Manuscript Number: **AMT-2024-2482**
Title: A Novel Methodology for Assessing the Hygroscopicity of Aerosol Filter Samples

Atmospheric Measurement Techniques

Reviewer 2

The manuscript was clear and relatively rigorous in the experimental setup. I like that the method does not seem costly, potentially allowing it to be applied more easily. One general comment: the authors mentioned a few times throughout the manuscript that this new method allows aerosol hygroscopicity to be related to chemical composition. It would be helpful to have a few short sentences of the chemical speciation methods that could benefit from these types of filter samples.

We would like to thank the reviewer for encouraging remarks and meticulous reading of this manuscript and for the thoughtful comments and constructive suggestions, which help to improve the quality of this manuscript.

A point-by-point response to the reviewer comments is provided below (in blue) along with the respective changes made in the revised manuscript (in **bold**)

We have added a paragraph explaining how we will link the measured hygroscopicity with the chemical composition from the same Teflon filter on **page 27-28, lines 625-641, to read:**

"The method developed in this study can be used to measure water uptake on the same samples used to measure chemical composition for ambient, indoor and chamber studies. For organic aerosol composition, Fourier-transform infrared spectroscopy (FT-IR), which is not destructive to the filter sample, can be used to quantify the organic carbon and organic functional groups present in the particles collected on Teflon filters (Anunciado et al., 2023; Boris et al., 2019; Debus et al., 2022; Li et al., 2024; Yazdani et al., 2021). Other non-destructive methods such as gravimetry for total mass, light absorption measurements to estimate elemental carbon (White et al., 2016) and X-ray fluorescence (XRF) to measure elements (Gorham et al., 2021; Hyslop et al., 2015) provide additional composition information. After the water uptake measurements are preformed, the filter sample can be extracted to measure inorganic ions, sulfate, nitrate and ammonium to complete the compositional measurements on the filter. Alternatively, simultaneous sampling of multiple filters including a Teflon filter, such as is done for the IMPROVE and the Chemical Speciation Network (Solomon et al., 2014) provide high quality speciation data. This integrated approach ensures that the chemical analysis corresponds to the air sample from which water uptake data is obtained. Furthermore, using modeled estimates of inorganic water uptake, the measured water uptake can be apportioned between organic and inorganic components."

See below for specific comments/questions.

1. Line 131: you already defined "mfs" in the abstract and used it on line 123, so no need to define it again here.

> Although mfs was defined in the Abstract, it is good practice to define it in the main text where it is first used. We have defined mfs in line 130.

2. Line 207: add a reference for the IMPROVE aerosol sampler (e.g., UC Davis or a previous paper that described this sampler in detail).

> Added reference, (Ruthenburg et al., 2014; Solomon et al., 2014) on **page 10, lines 255-256.**

3. Line 217: what is considered "sufficient mass to produce measurable water uptake"? I would suggest the author to put something more quantitative here (e.g., at least 100 mg of each compound was collected on a Teflon filter...).

> We have added a quantitative value based on our observations on page 10, lines 269-272, to read:

> **"Following this, each compound was collected on a Teflon filter using an IMPROVE aerosol sampler with sufficient mass (more than 50 μg, based on observations of sodium chloride's water uptake, as discussed in section 3.3) to produce measurable water uptake in the sample above its deliquescence RH (Table 1)."**

4. Line 219: change "was" to "to be"

> For better clarity, we revised the **lines 273-274 on page 10-11, to read**:

> **"ensuring they were contamination-free for subsequent runs."**

5. Line 223-225: I suggest changing "the collected samples" to "the collected dry samples" for clarity. It was clear when I read the next section but a little confusing when I just read this sentence on line 223-225.

> The samples collected from the aerosol generator and sampler were not completely dry at the time of collection, as there was likely some water present. To ensure complete dryness, we placed the samples in a desiccator. After desiccation, these are dry particle-loaded filter samples.

