Response to reviewer comments on "**Quantitative Chemical Assay of Nanogram-Level PM Using Aerosol Mass Spectrometry: Characterization of Particles Collected from Uncrewed Atmospheric Measurement Platforms**"

We thank the editor and the reviewers for their thoughtful and constructive comments and we have revised the manuscript accordingly. Listed below are our point-to-point responses (in **blue**) to the comments (repeated in black) and changes of the manuscript (in **red**).

Responses to Reviewer #1:

In this manuscript the authors report the development of a micronebulization-AMS (MN-AMS) technique that can provide quantitative analysis of nanogram level of organic and inorganic substances by utilizing an isotopically labeled internal standard ($^{34}SO4^{2-}$). Its major advantage is the less requirement of liquid volume for stable aerosol generation. As a result, it will meet the needs of applying AMS on offline chemical analysis of weight-limited PM samples from uncrewed atmospheric measurement platforms (UxS). Overall the manuscript is well written and the analysis is fairly easy to follow. I really enjoyed reading this article because it provides enough details of the experimental design, and also because the authors take an effort to validate the methods via multiple comparisons to other techniques such as IC, ACSM and SIMS. Therefore, I strongly support the publication of this work. Below are several minor comments that I would like to further discuss with the authors.

Minor comments.

1) Lines 227-229: Comparisons are made between the standard atomizer and the micronebulizer by atomizing a solution of sucrose and ammonium sulfate. The mass spectra derived from each atomizer show a high degree of similarity. What are the concentrations of sucrose and ammonium sulfate applied in this solution?

The concentration of both sucrose and sulfate (from ammonium sulfate) are 1 mg L^{-1}. This information will be added to the text in section 3.1.1.

Did the authors try different inorganic-to-organic mass ratio for this validation? Since atmospheric aerosol particles usually exhibit different morphologies and have complex chemical compositions, a validation by using a more complicated solution extracted from atmospherically relevant particles may be worthwhile. If this kind of sample is not available, adding some SVOCs, nitrogenated organic compounds, or chlorine species into the current solution could be some options. This validation can be critical, since one focus of this study is the micronebulization system, and Sections 3.2 and 3.3 are field applications rather than standard lab validations.

We did not compare more complex solutions in both the standard atomizer and micronebulizer. Given the limited availability of filter and impactor samples, we were unable to analyze the PM extracts using both the standard atomizer and micronebulizer. While such an analysis could help with the validation of our technique, both the standard atomizer and micronebulizer use the same physical principles for aerosol generation and are unlikely to give significantly disparate results.

2) Lines 299-308 in the main text and Figure S4 in the SI: I am wondering if it's reasonable to conclude "Overall, the chemical compositions of the filter extract and the impactor extract are similar". In Figure S4 c), the fractions of total organic and "Chl" look quite different between the filter and impactor samples.

The lines in question are meant to refer only to the mass spectral similarity, not to the total PM composition. The text will be updated to clarify this point. There are more significant differences when looking at the fractional contribution of the different PM components, and the possible reasons for this are discussed in the text.

The contamination from methanol is mentioned as one reason for higher concentrations of organic matter in the filter sample. Could the authors help explain why filter extracts contain more methanol but have less total organic matter?

During filter extraction, more methanol was used compared to the impactor extractions, and the final concentration of methanol was higher in the filter extracts. While this is not explicit in the manuscript, the filter sample shown in Figure S4 had a higher absolute mass concentration of organic material. What is shown in Figure S4c is that the filter sample had, as you point out, a lower fractional contribution of organic material compared to the impactor sample.

Will more methanol residuals contribute to more total organic matter in Fig. S4 c)?

Yes. Preliminary work looking at the HR-AMS organic signal from different organic solvents at different concentrations did show a dependence on the final concentration of the solvent. Methanol concentrations ≤ 10 % show a low, but consistent, background organic signal. Above that concentration and the background signal begins to increase rapidly. Because of this preliminary data, all filter and impactor extracts had a final methanol concentration ≤ 10 % v/v.

The similarity is also evaluated in the Figure S4 b), and it looks like the normalized signals are more consistent to each other in the region of both x and y values < 0.015? Is this similarity mainly from the methanol signals?

