

Reviewers comments in black

Replies to comments in blue

Changes to document in green

Reviewer #2

The manuscript by Oxford et al. presents a method for measuring water content of PM_{2.5} filter samples collected by the SPARTAN network. If successful, extending a global filter sampling network to quantify aerosol water content would provide valuable information for atmospheric aerosol research. However, in its current form, I believe that the manuscript has several fundamental technical issues that should be addressed before the methodology can be considered sufficiently validated for publication.

Reply: We have extensively revised the manuscript to address these concerns. The responses to each item are below as well as the final response.

1) Lack of validation using standard chemical compounds

Validation using well-characterized reference compounds is a standard practice in hygroscopicity measurements because it demonstrates that the measured water uptake is physically meaningful and that the measurement system performs correctly. Measurements of atmospherically important compounds, such as ammonium sulfate, sodium chloride, and sucrose, are routinely conducted for this purpose, with ammonium sulfate being one of the most commonly used standards. I was unable to identify such validation measurements in the manuscript. Therefore, measurements of standard compounds should be conducted and compared with well-established literature data to demonstrate the validity of the measurement approach.

Reply: Indeed, validation is essential. We have extensively expanded the description of this measurement system to demonstrate its fidelity as indicated in response to your comment 3) below. We also confirm that the inferred water uptake is physically meaningful by comparing the algebraic relationship to previous reference measurements using the same method (gravimetric measurement followed by Ion Chromatography measurement, McInnes et al. (1996)) as shown in Supplemental Table S3. The distribution of our growth

results offers additional validation of the entire study (measurement system plus algebraic solution) using their ammonium sulfate and lab generated sea salt measured in the same manner. We have rephrased the paragraph describing this comparison.

Main document (lines 541 to 547): “We compared our growth category results to prior measurements of water fraction at 40% RH for lab generated sea salt (83% sodium chloride) and ammonium sulfate on PTFE filters (McInnes et al., 1996) (Supplemental Table S3). The predicted water content distribution from the high growth category overlaps with the distribution of measured water content of lab generated sea salt, and the predicted water content distribution from the medium growth category overlaps with the distribution of measured water content of ammonium sulfate providing confidence in the physical meaning of the study results.”

2) Limited RH range

According to the Introduction, the purpose of the study is to quantify the water content of PM_{2.5}. However, the measurements were limited to a relatively narrow RH range (35–55%). This RH range does not cover the deliquescence relative humidity (DRH) of major atmospheric inorganic aerosol components such as ammonium sulfate and sodium chloride, where substantial water uptake occurs. Furthermore, multiphase chemical reactions that are important in the atmosphere are generally promoted under higher RH conditions. The reported mass growth factors (Figure 3) remain below approximately 1.05 throughout the investigated RH range, whereas ambient aerosol particles are frequently exposed to much higher RH in the atmosphere. Consequently, the atmospheric significance of the reported measurements remains unclear. Most hygroscopicity studies measure water uptake up to approximately 85–90% RH in order to characterize the full hygroscopic behavior of aerosol particles. If the authors believe that restricting the measurements to 35–55% RH is sufficient for the intended scientific objectives, a strong scientific justification should be provided. Otherwise, I suggest expanding the measurable RH range.

Reply: Thank you for highlighting a source of confusion. Our goal is not to assess the water content of ambient PM_{2.5}. Rather our goal is to assess the water content of PM_{2.5} on PTFE filters at low RH as indicated by the title. The introduction has been altered to clarify that

the objective is the estimation of water content in $PM_{2.5}$ aerosol mass measured on filters by networks (e.g. IMPROVE, SPARTAN). Since the sampling networks weigh filters between 30 to 55% RH, these results accomplish the intended objective. Additionally, we add a line to the conclusion to guard against applying the results to relative humidities higher than 55%.

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 112-129): “...Measurements of water mass, however, remain absent from filter-based $PM_{2.5}$ measurements made by air quality networks such as Interagency Monitoring of Protected Visual Environments (IMPROVE) or the Surface PARTiculate mAtter Network (SPARTAN).

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.”

Main document (lines 164 to 166): “We report the water mass fraction as a function of composition and RH between 35% and 55% RH. We then use the developed relationship to predict water content for the network at 35% RH, corresponding to the center of the RH range of the United States Environmental Protection Agency protocol.”

Main document (619-620): “The water mass associated with $PM_{2.5}$ filters at low laboratory RH as a function of ambient composition had not been well quantified.”

Main document (Lines 631-632): “Application of this relationship to studies should be limited to RH below 55%.”

