

Reviewers comments in black

Replies to comments in blue

Changes to document in green

Reviewer #3

Review of Oxford et al. “Gravimetrically measured water content of filter sampled fine particulate matter at low relative humidity: Insight from the Surface Particulate Matter Network (SPARTAN)

This manuscript describes experimental studies to estimate aerosol water content at low relative humidity using filters obtained from the SPARTAN network. The aerosol water growth categories were separated into low, medium, and high, and the chemical composition of the filters was also split into three hygroscopic categories. The hygroscopic growth models were applied to other sites in the network to gain an understanding of the water content on the filters at low RH (~35%) at each site. The strengths of the study include the experimental design, especially accounting for evaporation of mass on the filter over time and exploring several water growth models to apply. However, it is necessary put the results into context of mass reconstruction. For example, the highest water content at 35% relative humidity was 5.5%. What is the typical uncertainty or closure in mass reconstruction? This water fraction is significantly lower than the “residual” fraction, which is the difference in reconstructed and measured mass and is assigned to organics. However, this residual also reflects and includes other sampling biases. In addition, the mass evaporated was in some cases similar in magnitude to the water content. To what degree can these results be used to improve reconstructed mass estimates when there is a large residual due to unmeasured mass species? I recommend addressing these issues before publication. Additional comments are below.

Reply: Thank you for sharing this source of confusion. The purpose of this paper is not to improve mass reconstruction. We instead seek to discover the water content on filters. This information has multiple applications, such as allowing a researcher the ability to reconcile different network laboratory RH conditions using a simple algebraic relationship. Additionally, the relationship gives users of chemical transport models the ability to reconcile water mass present in the measured mass concentrations with modeled dry mass concentration.

Abstract (lines 82 to 84): “Water, a portion of PM_{2.5} mass, is difficult to measure, especially at the low laboratory relative humidity (RH) used during PM_{2.5} mass measurements.”

Main document (lines 126-129): “Knowledge of the relationship of water content on PM_{2.5} filters as a function of laboratory RH and composition is needed to rigorously evaluate air quality models and understand differences in water mass across monitoring networks.”

Since the residual is dominated by organic matter (lines 297-300), the water mass fraction will become useful after applying parallel efforts to quantify the organic content on SPARTAN filters. We are beginning to use Fourier Transfer InfraRed (FTIR) spectroscopy to quantify OC and OM (Debus et al. 2022) as mentioned in this paper. Additionally, we recently submitted a manuscript (Ren et al. 2026) on using an offline Aerosol Mass Spectrometer to quantify organics on PTFE filters. We intend to incorporate OC and OM measurements into our reported mass reconstruction, significantly reducing the currently large residual. When incorporation of organics occurs, the work in this document becomes relevant to what remains in the residual.

Debus, B., Weakley, A., Takahama, S., George, K., Amiri-Farahani, A., Schichtel, B., Copeland, S., Wexler, A., and Dillner, A.: Quantification of major particulate matter species from a single filter type using infrared spectroscopy - application to a large-scale monitoring network, *Atmos. Meas. Tech.*, 15, 2685–2702, 10.5194/amt-15-2685-2022, 2022.

Ren, Yuxuan, Randall V. Martin, Jhao-Hong Chen, Christopher R. Oxford, Brent J. Williams, Rodney J. Weber, and Lu Xu. "Development of an offline Aerosol Mass Spectrometry method for organic aerosol characterization in a globally distributed Surface Particulate Matter Network." *EGUsphere* 2026 (2026): 1-43.

We added the following paragraph to the uncertainty portion of the document. This paragraph confirms the residual as primarily organic as well as confirming that this residual is large.

Main document (lines 641-644): “Such an algorithm will also aid mass reconstruction algorithms of particulate matter on PTFE filters, in concert with ongoing efforts to advance characterization of organic matter on these filters (Debus et al., 2022; Ren et al., 2026)”

Line 73. Consider changing sentence to “... to develop a relationship of mass...”

Reply: Done.

Line now reads: “...collected around the world were used to develop a relationship of mass as a function of relative humidity.”

