Response to Reviewers Comments

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

Atmospheric Measurement Techniques

Reviewer 1

This study introduces a new way of quantifying hygroscopicity of aerosol particles collected on Teflon substrates. The paper is interestingly written, specifically Section 2, in such a way to take the readers on a ride to see what worked and didn't work on their way to the final desired method that seems robust based on their analysis. The paper is important in that hygroscopicity is a critical aerosol parameter to quantify and new methods are helpful especially if they can be easily related to composition. They clearly have done a lot of tests and show that their method is effective based on comparisons with literature.

> 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**)

I found the paper a bit confusing at times, especially Section 2. If someone scans the abstract and conclusions it isn't even clear what the method really is other than knowing there are Teflon filters involved. I suggest the authors try to be a bit more clear in different key parts of the paper how their method works (abstract and conclusions in particular). Section 2 is full of good details but can benefit from a bit more of a clearer picture of the method using potentially a figure (see a comment below about this). I am supportive of publication but hope the authors can address my comments below first.

> We have added methodology in the abstract on **page 02, lines 41-52, to read:**
>
> **"Constant humidity solutions (CHS), including potassium chloride, barium chloride dihydrate, and potassium sulfate, were employed in the saturated form to maintain the relative humidity (RH) at approximately 84%, 90%, and 97% in small chambers. Our preliminary experiments revealed that, without the pouch, water uptake measurements were not feasible due to rapid water loss during weighing. Additionally, we observed some absorption by the aluminum pouch itself. To account for this, concurrent measurements were conducted for both the loaded and blank filters at each RH level. Thus, the dry loaded and blank Teflon filters were placed in aluminum pouches with one side open and placed in RH-controlled chambers for more than 24 hours. The wet-loaded samples and wet blanks were then weighed using an ultramicrobalance to determine the water uptake by the respective compound and the blank Teflon filter,. The net amount of water absorbed**

by each compound was calculated by subtracting the water uptake of the blank filter from that of the wet-loaded filter."

We have added methodology in the conclusion part on **page 27, lines 610-616, to read:**

"Laboratory hygroscopic measurements were conducted for ammonium sulfate, sodium chloride, glucose, and malonic acid. Constant humidity solutions were employed to maintain specific RH and enable measurements as high as ~97%. While conducting water uptake measurements, we encountered problems, including water loss from the filter when moving from high RH to room RH for weighing, and absorption by the pouch used to contain the water loss from the filter sample. These problems were successfully addressed by placing the sample filter in an aluminium pouch and accounting for water absorption by the pouch itself."

Comments:

1. Line 34-35: for where it says "For ambient and chamber studies, HTDMA measurements provide water uptake and particle size information but not chemical composition.", note that the next sentence claims there is a gap being filled in this study but I would disagree since this new method still just aims to quantify hygroscopicity (just like a HTDMA) and cannot additionally measure composition. I would fix this disconnect in line 34-35 and the next sentence claiming a gap is being filled. Or rather, revise the next sentence to better articulate what is the novelty of this work.

Here's a revised text to clarify the novelty of our work. The text on **page 02, lines 33-38, to read:**

"For ambient and chamber studies, HTDMA measurements provide water uptake and particle size information but not chemical composition. To fill in this information gap, we have developed a novel methodology to assess the water uptake by particles collected on Teflon filters. This method uses the same filter sample for both hygroscopicity measurements and chemical characterization, thereby providing an opportunity to link the measured hygroscopicity with ambient particle composition."

2. Line 36: do the authors mean "water uptake on particles…"?

We have corrected to "water uptake **by** particles" on **page 02, line 36.**

3. Highlights: It is always dangerous to claim things like this is the "first" study to ever show something. In this regard, I am aware of other published works that quantified hygroscopicity of aerosol using Teflon substrate samples. Please revise this highlight and similar claims in the paper and also provide more credit in the literature review towards studies that used Teflon substrates to examine hygroscopicity.

 "This is the first study to assess the hygroscopicity of particles collected on Teflon filters at near-saturation levels using constant humidity solutions."