3) Insufficient technical description to demonstrate the validity of the methodology

The technical description is not sufficient for readers to evaluate the validity of the proposed measurement approach. For example, the manuscript does not adequately describe how RH was generated and controlled. In addition, information regarding RH stability, such as representative RH time series during equilibration and the standard deviation of RH, is not provided. Combined with the absence of validation using standard compounds, these omissions prevent the reader from assessing whether the proposed methodology accurately measures aerosol-associated water. Consequently, the technical validity of the methodology has not yet been demonstrated.

Reply: We have added to the supplement the RH control method of both the AH500 system and the environmental chamber. We also added the mean and standard deviations for both temperature and RH (AH500 system) for all periods during the experiment. We also added an alternate description of the weighing method to help understanding of the AH500 system. This description is located in Supplemental Text S3.

“Supplemental Text S3: AH500 system and environmental chamber

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.

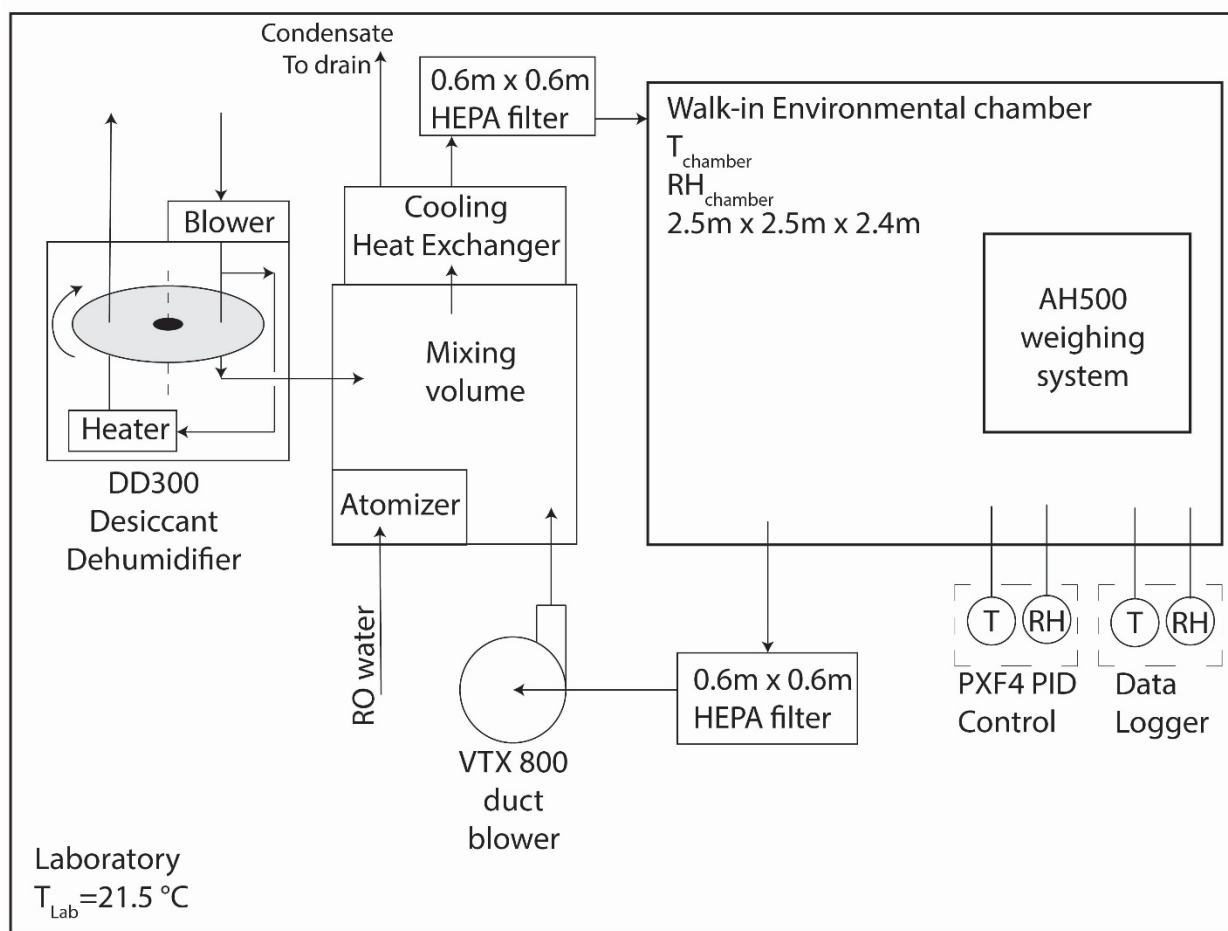


Figure S2. The environmental control system for the walk-in environmental chamber. RO water is reverse osmosis water. DD300 indicates the EBAC Industrial Products Desiccant Dehumidifier. The VTX800 indicates the Vortex duct blower. The PXF4 PID control indicates the Fuji electric PID controllers used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