I would agree that the correlation is tighter in this low-signal range (< 0.015). This region contains mostly higher m/z ions (~> 80 m/z) with a small number of low m/z ions. When examining the organic mass spectra of aqueous solutions containing 5 mg L^{-1} sulfate and 10 % methanol, it is comprised almost exclusively of ions with m/z values < 100, and most of the signal is from lower m/z ions (< 70). Thus, while the methanol likely makes some contribution in the region you point out, the contribution is small. Rather, correlation in this region is more likely driven by similarities in the PM collected on both the filter and impactor.

Is it possible to make a comparison without methanol-related signals? As the authors mentioned in lines 297-299, the comparison between the filter (PNNL_F8) and the impactor (PNNL_I3) assesses biases either in the sampling system or the extraction procedure. For me it's totally ok if two samples do not show apparent similarities due to many factors.

Depending on the mass of PM collected (and thus the PM concentration in the extracted solution), this methanol subtraction can be difficult. The methanol mass spectrum at low concentrations (<10 %) is very consistent, but if the PM mass concentration is very low, the uncertainty with respect to subtraction could be quite large. This may have been the case with the PNNL samples as the collection times were short (3 hr). We have no data from other instruments

to compare the PNNL samples to, and very few samples for analysis, so we chose not to perform a methanol subtraction at this time. In the future, with more samples and more supporting measurements, this type of subtraction will be explored in more detail.

We agree that a lack of total agreement between different sample types is okay in this case. As you say, and as is discussed in the manuscript, there are a number of factors that will contribute to the differences in PM composition seen by the filter and impactor samples.

Some random thinking. What about the RH of that day and the particle viscosities? Is it possible that the impactor preferably holds more viscous particles that have larger mass fraction of organic matter?

This is an interesting question. We do not have data on RH at the time of sampling or particle viscosities for the PNNL samples in this manuscript, so we can only speculate.

Prior work comparing filter and impactor sampling does suggest a relatively strong RH-dependence on particle collection [1]. Particle bounce seems to be more of a problem for impactors compared to filters, and particle bounce becomes more significant at lower RH values. Given the unknown RH and particle viscosity at the time of sampling, it is possible the filter and impactor were sampling different particle populations (or, rather, the impactor was sampling a subset of the particles sampled by the filter).

3) Lines 330-331: "The organic mass spectra patterns from the two approaches are similar too for the indicated sampling periods (Fig. 5 b-e and Figure S5 a-d)." Is there a way for us to quantify the similarity between mass spectra obtained from MN-AMS and ACSM? I did not see r^2 in Figure 5 b-e as noted in Figure S5. Also, is r^2 a good way to represent similarity?

The r^2 referred to in the text was previously in the figure in question in earlier versions of the manuscript. After we decided not to include the r^2 values, this reference in the figure caption was accidentally left in. Thank you for pointing this out, it will be removed to avoid further confusion.

To your broader point about quantitative comparison between the MN-AMS and ACSM mass spectra: The quantitative comparison between the AMS and ACSM organic mass spectra, as based on a simple regression analysis, can be misleading due to the differences in sampling used between the real-time and offline analyses, as well as differences in mass spec fragmentation between the two instruments (noted in prior studies). Without the proper context of the differences in instrumentation, a low r^2 implies a worse correlation that may actually be the case. To avoid misinterpretation, we chose to remove the r^2 values from the figure and focus on the quantitative comparison in bulk composition as measured by the MN-AMS and ACSM.

Simple regression analyses, like the one referred to here that was ultimately removed from the manuscript, can suffer from biases (e.g. fitting can be heavily driven by high signal ions) partially eliminated by more complex statistical techniques. The spectral similarity index and contrast angle are more robust techniques, but they do not solve our original problem which was properly framing the correlation to avoid misinterpretations.

As in Figure S4 b), if we use r^2 to show similarity, what does the slope mean in the fitting? If we use the same method in Figure S4 b) to estimate the similarity between mass spectra of MN-AMS and ACSM, should we use a slope of 1 to do the fitting? If not, does the slope represent the systematic over- or under- estimation between those two methods?

In a simple regression analysis, the slope would give some indication of under/over-estimation. However, as discussed in the previous comment response, interpretation of both the r^2 and slope is not trivial in this case. Differences can arise from PM sampling, instrumental differences, and methods of data treatment. We certainly do not expect perfect agreement due to these differences and chose to remove the r^2 analysis entirely in favor of a qualitative comparison of the organic mass spectra derived from the MN-AMS and ACSM.

4) Line 222: What temperature the spray chamber is heated up to? Will some dissociation reactions occur at this temperature?

During PM extract sampling, the spray chamber was ~50 °C.