"Various techniques exist to measure the hygroscopic growth of aerosol particles. These include methods such as the Humidifier Tandem Differential Mobility Analyzer (HTDMA), Electrodynamic Balance (EDB), Differential Aerosol Sizing and Hygroscopicity Probe (DASH-SP), and direct mass measurements of water uptake by particles collected on aerosol filters. These techniques have been extensively reviewed in previous studies by Kreidenweis & Asa-Awuku (2014) and Tang et al. (2019). Among these, the most employed methods are the HTDMA (Boreddy et al., 2014; Laskina et al., 2015; Mikhailov et al., 2021) and EDB (Chan et al., 1992, 2000; Cohen et al., 1987; Kohli et al., 2023; Peng et al., 2001; Steimer et al., 2015; Tang & Munkelwitz, 1991). EDB measures the change in mass of individual charged particles of known composition, which are levitated in a gaseous atmosphere by means of an electric field created by imposing voltages on the electrodes (Cohen et al., 1987; Kohli et al., 2023). When the mass of a levitating particle undergoes evaporation or condensation due to a change in RH, it becomes proportional to the DC voltage required to balance the particle in a stationary position. The particle's mass fraction of the solute (mfs) can then be determined by measuring the particle's balancing voltage with that of a reference state of known composition (Peng et al., 2001). However, EDB is limited to analyzing single particles and is not suitable for studying the water uptake of ambient samples. HTDMA measures the change in particle size distribution in response to varying humidity levels and can be used to measure ambient aerosol. By exposing aerosol particles to controlled humidity levels and measuring their sizes before and after exposure, HTDMA assesses the extent of hygroscopic growth as a function of particle size. This method measures the change in the diameter of the particles, from which parameters such as mfs and solute molality are estimated. However, this method faces challenges in measuring RH conditions exceeding 90% (Marsh et al., 2019), an RH regime that can lead to very high water uptake and is not applicable for measuring the hygroscopicity of particles collected on aerosol filters. An alternative to HTDMA is the DASH-SP, which can measure hygroscopic growth at RH levels as high as 95% and perform rapid, size-resolved measurements of subsaturated particle hygroscopicity (Shingler et al., 2016; Sorooshian et al., 2008). However, DASH-SP is impractical for measuring the hygroscopicity of particles collected on filters.

Quartz crystal microbalances (QCMs) offer a direct method for measuring water uptake by aerosol particles collected on filters. These instruments utilize the Sauerbrey equation to quantify mass-based hygroscopic behavior of particulate matter (Tang et al., 2019 and reference therein). Jose et al. (2024) demonstrated the

application of QCM technology to measure hygroscopic growth of size-resolved aerosol particles on Teflon filters at RH levels up to 93%. The experimental protocol involved transferring collected particles to the QCM sensor via direct contact by placing the filter onto the sensor and gently pressing it with a cotton. However, the Sauerbrey equation's accuracy may be compromised when the deposited film lacks rigidity or exhibits poor surface coupling, potentially introducing systematic errors in hygroscopic property estimations (Tang et al., 2019). Alternative methodologies, including physisorption and katharometer analyzers, have been employed to quantify water vapor concentration changes resulting from particle-water interactions on aerosol filters (Ma et al., 2010; Mikhailov et al., 2011). Notably, physisorption analyzers typically necessitate substantial sample masses ($\geq$1 mg), which limits their applicability in atmospheric aerosol studies (Gu et al., 2017). Moreover, both physisorption and katharometer techniques are characterized by extended experimental durations, often spanning several days (Gu et al., 2017; Mikhailov et al., 2020). The precision of katharometer methods in quantifying water adsorption within nanoscale layers remains a subject of ongoing investigation (Tang et al., 2019), highlighting the need for further refinement of these analytical techniques.