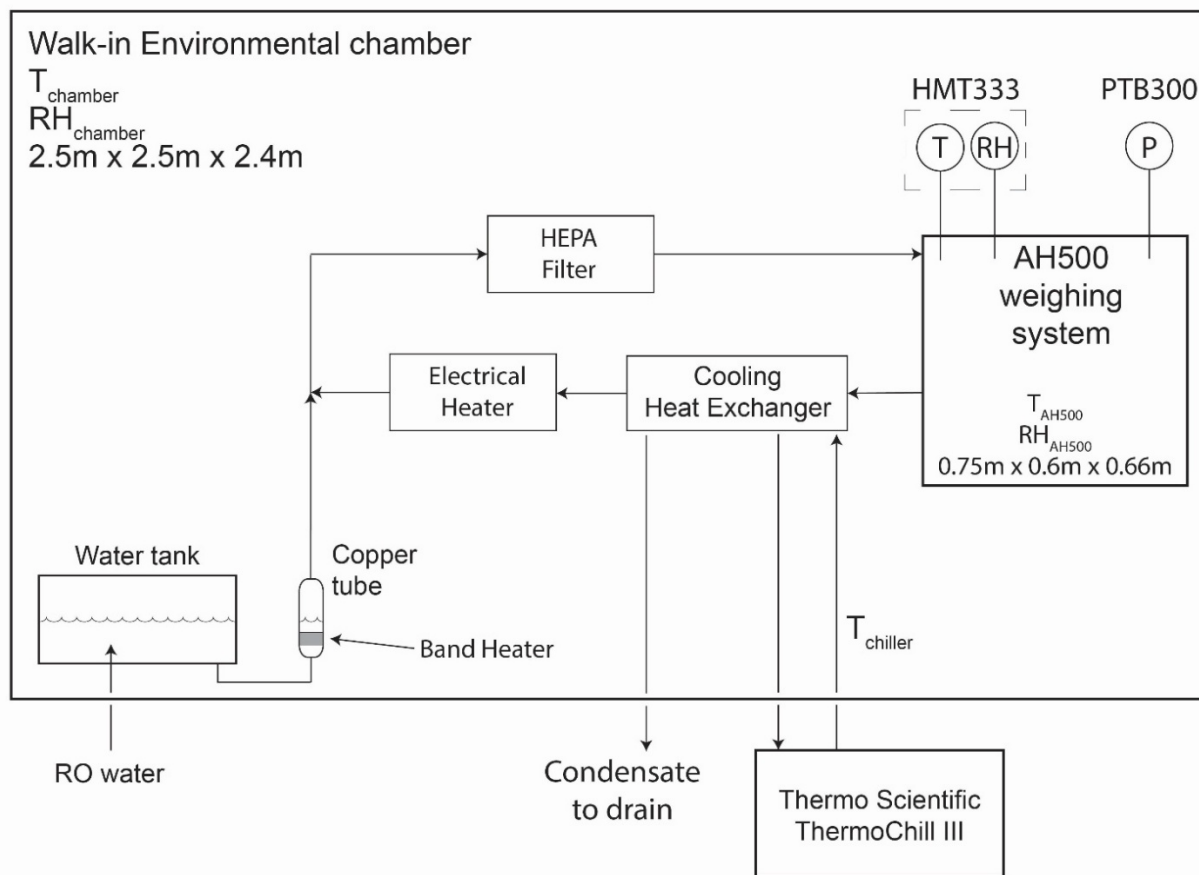


Figure S3. The AH500 environmental control system. The ThermoChill chiller resides outside the walk-in environmental chamber. RO water is Reverse Osmosis water. HMT333 is an RH and temperature measurement transmitter. PTB300 is a barometer.

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, 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.

Supplemental Text S3.2: Filter Handling and Group-Subgroup Description

The AH500 uses a system of carriers to move individual filters inside the environment. Only one filter resides on each carrier, and the filter's outer support ring rests on the carrier's three small tabs (Figure S4). The thickness of each carrier as well as the location of the tabs ensures that deposition area does not touch other filters nor the carriers, and the air may move around the filters unimpeded.

