 hours over multiple days. I would delete this phrase.

Line 34-35 and throughout paper: Please format the citations properly, i.e., remove the extra parentheses and don't include the author's name if it is right before the citation.

Lines 120-125: Since you include this data in the paper, please include the sampling dates and times in Table S1 and give the samples names. In Figure S7, you refer to SGP impactor 2, but it is not clear if you are referring to one sample or the average of multiple samples. Also, it is not clear if this is one stage (which size cut?) or multiple stages averaged together. Please specify in the text that the four-stage impactor samples were collected at SGP. Delete "Note that" at the beginning of the last sentence.

Line 128: Please use one system of units.

Lines 129-132: Why is the filter extraction/sonication performed in two steps?

Lines 144-148: In this description of the AMS, please mention that you were using N₂ as the carrier gas for the nebulization. This is important for interpreting the mass spectra in Figure 2b.

Figure 2: Please use more different colors in (a) and (b) for SO₄²⁻ and ³⁴SO₄²⁻. e.g., red and black. It is hard to tell them apart.

Lines 162-167: What was the point of the SIMS analysis? Is it preferential to N containing organics? Are there any references for applying this technique to ambient aerosol samples? I do not understand what the SIMS analysis adds to this paper.

Lines 176-184: This description in the text is not consistent with the modified frag table provided in the SI. For example, text says CO=CO₂, but frag table has CO=0.75*CO₂. Why the nonstandard multiplier? Text says that S is removed from the parameterization, but it is still in the frag table as calculated from SO and SO₂. Please correct either the frag table or the text! I would also rephrase the end of the sentence on lines 181-183 which seems confusing for non-AMS experts. Instead of "parameterized to the ³⁴SO₂ and ³⁴SO ions and the parameterizations for the S and ³⁴S were removed" maybe this works better: "parameterized to the ³⁴SO₂ and ³⁴SO ions. The signals for S and ³⁴S were determined directly from the high-resolution fits. Direct measurement of S is possible when N₂ is used as the carrier gas."

Line 193: Should that be [³⁴SO₄] instead of [X] in the numerator?

Lines 198-206: You describe the IC analysis of ³⁴SO₄ spiked samples, but you do not show any data for either the known laboratory solutions or the ambient samples. Please include a comparison of the IC and AMS SO₄ for at least some samples. This could be a table in the SI and should be referred to in lines 225-226 where you mention additional validation with IC analysis.

Line 211 and elsewhere in the paper and SI: It's a "collision-type" atomizer, not "collision-type"

Line 212 and line 216: I would remove editorializing comments like "sorely" and "apparently."

Line 222: What temperature is the spray chamber? Is it warm enough to evaporate NH₄NO₃ and lead to the lower reported recovery for NO₃ in Table S3?

Lines 243 to 247 and Figure 3: Why does the data roll over at higher mass loading? I would add a sentence describing how you calculate NE. It's also not clear how you get a single value for NE from curved data. Is it the slope? Average of the ratios, in which case you should include the standard deviation? Refer to Table S3 when you mention the NE values. I would reorganize the caption to Figure 3. By the time you get to referring to the ratio between the two values, it is not clear if you are referring to (a) or (b). And there's a typo – "as in Fig. 1b" should be "as in Fig. 3b."

Lines 281-282: Figures 2a and 2b are reversed.

Line 286: I would add "on the ground" to the heading to make it clear these were not UAS samples.

Lines 294-5: Did you subtract total organic mass for the blanks or subtract the mass spectrum for the blanks? The latter might help resolve whether the methanol contaminants are the cause of the differences between the filter and impactor. It's a bit confusing that you had more organic in the impactor blanks, but less methanol.

Lines 311-317: I'm very confused by the UAS sampling. Table S1 has dates between 11/15 and 11/18, but Figure 4 shows a flight track on 11/13 and Figure 5 shows additional grey bars on 11/9 and 11/11. Is Table S1 incorrect? I'm also confused about whether you have one UAS filter sample or multiple filter samples because sometimes you use singular and sometimes plural in the text. Did you really fly a single filter over 9 days? How did you prevent adsorption of gas-phase species when the UAS was not flying? In Figure 5, is the pie comparison for the filter using the ACSM data for only the indicated grey bar or for all the grey bars averaged together? Please clarify in the caption.