Line 124. Differences in what across monitoring networks?

Reply: The intent was a difference in water mass. The entire paragraph has been changed to focus on change in water mass.

Main document (lines 126 to 129): “Water mass associated with deposited $PM_{2.5}$ aerosol depends on both the relative humidity (RH) of the laboratory air at the time of gravimetric measurement, and the composition of the deposited aerosol. Ionic components, metals, elemental carbon, and organic matter have different affinities for water (McMurry et al., 1996), and fractional differences in these components across filter samples alter that total water mass. Additionally, laboratory conditions defined by standard network protocols vary, with the US EPA using 30-40% RH (Register, 2020), Canada using 35-45% (Dabek-Zlotorzynska et al., 2011), and Europe using 45-50% (Standardization, 2023). Air quality models used for $PM_{2.5}$ prediction and to relate satellite observations of aerosol optical depth with ground-level $PM_{2.5}$ require information on the water content of $PM_{2.5}$ at measurement conditions to reconcile calculated $PM_{2.5}$ concentration with observations (van Donkelaar et al., 2010; van Donkelaar et al., 2024). Knowledge of the relationship of water content on $PM_{2.5}$ filters as a function of laboratory RH and composition is needed to rigorously evaluate air quality models and understand differences in water mass across monitoring networks.”

Line 130. Consider changing “water mass” to “water mass fraction” since the values in the parentheses are water fractions.

Reply: Done. We changed to percentage as the numbers quoted are percentages.

Line now reads: “Canepari et al. (2013); (Canepari et al., 2017) applied this method to measure percentage water mass on filters at 50% RH from...”

Line 134. What does “lacked mass resolution” mean in this context?

We meant that the study could not resolve (accurately estimate) water mass on the filters at low RH.

Line now reads: "...and from a boreal forest near St. Petersburg, but the method could not accurately determine water fraction at low RH (Tang et al., 2019a)."

Line 141. Do the authors mean "used gravimetric measurements" ?

Reply: yes.

Line now reads: "McInnes et al. (1996) used gravimetric measurements on several marine samples, finding..."

Line 142. Are these RH values laboratory or ambient?

We mean laboratory. Thank you for catching the ambiguity of our statement. The adjective "laboratory" has been added.

Lines now reads: "...Cheeka Peak increased 9% by mass when laboratory RH increased from 9% to 35%, and samples from an ocean cruise increased 29% by mass when laboratory RH increased from 19% to 47%;..."

Line 159. When did the SPARTAN network begin operation?

Reply: 2012.

Lines at beginning of Materials and Methods: "SPARTAN has measured the mass concentration and chemical composition of ambient PM_{2.5} and PM₁₀ across globally-distributed sites since 2012."

Line 170. Include "a" after "plus".

Reply: done

Line now reads: "...7 sample filters plus a traveling field blank."

Line 191. How long of a period occurs between sampling and analysis?

Reply: the length of time between sampling and completed analysis is 6 to 12 months.

Line 275. How are method detection limits determined?

We should have said “minimum detection limit” as defined in Chow and Watson, 1999.

Line now reads: “...the water samples measured more than 10 times minimum detection limit (Chow and Watson, 1999) of any of the 13 measured species...”

Line 286. Why were FT-IR OC not used instead of assigning the residual to organics?

As written, organics contain more than just OC mass, which includes oxygen, hydrogen, and other elements. We are trying to incorporate that mass into our calculations as well.

Line 317. This terminology is somewhat confusing. I needed to reread this several times to get the difference between a group and a subgroup.

We have placed a second description of the meaning of “group” and “subgroup” in the supplement explaining the definitions in terms of the AH500 system. This description is referenced in the main text.

Supplemental Text S3.2 (lines 220-239):



“Figure S6. The AH500 system. The silos are labeled A through F. A barcode reader is used to identify each filter. The picture shows the back side of the scales. All items behind the shown door exist inside the controlled environment described by Figure S4.