Analytical balances have been employed to measure the mass change of particles collected on aerosol filters due to water uptake under controlled conditions. For instance, McInnes et al. (1996) used a semi-dynamic method to measure the water uptake of particles collected on Millipore Fluoropore filters, with the microbalance housed in a chamber controlled for humidity and temperature. They maintained a 33% RH using a saturated solution of $MgCl_2 \cdot 6H_2O$, with the lowest RH achieved via nitrogen cylinders. The aerosol water uptake at 33% RH was calculated as the difference in mass between higher and lower RH conditions. However, most organic and inorganic compounds do not take up significant water at 33% RH. Similarly, Hitzenberger et al. (1997) employed a semi-dynamic method to measure aerosol particles collected on aluminum foils, maintaining RH levels between 45% and 95% using varying concentrations of $CaCl_2$ solutions in a housed chamber. Nevertheless, actual humidities inside the chamber were lower than the water activities of the $CaCl_2$ solution, due to a narrow chamber opening, resulting in differing growth patterns for two samples collected at the same location and time of the year (Hitzenberger et al. 1997). Housing microbalances in chambers with high humidity (>80% RH) is also problematic, as the high moisture can corrode electronic components, affecting measurement accuracy and stability. However, many atmospheric aerosols, especially those with deliquescence relative humidities (DRH) greater than 80%, undergo rapid water uptake at RH >95% (Kreidenweis & Asa-Awuku, 2014). Therefore, there is a need to develop robust laboratory techniques capable of measuring composition-dependent water uptake of aerosols collected on Teflon filters under near-saturated conditions."

4. Line 123: define "mfs" here instead of in line 131.

As suggested, we moved the 'mfs' definition and it is on line 130 in the revised manuscript.

5. Line 133: Although not as common as the HTDMA, the authors can acknowledge the DASH-SP instrument that can go above 90% and measure sometimes near 95% (doi:10.1002/2015JD024498).

We have added DASH-SP instrument in our detailed literature review on **pages 5-6, lines 140-143, to read:**

"An alternative to HTDMA is the DASH-SP, which can measure hygroscopic growth at RH levels as high as 95% and perform rapid, size-resolved measurements of subsaturated particle hygroscopicity (Shingler et al., 2016; Sorooshian et al., 2008)."

6. Line 136-138: at this point the reader is confused as to whether you are claiming your technique measures just water uptake properties or water uptake AND composition. The hints in the text claim it will do both and so if the method is just for water uptake properties, it would be good to be more explicit and drop the hints earlier in the text. My sense from reading the paper is that the paper focuses on just the water uptake measurement and that composition can separately be done with other techniques, which is the advantage of filters.

Thank you for your insightful comment. We appreciate the opportunity to clarify our study's focus. You are correct that our primary objective in this study is to measure water uptake properties of the particles collected on aerosol filters. We have revised our statement to explicitly reflect this on **page 07, lines 183-186, to read:**

"This study's objective is to devise a methodology for assessing the water uptake of organic and inorganic aerosol in samples with known chemical composition. Samples collected on Teflon filter are commonly used for gravimetric and chemical analysis, and we developed a method to measure water uptake on the same filter enabling correlation chemical composition with hygroscopicity."

7. Line 179: should be "…Lide (2004) provided…"

We corrected the sentence on **page 09, line 230, to read:**

"In the CRC Handbook (Volume 85), Lide (2004) provided integer RH values for CHS at 25°C."

8. Line 219: potential typo around "leaving it was…."?

Thank you for pointing that out. The sentence was corrected for clarity. We revised the sentence on **page 10-11, line 273-274, to read:**

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

9. Line 249: Doesn't read well to see "from 97.5% RH". Do the authors mean "at 97.5% RH"?

Revised the sentence for clarity on **page 12, line 303, to read:**

"Weight of the filter and mass of water lost while weighing glucose at 97.5% RH."

10. Line 311: should be "represent" and not "represents"

Corrected: 'represents' changed to 'represent' on **page 15, line 365**.

11. Line 327: "weigh" should be "weight"

Corrected: 'weigh' changed to 'weight' on **page 16, line 381**.

