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 #2:

This manuscript presents a method to atomize small volumes of sample into an AMS for offline analysis. The spray is continuous and requires about 100 uL of liquid volume, and shows good comparison with online methods (ACSM). Offline analysis of aerosol samples is beneficial because it allows for characterizations to be made on samples that are significantly easier to collect (compared to flying an AMS). The paper is clear and well written and the work will be of interest to the readers of AMT. My main concerns are some needed clarifications and some corrections to statements made in comparison to prior work. Once these concerns are resolved, I recommend publication in AMT.

1) In the abstract and conclusions, the authors list a detection limit in nanograms. However, these samples are coming from solutions and it is not clear what the sample volumes are that these correspond to. If it is the same sample volume used everywhere, please make that more clear. Otherwise, please report the sample concentrations as well as the masses to improve reproducibility of the work.

Thank you for pointing out this lack of clarity. The sample volume is dependent on the syringe pump flow rate and HR-AMS averaging time. The HR-AMS averaging time was constant across all data points at 1 min. All UxS samples (i.e. all samples from PNNL and SGP) used the same flow rate of 50 µL min^{-1}, leading to a sample volume-per-HR-AMS data point of 50 µL. For the MN-AMS data from standard solutions (i.e. Figure 3), a variable flow rate was ranging from 13-53 µL min^{-1}. However, the data here is based on integrating the AMS-measured mass concentration for the entire 400 µL sample volume that was loaded into the syringe. So for the detection limits, the total volume-per data point on Fig. 3 is 400 µL although the sample concentration and nebulized volume-per-AMS run changes. This is described in lines 242-247. To improve the clarity regarding the detection limits, the following text will be added to the end of section 3.1.2:

Additionally, the low concentration samples analyzed here ([sucrose] = [SO_4] = 0.06 mg L^{-1}) sampled at the lowest usable flow rate (13 µL min^{-1}) were used to estimate the detection limits discussed later.

2) On page 3, it is noted that "Since the nebulization efficiency (i.e. the ratio between the mass detected by the AMS compared to the mass of solute nebulized) of the common aerosol generation systems is low, e.g., ~ 0.02% for an ultrasonic atomizer utilized by O'Brien et al. (O'Brien et al., 2019), liquid volumes of several milliliter and tens of micrograms of sample mass are usually required for continuous aerosol generation and AMS analysis (O'Brien et al.,

2019; Sun et al., 2011).” This statement is incorrect for O’Brien et al.. The efficiency is correct, however, the technique used a discrete injection, not continuous flow, and only 4-5 microliters of solution were used per injection. This should not be scaled to flows for a continuous injection as it misrepresents the method and over-estimates the volumes needed.

There is a lack of clarity to this sentence that we will correct. The nebulization efficiency does indeed refer directly to the data in O’Brien et. al. However, the “liquid volumes of several milliliter and tens of micrograms of sample mass” is meant to refer to the more commonly used collision-based atomizers (e.g. the TSI 3076). The statement is paraphrased from the introduction of O’Brien et. al, but is not meant to refer to their data specifically. You are correct that their low-volume, discrete injections should not be scaled to continuous flow systems with respect to sample volume/mass. The sentence you quote will be rewritten as follows to avoid this confusion:

The nebulization efficiency (i.e. the ratio between the mass detected by the AMS compared to the mass of solute nebulized) of aerosol generation systems is low, e.g., ~ 0.02% for an ultrasonic atomizer utilized by O’Brien et al. [1]. Additionally, liquid volumes of several milliliter and tens of micrograms of sample mass are usually required for continuous aerosol generation and AMS analysis [1,2].

3) The comparison of the UAS samples is welcome and interesting. In section 2.2, how were the blanks collected, handled, and prepared? In section 3.2 it is noted that the normalized blanks are subtracted from the samples. Were these mass subtractions only, or were the spectra subtracted as well? What did the blank spectra look like compared to the samples?

The blank filters and impactors were handled and prepared identically to the collected filters and impactors. A sentence mentioning this is currently in section 3.2, but will be moved to section 2.2 where the extraction of the filters and impactors is discussed in more detail.

For the blank subtraction, this was a mass subtraction only. The blank filters and impactors were similar to the mass spectra of solvent blanks comprised of $^{34}SO_4$ and methanol (at the same concentration range used for the filter/impactor extraction), suggested most of the background organic signal is derived from the methanol used during extraction and not from material adsorbed to the filters or impactors.

4) The use of isotopically labeled sulfate is a nice quantification method. Have the authors explored the ability to quantify with sulfate when ions like sodium or potassium are present in the sample? These can form salts with high vaporization temperatures and may be a concern for quantification.

We have not explored quantification with isotopically labeled sulfate when sodium or potassium are present in solution.

5) I appreciate the comparisons between he different HR spectra, but I would like more comparison with the online ACSM data. Figure S5 shows the ACSM data for I believe the same time periods as those in Figure 5. However, it is very difficult to directly compare. Please add a figure in the supplemental that is a direct comparison between the two (with the HR data unit

mass). The caption on Figure S5 also notes some r squared values that I cannot find in Figure 4. Please correct this.

The r^2 referred to in the text was previously in the figure in question in earlier versions of the manuscript but was later removed. The r^2 values have been added back to Figure S5. Additionally, as you suggest, we have improved the comparison between the AMS and ACSM organic mass spectra. Figure S5 now includes an overlay of the HR unit mass AMS data. The discussion regarding the comparison between the two instruments has been similarly expanded on. Section 3.3 now includes the following text:

The comparison between the MN-AMS and ACSM organic unit mass spectra is shown in Figure S5. The agreement between the MN-AMS and ACSM measurements is moderate ($0.5 < r^2 < 0.8$). However, it is important to remember the differences in PM sampling between the MN-AMS and ACSM (filter and impactor extraction of $PM_{2.5}$ vs real-time PM_1)and that the two instruments may have different sensitivities to certain organic species resulting in discrepancies for co-located AMS and ACSM measurements (e.g. [3]). Many of the most divergent ions measured in both instruments are C_xH_y ions that have a significantly higher signal in the MN-AMS. This may suggest chemical differences in the $PM_{2.5}$ and PM_1 size regimes.

6) On page 15 no mention is made of differences that can be due to extraction and solubility of the samples. This may not be too large of a concern at SGP, but it may be a concern at other field sites and should be mentioned.

We agree. Issues with PM solubility were briefly discussed earlier in the manuscript when talking about the samples from PNNL, but it is worthwhile reiterating this point with the SGP samples, partially because these samples were discussed in much more depth than the PNNL samples, and because it certainly could account for some of the differences seen between the MN-AMS and ACSM datasets. The following text will be added to the manuscript in the section comparing the MN-AMS data to the ACSM data:

Last, it is possible that the extraction process, using both methanol and water, is a source of discrepancy between the MN-AMS and ACSM datasets as both organic and inorganic PM exhibits a range of solubilities in different solvents [4]. While the MN-AMS data resembled the online ACSM measurements to a high degree, differences in recovery of specific PM components when comparing offline to online results should be considered [5].

References

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