The group-subgroup language can be confusing, so here we present an alternative description of groups and subgroups in the context of the AH500 photos above. All filters from an experiment (usually 12) are placed in individual carriers, and the carriers are stacked in silo C (Figure S6). The AH500 RH is set, and the system waits for at least 24 hours to equilibrate the filters to the set RH conditions. After equilibration, the system calibrates the scales and weighs the reference weights. Then, after the calibration step, the system weighs each individual filter in silo C 3 or 5 times and stacks the carriers (with filters) in silo D. This process of calibrating the scales and weighing each filter in a silo is called a subgroup. After the first subgroup, all filters reside in silo D. Then, the system recalibrates the scales and weighs the reference weights. Then the system weighs each filter in silo D and stacks the carriers in silo E (subgroup 2). This subgroup process repeats 8 times with filters passing through silos C through F twice finishing where they began in silo C. This complete process of 8 subgroups is called a group. Once the group is complete,

a new RH may be chosen, and the process repeats. In an experiment, the filters never leave the AH500 environment.”

Main text (line 334): “An additional description of group and subgroup is in Supplemental Text S3.2.”

Line 325. Figure 1 reads “average aggregate mass” but here there seem to be two separate things, “average net mass” and “aggregate net mass”. Confusing. All occurrences corrected to average aggregate net mass.

We have now changed all occurrences to the phrase “average aggregate net mass”, including the column header in Table 2.

Line 328. At what RH were the filters equilibrated?

Reply: added “to the set RH” in sentence.

Line now reads: “Once at setpoint, the filters equilibrated to the set RH at least 24 hours before weighing all weighing subgroups.”

Line 333. “relative humidity” and “RH” are used interchangeably. I suggest “RH” since it’s already been defined. All occurrences of relative humidity changed to RH.

All remaining occurrences of “relative humidity” existing after the definition of RH, have been changed to RH.

Line 336. Table 1. What does “7(1st) 8(all others)” mean? This refers to the number of subgroups in a group.

Our first experiment had a programming error that only included 7 subgroups per group. This programming error was corrected in all subsequent subgroups.

Caption to table 3 now includes: “...a programming error in the first group created a subgroup of 7. The error was corrected, and all subsequent groups contained 8 subgroups.”

Line 342. Why 20% or 35%? Why not use one value? How is RH measured and what is its uncertainty?

The environmental chamber could not achieve 20% RH unless the laboratory was near that RH, which only happens in winter. This is now mentioned in Supplemental Text S3.1. A description of how RH is controlled in the environmental chamber and in the AH500 system are included in the supplement. Table S3 now includes average and standard deviations in temperature and relative humidity for all experiments.

Supplemental Text S3.1: Relative Humidity and Temperature Control

All filters are weighed inside the AH500 environment which resides inside a walk-in environmental chamber inside a laboratory at Washington University in St Louis (Supplemental Figure S2). The relative humidity (RH) control system for the walk-in environmental chamber recirculates air through an inlet and outlet HEPA filter using a VTX800 duct blower (Vortex). The air passes through a mixing volume where Reverse Osmosis water is atomized to increase RH, and a DD300 Desiccant Dehumidifier (EBAC Industrial Products) to reduce RH by drawing air from the laboratory and drying the air. Air leaving the mixing volume exits through a heat exchanger that cools the air, if needed.

The DD300 desiccant drier uses a rotating desiccant wheel to dry incoming air. The incoming air from the laboratory passes through the warm desiccant wheel and into the mixing volume. The desiccant wheel then rotates the wet desiccant to the drying position where hot air passes through the wheel discarding hot, humid air into the laboratory.

The temperature and RH are controlled by two PXF4 proportional-integral-derivative (PID) controllers (Fuji electric). Also attached to the system is a Hygrolog data logger (Rotronic) which records the temperature and RH inside the walk-in chamber. Both the PID controllers and the data logger use HC2A probes (Rotronic) which are co-located within the chamber.