12. Section 2 was a bit of a tour into the authors' process to arrive at their final method and I wonder if they can benefit from some visual schematic of what their method boils down to in order to make it more visual for readers. Sometimes new instrument papers show a flow diagram and I am wondering if their method can be shown as such. I worry that Section 2 becomes a bit tedious and if the authors can make it easier to understand what their method is. The conclusion section for instance doesn't even summarize the method leading readers in suspense – consider explaining the method briefly.

We appreciate your thoughtful feedback on Section 2 and the presentation of our methodology. Your suggestions for improvement are valuable and we agree that enhancing the visual representation and clarity of our method would benefit readers. Hence, we added a flow diagram depicting the developed water uptake methodology in this study on page 18:

Lines 422-423: **"Figure 6 illustrates finalized water uptake methodology derived from the laboratory experiments conducted in this study."**
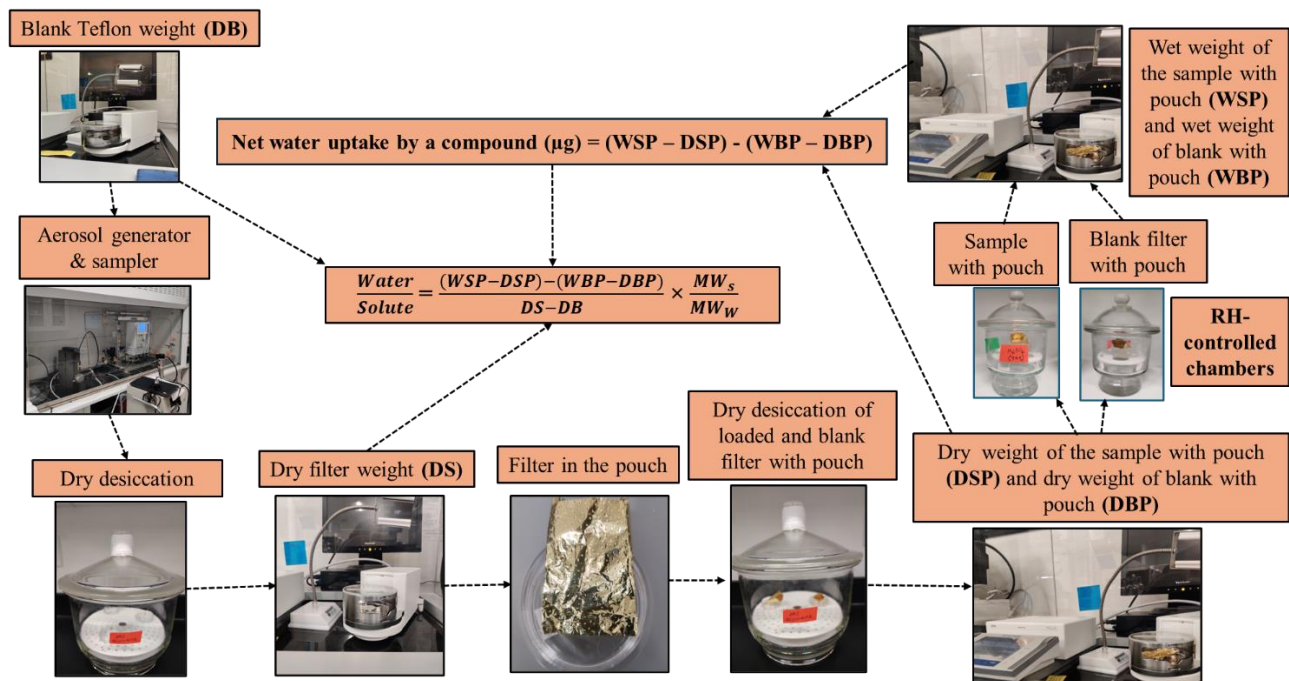
Figure 6. Water uptake methodology developed in this study

13. Line 464-465: please be consistent in having spaces between numbers and units. This issue occurs throughout the paper.

> We have made the necessary changes to ensure consistency in spacing between numbers and units throughout the paper.