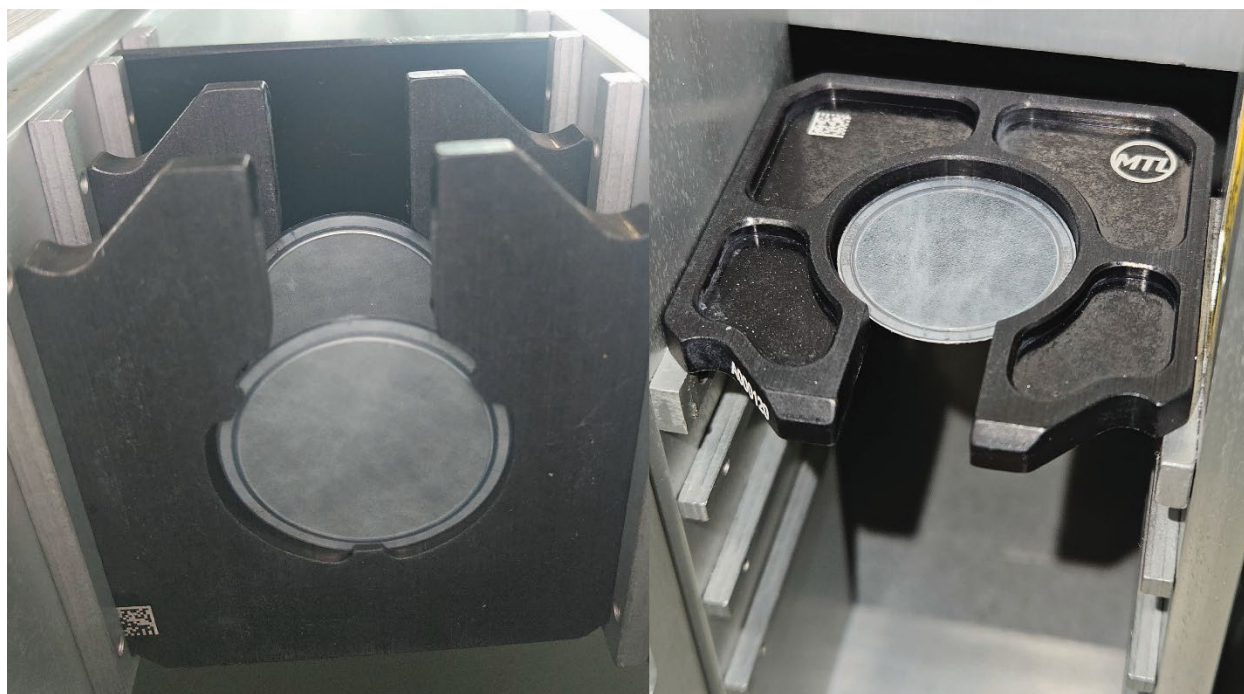


Figure S4. Picture at left displays the two black carriers from below. Picture at right (taken from above carrier) displays a black carrier and filter resting at the bottom of the silo.

The carriers are stacked inside 1 of 6 silos identified by a letter code. Silos A and B were not used in the study. For this study, there are never more than 12 filters/carriers inside the environment, which are easily stacked within a single silo (silo capacity is 100 carriers). A robotic arm picks a carrier from the bottom of a stack inside the silo and passes the filter under a barcode reader for filter identification. The robotic arm places the filter on a brass stand inside the scales to weigh the filter (Figure S5). This weighing process repeats 3 (Halifax and Beijing) or 5 times (Fajardo, Bujumbura, and Abu Dhabi). Then the robotic arm removes the filter from the scales and places the filter/carrier on the bottom of the next silo with the filter resting on the tabs. For example, the robot picks a carrier from the bottom of silo C, weighs the resident filter, and then returns the carrier to the bottom of silo D.