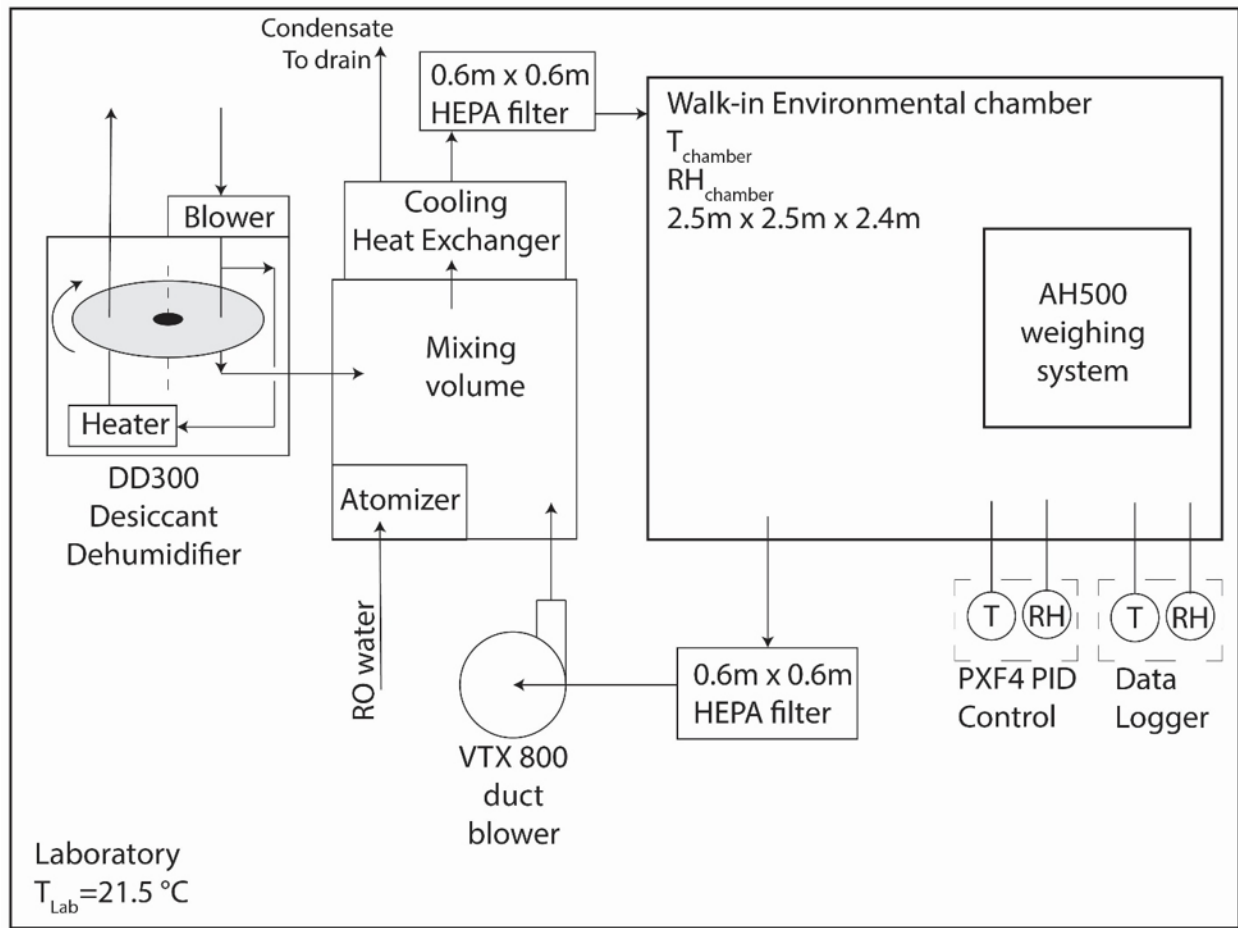


Figure S2. The environmental control system for the walk-in environmental chamber. RO water is reverse osmosis water. DD300 indicates the EBAC Industrial Products Desiccant Dehumidifier. The VTX800 indicates the Vortex duct blower. The PXF4 PID control indicates the Fuji electric PID controllers used for RH and temperature control.