> For clarity, we have replaced the sentences at page 11, lines 274-278, to read:

> **"Following sample collection and prior to post-weighing, the collected samples were placed in a dry desiccator for a minimum of 24 hours to remove any residual water. Pre-weights and post-weights of filters were recorded at least thrice on three separate days using a high-precision ultra-microbalance with a readability of 0.1μg (model XP2U, Mettler–Toledo, USA) before and after sample collection."**

6. Line 254: is there any concern of water interacting with the dry particle-loaded filter in the chamber differently when it is in an open pouch vs. when it is not inside a pouch? Why not put the filter in the pouch after 24hrs of being inside the chamber?

> The interaction of water with the dry particle-loaded filter in the chamber is essentially the same, whether it is in the pouch or not. However, placing the filter in the pouch from the start offers advantages, including *Minimized water loss:* Fig. 2(a) demonstrates water loss is exponential. If we were to place only the filter in the chamber for 24-hours and then transfer it to the pouch, there would be significant water loss during the transfer process; this could introduce variability and potential inaccuracies in our measurements, and *Measurement accuracy:* keeping it pouched from the start eliminates an additional handling step, reducing potential errors.

7. Line 328-329: along the line of the previous question, could the theoretical increase in the mass of air higher than the measured values due to the RH inside the pouch being different from the RH inside the chamber? i.e., there was not an efficient amount of water entering the pouch over the 24 hours of it being in the chamber.

> The discrepancy between theoretical and measured air mass values can be attributed to RH changes during sample transfer and weighing. For theoretical calculations, we assumed that the chamber RH persisted in the pouch during weighing. However, in practice, the air in the pouch exchanges with room air during handling, including when we open the chamber, transfer the pouch for weighing, and during the weighing process itself. This lowers the RH in the pouch, resulting in lower measured air masses compared to theoretical predictions. The 24-hour chamber exposure allowed sufficient water vapor ingress; the observed difference is primarily due to air exchange in the pouch during post-chamber handling rather than inadequate equilibration within the pouch.

8. Line 370 Figure 5: I suggest putting error bar on the bar graphs to reflect the uncertainties in measured water mass. Also, were the measurements made at roughly the same time every day over the 5-day period?

> Each day's water mass measurement was based on a single observation, so we cannot provide error bars.

> Measurements were not conducted at fixed daily times; instead, each sample was allowed to equilibrate in the chamber for more than 24 hours before measurement. Our observations indicate that a period exceeding 24 hours is sufficient for equilibration; whether the duration is 48, 72, or 96 hours, the water uptake remains consistent.

9. Line 374: "mfs" and "GF" are defined in the abstract so no need to define them here.

> We believe it is beneficial to mention this information in the main manuscript when it is first discussed, even though it is already present in the abstract. This is because the

abstract often stands alone, and readers may not always refer to it when reading the full text.

10. Line 378: mass fraction "of" solute.

Added missed 'of' in "mass fraction "of" solute" at line 436

11. Line 381-382: I think you are missing Eq. (6). There was Eq. (5) on line 317 then Eq. (7) here.

Thank you for pointing out that. Corrected the sequence of equation numbers in the whole manuscript.

12. Line 411: edit MW unit to be "mol/mg" from "mol/gm"

Edited.

13. Line 419-424: from Eq. (17) to Eq. (22), when you took partial derivatives of the (W/S) ratio for each input variable, why did you eliminate the term (MW_s/MW_w)? For example, Eq. (17) should be abs(1/ (DS-DB)) * (MW_s/MW_w).

In this case, the molecular weights of the solute and water are constant. Therefore, they do not need to be considered when estimating the partial derivatives of the W/S ratio for each input variable.

14. Line 523 Figure 6: It may be nice to put the species label on the panel itself (e.g., Ammonium sulfate on panel a). I would make the markers larger and add error bars for both %RH and GF uncertainties.