14. I wonder if the comparisons in Section 3.2 would be better presented in the form of a table.

Figure 6: This can be improved as it is hard to see the markers and there is a ton of wasted space in each panel. Consider using the space better to zoom in more on the action.

> We have improved Figure 6 (in revised manuscript, it is Figure 7) by utilizing the previously wasted space, making the markers more visible, and zooming in on the relevant data. We have chosen to maintain the current format in Section 3.2, as we believe it best illustrates the trends in our data.
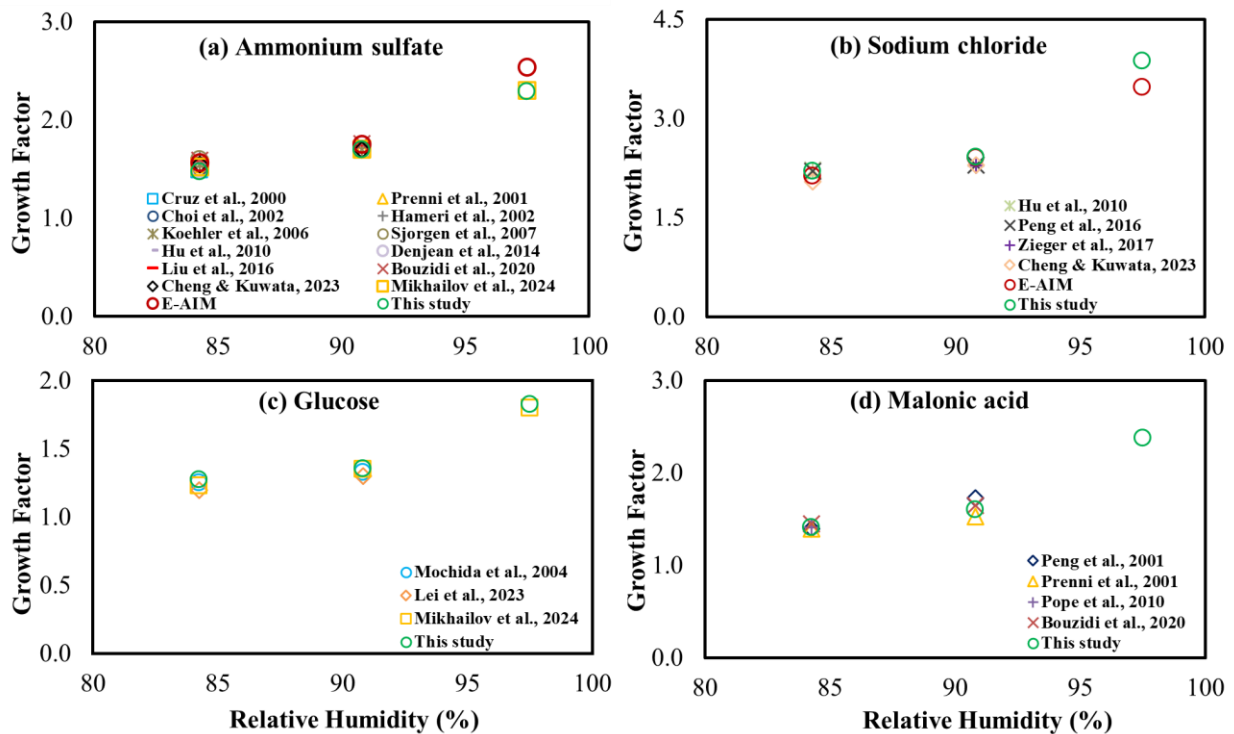
Figure 7. Comparison of estimated growth factor for (a) Ammonium sulfate, (b) Sodium chloride, (c) Glucose, and (d) Malonic acid with previous studies

15. Line 541: double period

> Removed the redundant period

16. Regarding sodium chloride: does a shape factor need to be accounted for in the authors' study?

> No, we don't need to account for the shape factor of sodium chloride in our study. Our method directly measures the mass of water uptake by particles on Teflon filters, which is independent of particle shape. This is unlike HTDMA (Hygroscopic Tandem Differential Mobility Analyzer) measurements, where the cubic crystal structure of sodium chloride can lead to an underestimation of the hygroscopic growth factor due to overestimating the dry particle diameter.