Figure S3 shows the environmental control unit for the AH500 system. Air is pulled from the AH500 environment and passed over the cooling heat exchanger. The chiller setpoint (T_{chiller}) is set 6 degrees cooler than the required dewpoint of the AH500 system for all but the Beijing experiment. Thus, the cooling heat exchanger both cools the air stream and condenses water from the air. The air is then electrically heated to setpoint. A copper tube filled with Reverse Osmosis water is electrically heated to introduce water vapor until RH setpoint is achieved. Finally, the conditioned air passes through a HEPA filter back into the AH500 environment.

The RH and temperature are monitored using a HMT333 system (Vaisala) with a HUMICAP capacitance probe (Vaisala). This system is calibrated using 3 saturated salts (NaCl [RH=75%], MgCl₂ [RH=33%], and LiCl [RH=11%]) every two years. A calibration occurred once during this study. Pressure is monitored using a PTB300 barometer (Vaisala). This barometer was added during the experiment to adjust for the pressure change when the walk-in chamber conditioning unit was active. When the DD300 system is actively drying the chamber, there is no designed outlet for the excess air. Thus, this active drying increases the pressure inside the walk-in chamber. Measurements from the PTB-300 estimate this increase at 0.25 hpa.

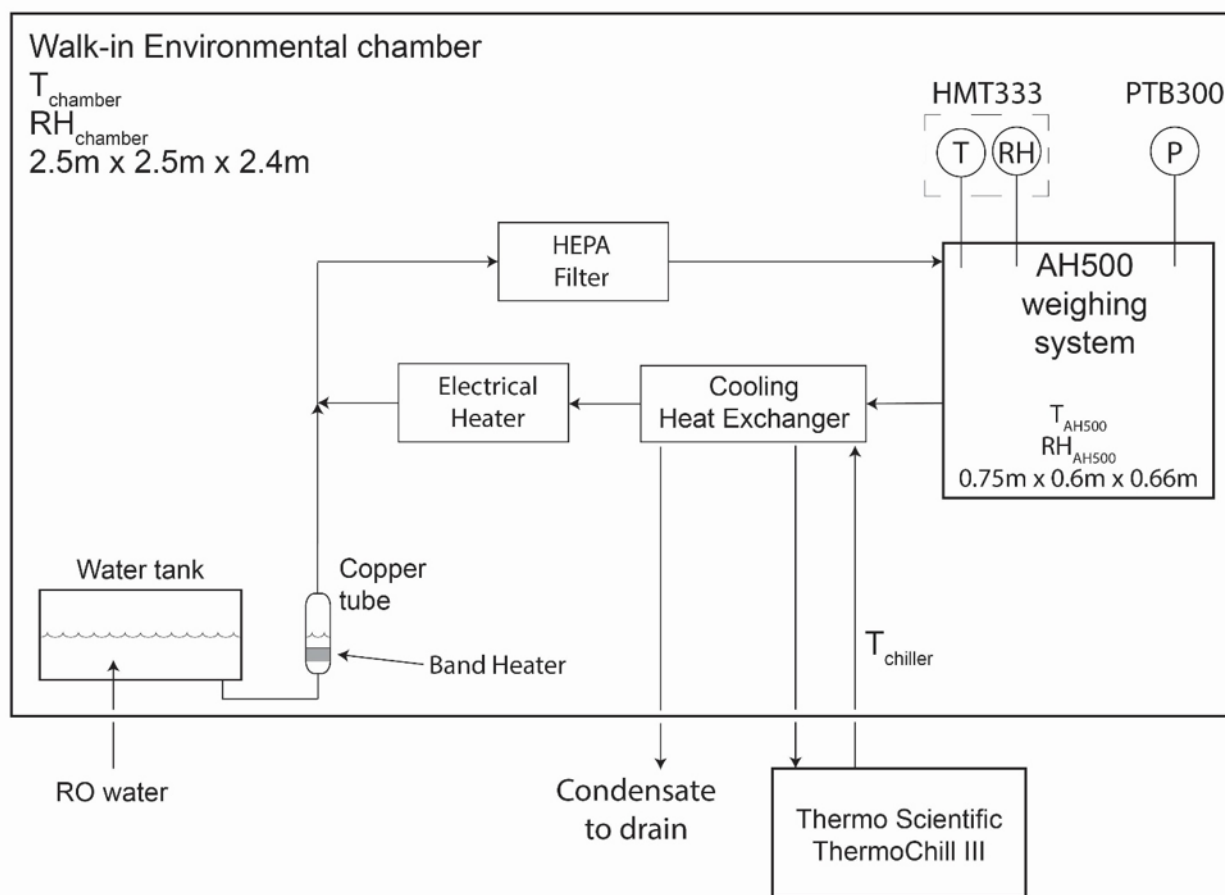


Figure S3. The AH500 environmental control system. The ThermoChill chiller resides outside the walk-in environmental chamber. RO water is Reverse Osmosis water. HMT333 is an RH and temperature measurement transmitter. PTB300 is a barometer.

Table S3. The temperature and RH inside the AH500 system during each experiment.

	Average RH	Std Deviation RH	Average Temperature	Std Deviation Temperature
Beijing	35.078	1.063	21.533	0.051
	44.793	0.98	21.532	0.034
	49.989	1.173	21.533	0.050
	49.312	1.111	21.549	0.169
	44.787	0.485	21.534	0.028
	35.023	0.937	21.543	0.150
Halifax	N/A	N/A	N/A	N/A
	N/A	N/A	N/A	N/A
	N/A	N/A	N/A	N/A
	54.097	2.198	21.536	0.047
	45.396	0.788	21.536	0.021
	35.248	0.712	21.534	0.028
Fajardo	35.287	1.018	21.533	0.044
	45.391	2.258	21.549	0.189
	54.155	2.391	21.537	0.061
	54.118	2.211	21.537	0.058