We appreciate your suggestions and have implemented them as follows: *species labels have been added to each panel, and marker sizes have been increased for improved visibility.*

Regarding error bars, we did not include them for the following reasons: %RH variation was negligible during measurements for each compound, and GF standard deviations are very small, as shown in Table 2. Adding these as error bars would not be visually discernible. We believe these modifications enhance clarity while maintaining concise data presentation. The complete obtained hygroscopic data in Table 2 complements this figure.
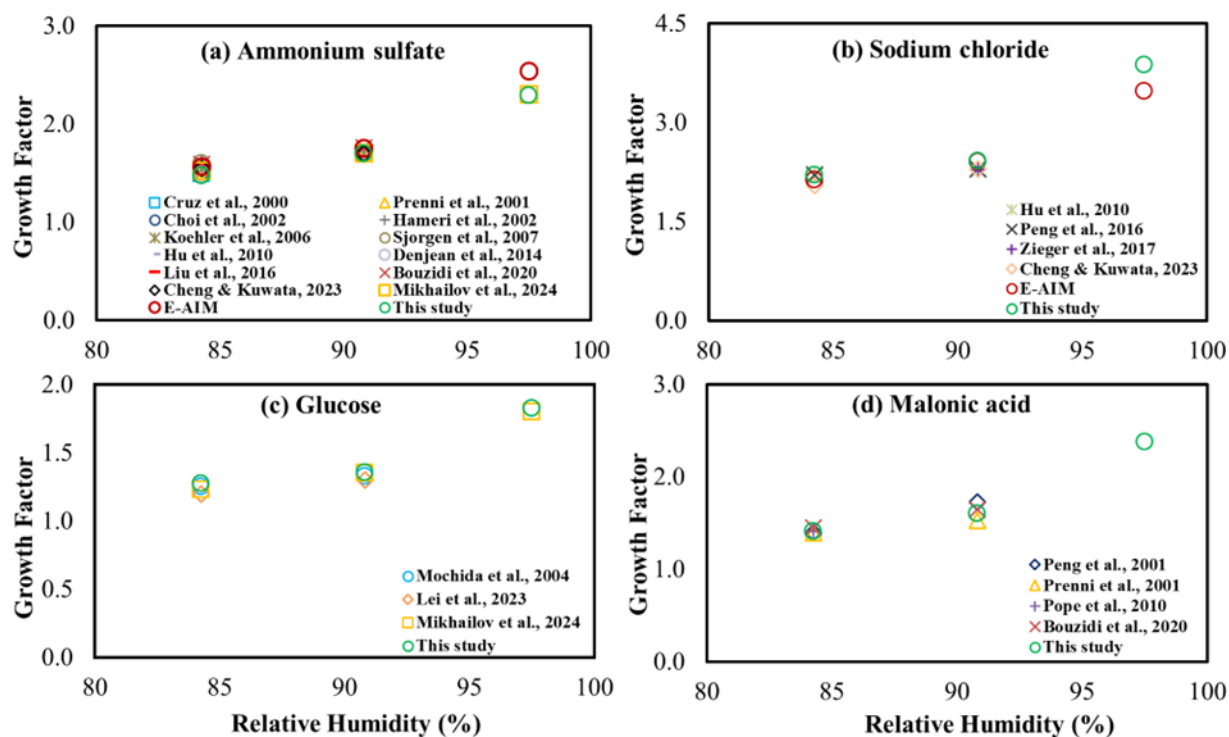
Figure 7. Comparison of estimated growth factor for (a) Ammonium sulfate, (b) Sodium chloride, (c) Glucose, and (d) Malonic acid with previous studies

15. Line 541: extra "."

Removed redundant period

16. Line 545-549: perhaps add this information to the SI and reference it at the beginning of the paper like on line 217 (see my comment above). In addition, it would be helpful if the authors have repeated the sodium chloride experiments with higher dry sample masses to confirm the hypothesis/statement on line 541: "The lower mass increases uncertainty due to the limitations in the precision of the balance).

We believe the current placement of mass information is appropriate, as it follows our uncertainty estimation process.

For compounds other than sodium chloride, we conducted hygroscopicity experiments with relatively higher masses, which demonstrated reduced uncertainty. These results sufficiently support our understanding of the mass-uncertainty relationship, obviating the need to repeat sodium chloride measurements with higher masses. We have removed the statement on line 541 as it is redundant given the surrounding context.