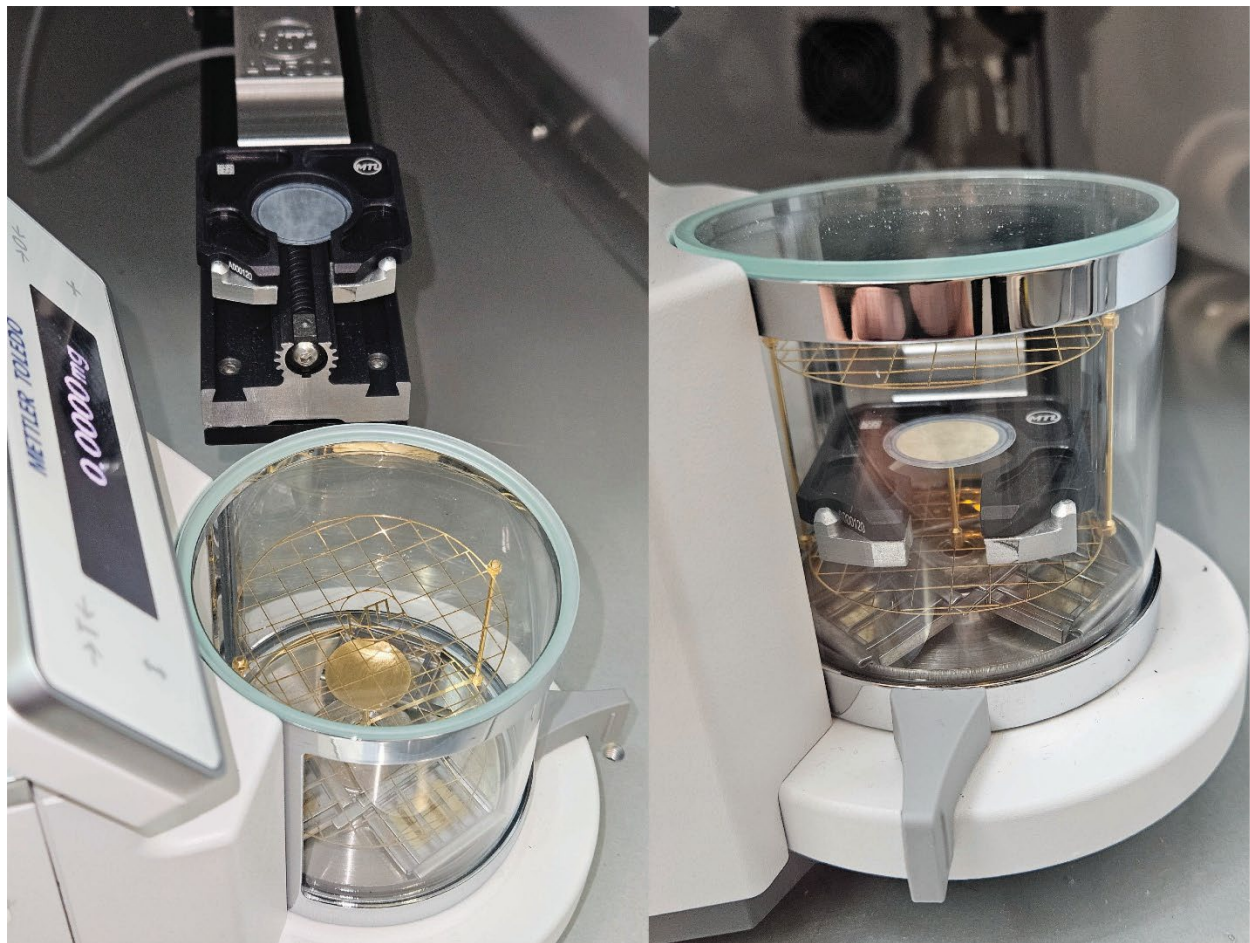


Figure S5. Picture at left shows robotic arm with carrier and filter. In the foreground is the scales with brass stand. The picture on the right shows the filter placed on the brass stand.



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.

Reply: The main document now references this additional information in the supplement.

Main document (lines 214 through 216): “A more detailed description of the environmental chamber and AH500 system can be found in Supplemental Text S3.”

Main document (lines 311 through 314): “We used the MTL AH500 system which includes a controlled RH chamber and the Mettler-Toledo XPR6UD5 balance to repeatedly weigh filters at multiple RHs. For a detailed description of the RH control of the MTL AH500 system and the environmental chamber, see Supplemental Text S3.1.”

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

Because these issues require substantial additional experimental validation rather than clarification or minor revision of the existing manuscript, I do not believe that they can be adequately addressed through a normal revision process. Therefore, I cannot recommend publication of the manuscript in its current form. Resubmission should be considered after the authors have fully addressed these fundamental technical concerns.

Reply: We have addressed the fundamental technical concerns as described above. The description of the RH control, for both the AH500 system as well as the walk-in environmental chamber, has been added. RH and temperature data for the AH500 system has been summarized for every experiment. Additionally, the limited RH range of our experiment directly corresponds with the limited RH range to which it is to be applied—the RH ranges used by active PM_{2.5} networks (e.g. CSN, IMPROVE, NAPS, SPARTAN). Application of the relationship to RH beyond the investigated range have been cautioned against. Finally, the study does compare its overall results to both ammonium sulfate and lab generated sea salt measured by McInnes 1996, which used a similar method to assess

water (gravimetric mass minus Ion Chromatography mass). We believe that these additions and clarifications address the concerns raised.