	45.096	1.939	21.536	0.055
	35.466	0.731	21.535	0.033
Bujumbura	35.007	0.397	21.545	0.024
	45.102	0.395	21.545	0.034
	53.395	0.886	21.549	0.052
	53.460	0.969	21.560	0.178
	45.098	0.474	21.545	0.031
	35.008	0.513	21.544	0.025
Abu Dhabi	20.644	1.016	21.613	0.317
	35.010	0.702	21.545	0.030
	45.094	0.258	21.545	0.028
	53.685	0.767	21.545	0.032
	53.630	1.300	21.545	0.030
	45.109	0.465	21.554	0.111
	35.005	0.273	21.543	0.041
	19.442	0.908	21.550	0.052

N/A – not available.

The RH and temperature response inside the AH500 system is summarized in Table S3 for the entire study. A capacitance probe failed during the ascending portion of the Halifax experiment, and the RH and temperature data is not available. The average temperature and standard deviation in temperature was stable throughout all experiments. In the Beijing experiment, the T_{chiller} is not adjusted with each RH setpoint change. This constant T_{chiller} limits the maximum achievable RH to 50%. For all subsequent experiments,

we changed T_{chiller} as described above, which increased the maximum attainable RH. The system was unable to achieve 20% RH without freezing the cooling heat exchanger in the AH500 system. Low humidity (20% RH) was capable only when laboratory RH was near 20% in the winter months, which was when the Abu Dhabi experiment was performed. In the Fajardo experiment, the RO supply water to the AH500 system was limited by a failing pressure regulator, which increased the RH standard deviation. The average RH remained unaffected.

Line 346/347. The “high, low, and medium growth samples” has not yet been defined.

The names of the sites have replaced the words "high, low, and medium"

Line now reads: “For the Fajardo, Bujumbura, and Abu Dhabi growth samples, there were...”

Line 349. So all filters were weighed from a given site at once?

Correct. We added discussion to the supplement (Supplemental Text S3.2) to aid understanding the weighing methodology. Supplemental Text S3.2 is presented above.

Line 358. Explain what is meant by factors like the ambient conditioning unit? Is the the room A/C or are you referring to something else?

Added this subject to the RH and Temperature discussion in the supplement (Supplemental Text S3.1).