Figure 4: I think you could move this figure to the SI. What is the blue blob around SGP? Is that UAS flight track or something else? And if it is UAS flight track, why is there a ring of much higher concentration around it? Is it a different altitude?

Figure 5: It would be easier to compare the pies if you start organics at the top. You could also size the pies by the mass loading. In the caption, delete one of the uses of "offline" in the first sentence.

Line 353: Somewhere earlier you should mention that the Q-ACSM is a PM₁ and a unit mass resolution instrument.

Line 381: "a small number of UAS-collected" suggests you analyzed multiple filters, but I think you only analyzed one. Please correct this.

Figure S2 a) caption: The description of the change in size distribution is not correct and not consistent with the text in lines 236-8 where you say that decreasing the concentration below 1 mg/L causes the size distribution to become too small to be effectively transmitted to the AMS lens. Please correct the caption.

Figure S3: This figure is very confusing. What is the data in between organics and SO₄? It is not identified in the legend. Please identify the lines in the legend! It would help to scale the zeros to the same place on the left and right axes. I'm going to assume that the unidentified trace is AMS SO₄, in which case it looks like the ratio of the AMS Org/SO₄ is 20:1, even though the solution concentrations are 5:1. That would suggest much lower NE for SO₄ than Org, which is not consistent with Figure 3a. I don't understand the caption to Figure S3 – how is this a range of solute concentrations? It looks like just one. Presumably, this data corresponds to a single point in Figure 3. Which one? There's a significant variation in the AMS Org signal (from 0 to 50 ug/m³) across this time series. Do you have an explanation? When analyzing ambient samples, do you integrate across the entire nebulization? Or do you use the region where the AMS signal is stable? For the left axis, how are you measuring the solution concentration and why does it decrease at the start of the nebulization? You also need to correct the description of this Figure in the text (lines 258-261) which refers to comparing both AMS modes and not what is actually in Figure S3 (sample data for one point in Figure 3).

Figure S4: Use the same units on the y-axis of (a) and the axes of (b). One is in percent and the other is fraction. Please include the mass loadings for the species as well as the fractional contribution in (c). Please note in the caption that this comparison is for samples PNNL_F8 and PNNL_I3. You have other pairs that are very similar in day/time, e.g., PNNL_F7 and SGP_I2. What does that comparison look like? You could also compare the sum of PNNL_F1 through F6 with PNNL_I1. What does that look like? I think this is worth a comment in the text.

Figure S5: It is odd that the Q-ACSM MS for Impactor 3 shows a lot more signal at higher m/z's, but this is not reflected in the HR-AMS data. Or maybe this is an artifact of the m/z transmission efficiency calibration in the Q-ACSM data? Did something change in the way the Q-ACSM was operating?

Figure S6: It looks like the C_xH_yNO peak at m/z 59 is mislabeled as CH₃NO₂. It is called C₂H₅NO in the text (line 357) and in Figure S7b. I am also concerned by the fit to m/z 59 that you show in Figure S7b. Did you really not fit the C₃H₇O and C₂H₃O₂ ions? You can't just arbitrarily leave out the organic ions because you want to see C_xH_yNO. Also, C₂H₇N₂ is a very strange ion and not in the C_xH_yN series that you are observing. I suspect that is really C₃H₇O. Please fit m/z 59 with the correct set of possible ions and then redo the MS in Figure S6 and Figure 5 (b-e).

Figure S7: Which AMS data are you using for the comparison with the SIMS data? Weren't they collected at different times? Does the SIMS preferentially detect $CxHyN$, but not $CxHyNO$? I don't understand how you have scaled the axes for the two signals. If your point is that the SIMS signal is comparable to the AMS CHN signal, then it seems like you should use the same relative scaling between right and left axes on all panels.