> We have added this is one of the advantages of this method on page 7, lines 195-197, to read:

> **"In addition, unlike HTDMA measurements, there is no need to account for shape factor of a compound, as this method directly measures the mass of water uptake by the particles collected on the Teflon filters."**

17. A key aspect of the paper that is missing is the application potential of this method. I would hope the authors can share a paragraph at least in a revision about how they envision this new method can be applied on a larger scale to help the research community. For instance, can this method meant to be employed with the IMPROVE network collection of measurements in the future? If not or even if so, how else can this be applied in future research by other groups. Some examples would be helpful to provide more impact to this paper.

> Thank you for your valuable feedback. We have added a detailed paragraph in the revised manuscript discussing the application potential of our method 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."

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.
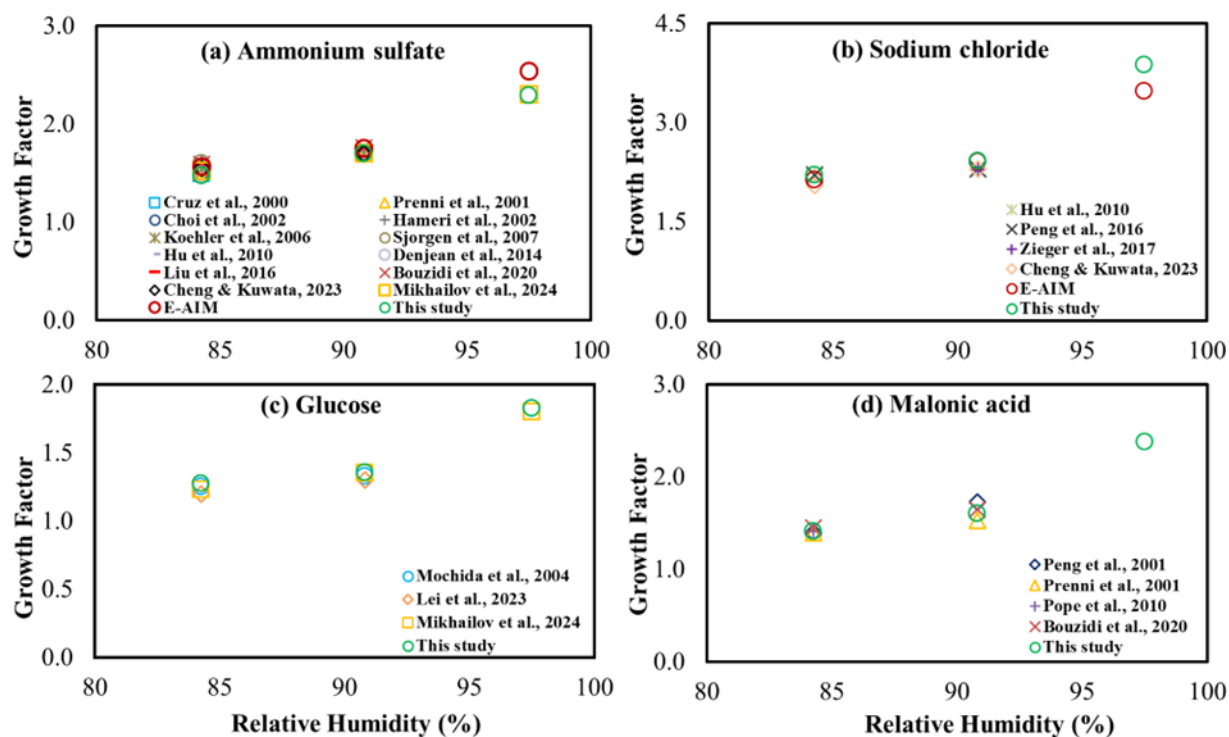
Figure 7. Comparison of estimated growth factor for (a) Ammonium sulfate, (b) Sodium chloride, (c) Glucose, and (d) Malonic acid with previous studies

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.