Supplemental Text S3.1 (lines 164 to 172) “The RH and temperature are monitored using a HMT333 system (Vaisala) with a HUMICAP capacitance probe (Vaisala). This system is calibrated using 3 saturated salts (NaCl [RH=75%], MgCl₂ [RH=33%], and LiCl [RH=11%]) every two years. A calibration occurred once during this study. Pressure is monitored using a PTB300 barometer (Vaisala). This barometer was added during the experiment to adjust for the pressure change when the walk-in chamber conditioning unit was active. When the DD300 system is actively drying the chamber, there is no designed outlet for the excess air. Thus, this active drying increases the pressure inside the walk-in chamber. Measurements from the PTB-300 estimate this increase at 0.25 hpa.”

Line 363. What is meant by “achieves independence of ascending or descending sections”?

Reply: When the bridging method is used, a single evaporation line is created from masses in the ascending and descending portions (35% RH) of the experiment. Thus, the ascending water mass depends on the single evaporation line which itself depends on data in the descending portion and vice versa. Ascending and descending data are not fully independent of one another. Independence is achieved by creating two individual evaporation lines (one evaporation line for ascending and one for descending). Thus, dependence and independence refer to whether there is a common evaporation line or two independent evaporation lines. We have simplified the discussion to refer to the evaporation lines alone.

Main document (lines 376 to 381) “The total AH500 measurement duration (weeks) for each sample was long enough to require estimation of aerosol evaporation in conjunction with hygroscopic measurements. Fig 1 shows the two methods used to estimate evaporation of the aerosol sample: 1) a bridging method using a common evaporation line which is suitable for shorter durations and 2) an individual method that creates two independent evaporation lines, one for ascending and one for descending RH sections, but requires a longer analysis period. ...”

Line 372. For which case is this being discussed?

Reply: We were referring to the individual method. We have broken this confusing paragraph into two paragraphs to simplify and focus the discussion. The second paragraph parenthetically refers to the individual method.

Main document (lines 390 to 394): “Our inference of the PM_{2.5} mass as a function of RH needs only one 35% weighing group for the ascending portion and one 35% weighing group for the descending portion of the experiment. We chose the closest 35% weighing group (temporally in Fig 1) to the 45% weighing group in all cases. The 35% weighing group in the ascending line uses the last (temporally) 35% RH weighing group in the ascending portion of Fig 1 (individual method). The descending RH-gravimetric relationship uses the first (temporally) of the last six 35% RH weighing groups (Fig 1, individual method). ...”

Line 372. It appears in Figure 1b that the slope of the line (extrapolated into the higher RH range) is used, not the 5th weighing group?

This confusing discussion has been split into two paragraphs. We intended the 5th 35% weighing group, which could be confused with the 5th weighing group temporally. We have changed the wording to use “last 35% weighing group.” Additionally, we have added a sentence at the beginning of the new paragraph to add context to the objective of these confusing sentences.

Main document (lines 390 to 394): “Our inference of the PM_{2.5} mass as a function of RH needs only one 35% weighing group for the ascending portion and one 35% weighing group for the descending portion of the experiment. We chose the closest 35% weighing group (temporally in Fig 1) to the 45% weighing group in all cases. The 35% weighing group in the ascending line uses the last (temporally) 35% RH weighing group in the ascending portion of Fig 1 (individual method). The descending RH-gravimetric relationship uses the first (temporally) of the last six 35% RH weighing groups (Fig 1, individual method). ...”

Line 480, Table 4. Do these values refer to a given site?

Reply: No. The values refer to the growth categories. We have added to the caption of Table 4 to help clarify the confusion.

“Table 4. The solved water fraction for the growth categories at three RH’s inferred from collective analysis across all sites. The numbers in parentheses are the 95% confidence interval (CI) at 35% RH. A-N-S-K represents Ammonium-Nitrate-Sulfate-Potassium.”

Line 569. Why does the “No” (white) not show up on the outer circles?

There was an error in the figure legend. The “No” in the legend has been removed.