It is certainly possible some dissociation reactions, as well as evaporation, may occur for particularly temperature-sensitive/volatile species. For example, the comparatively high detection limit for nitrate in this study may be the result of nitrate evaporation occurring in the spray chamber. We are currently investigating the temperature dependence of NO_3 measurements in our system. For organic material, losses due to evaporation, as opposed to dissociation reactions, are a larger concern. Prior studies examining organic aerosol (OA) volatility show a wide range of results depending on OA source, aging, etc. Given the results shown in Figure 6, the 50 °C heating did not seem to introduce large measurement errors within our limited set of samples. This could be partially due to the short residence time of the particles within the cyclone. However, more work should be done to assess the spray chamber temperature dependence of different PM components as evaporation can be significant even at 50 °C.

5) Lines 236-238 in the main text and Figure S2 in the SI: I saw for the concentration of 1.75 mg L^{-1} there is already a considerable fraction of particle mass outside the 100% transmission range of the AMS. I am wondering how large is this fraction and how this will influence the sensitivity of AMS? Will the transmission drop significantly once the particle diameter is below 100 nm? Also, what about the case for the concentration of 1 mg L^{-1}?

The 100% transmission range for spherical particles in the AMS inlet is ~70-500 nm. We have no measurements of particle shape derived from our micronebulizer, but we can still use this range as a guide. For the 1.75 mg L^{-1} sample, the fraction of area outside of this range is less than 5% of the total area. Given this low fraction, the effect on the AMS sensitivity is likely to be correspondingly low.

Transmission efficiency of spherical particles begins to drop rapidly below ~70 nm, although there is still substantial transmission (>10 %) of particles from 30-70 nm. This does not begin to be a significant fraction of our generated particle distributions until the total PM liquid concentration drops below 1 mg L^{-1}. Below this concentration, the peak particle size drops below

100 nm and a significant fraction of generated particles is outside of the 100% transmission region. This would begin to significantly affect the method sensitivity.

6) Lines 140-141: In Figure 1. b). Is it better to present different parts in number and list their names aside as a legend? Readers might not be able to clearly see the setup underneath the text of "Spray chamber heater".

We thank the reviewer for the figure suggestion. While we tried not to occlude key aspects of the setup with the labels, this suggestion would improve overall readability. Below the "Spray chamber heater" text is a standard laboratory scissor jack.

Is the condensation liquid reusable? This is hidden by the text on the graph.

We have not attempted to reuse the condensation liquid. Excess liquid generated by the common, collision-based atomizers is reusable as this liquid volume is quite large. Here, even without spray chamber heating, the condensation volume is small relative to the already small sample volumes of < 1 mL. Condensation only became noticeable after continuously nebulizing multiple samples in a row. We could collect the condensation, but reusing it without dilution to increase the volume to a usable level (~100 uL with the setup as shown in Fig. 1b) is likely not feasible.

Typos or Formats

1) Line 14 in the Abstract, "as low as 10 μL" is not consistent with line 380 "as low as 100 μL"

The "100 μL" has been corrected to 10 μL.

2) Line 193: The [X] item in equation (2) seems not quite right.

It is indeed incorrect. The equation has been updated to the following:

$$[X]_{liquid} = [X]_{AMS} \times \left(\frac{[^{34}SO_4]}{[^{34}SO_4]_{\mathrm{AMS,adj}}}\right)$$

3) Line 228: "similarly" or "Similarity"?

The line should read "similarity". It has been updated as follows:

...high degree of similarity…

4) In Figure 5(a), the pie charts can be rotated in a way so that the readers can make easy comparisons, especially for the green parts representing organics. Top boundary for the green portion can be vertical.

We thank the reviewer for this suggestion. The current version has the alignment on the horizontal, starting with the red (sulfate) portion. Having the alignment be on the vertical, with the largest fraction of each sample being aligned (the green, organic portion), is a good suggestion. The figure has been updated so the fractions of each pie chart are aligned on the same vertical, starting with the green, organic portion.

5) Figure S6 (b), "CH3NO2" should not be at m/z=59?

Correct, this ion is actually C2H5NO. Thank you for this correction.

References

(1) Nie, W.; Wang, T.; Gao, X.; Pathak, R. K.; Wang, X.; Gao, R.; Zhang, Q.; Yang, L.; Wang, W. Comparison among Filter-Based, Impactor-Based and Continuous Techniques for Measuring Atmospheric Fine Sulfate and Nitrate. *Atmos. Environ.* **2010**, *44* (35), 4396–4403.