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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Water content of aged aerosol" *by* G. J. Engelhart et al.

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1. *The goal of the article and supporting research, to determine the state, water content and volume growth factors and compare results among two instrumental methods and models, is valuable. The investigation of the AMS signals as a means of determining aerosol water content directly as well as via models is useful to the extent that it may supplant a separate measurement scheme, e.g. DAASS or similar. The DAASS method, operation and data analysis were adequately presented and included the relevant parameters. Comments regarding the details of the AMS operation and data interpretation with respect to water vapor and aerosol water have been submitted by AMS experts far beyond my level and I will not comment further.*

This is an accurate assessment of the objectives of our paper and its contents.

2. *The experimental and analytical method with respect to the AMS particulate water determination seems to be flawed in one respect, however. The RH to which the aerosol was equilibrated at the inlet to the AMS was not ambient RH as in the DAASS nor was it measured or calculated from temperature and dew point temperature as far as I can tell from the manuscript. The only reference is that the aerosol in the AMS sample inlet was equilibrated to "around 25 deg. C" in the air conditioned field laboratory. Without a measured RH how was the AIM model initiated? Without knowledge of the AMS inlet RH how can a quantitative comparison be made to the DAASS where considerable effort was made to control and know the ambient RH and matching instrumental RH? Clearly there was reasonably good correlation of AMS vs. DAASS particulate water. Given the uncontrolled AMS inlet RH this is surprising. Is it a coincidence resulting from the fact that the aerosol chemistry was relatively stable (see acidity ratio) thus the two water contents varied similarly over time even though they were made at different RHs? Or was it simply due to the fact that most of the data was collected when the ambient RH was in the range of 30 to 60 percent where change in particulate water with RH is not large? Or a combination of both effects? The regression slope of 0.44 is likely due to a lower RH at the AMS inlet, knowing what I know about average ambient temperatures cf. lab temperature of 25 C at Heraklion in May. Without the thermodynamic data, other than one example day, Fig. 3, it is hard to speculate further. As the authors stated, "This may explain some of the observed disagreement at high water content . . .". But there is more that could be said than that. If these points are explained or corrected and discussed, then the paper will be acceptable and publishable.*

This is a critical point for the paper that apparently requires additional explanation. The RH values at which the DAASS and the AMS measured the atmospheric aerosol water concentration were different. As the referee suggests, the DAASS measurement was performed close to the ambient RH while the AMS at the corresponding indoor RH (the RH for the ambient absolute water vapor concentration and room temperature). Figure 6 suggests that the two water concentrations were correlated. The correlation

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was mainly due to the aerosol itself; for example during high sulfate periods both the DAASS and AMS measured high aerosol water concentrations. Of course, some of the correlation is due to the fact that both measurements took place under the same absolute water vapor concentration. This is now explained in the revised paper.

A more important result is the comparison of the AMS water concentration and AIM. For this comparison the corresponding indoor RH was used. This was the RH at the AMS inlet and was different from the ambient RH. We now clarify, both in the text and in the corresponding figure captions, that Figure 6 compares measurements and the ambient and "indoor" RH, Figure 7 and 8 is at the DAASS RH (close to ambient), and Figure 9 is at the "indoor" RH. Additional information about the average indoor and ambient temperatures has been added to clarify this point. The final conclusion here is that the AMS provides valuable information about the aerosol water concentration at the indoor RH. This is now explained in the abstract, main text, and conclusions of the paper.

3. *Minor points to be addressed are listed below with reference to the text of the article, in quotes. "An overview of the FAME-08 field mission with details on each of the measurements described below has been presented by Pikridas et al. (2010)." A one sentence summary of the goals of FAME08 within EUCARRI would put this work in the larger context.*

This following sentence has been added in the revised paper: "Specifically, FAME-08 investigated the physical, chemical and optical properties of aged European aerosol. The field mission's focus on a remote area complements other regional pollution measurements of the EUCAARI campaign (Kulmala et al., 2009)."

4. *The sampling station is located at a 250 m elevation far from any major local anthropogenic sources; the closest urban center is Heraklion, which is approximately 50 km to the west. The island's location in the Eastern Mediterranean makes it an ideal lo-*

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cation." Quantify the distance from major sources and the size of the city of Heraklion. No site is "ideal" though it may in fact be very good.

We have added "with an approximate population of 150,000" to the text. We have improved our word choice to "excellent" to reflect that all sampling locations have their shortcomings, but this one does not suffer from some of the worst.

5. *"The difference between the ambient and dry mode aerosol volume distributions is equal to the particulate water concentration." .... is interpreted as the particulate water concentration.*

Updated as suggested.

6. *"Permapure HD-2000) with final polishing via a carbon cap, silica gel dryer and a HEPA filter." Carbon capsule? Describe. Discuss the effect of the drying method and removal of organic vapors with the carbon capsule on volatile compounds other than water.*

Whatman, the manufacturer of the commercially available activated carbon capsule used in this study, has been noted in the revised paper. The countercurrent streams in the sheath and sample air drying paths flow rates were required to be low in order for water to diffuse across the Nafion membrane in the Permapure dryer. This cleaned air does not contact the sample aerosol directly. The low humidity air was generated by using a generator to compress air to provide flow to a heatless dryer. The model number is provided for further information, but in short, the dryer consists of two chambers filled with highly absorbent desiccant. The chambers alternate between drying the sample and being regenerated by the active chamber. The carbon capsule is the next step to remove all volatile organic compounds. The carbon capsule is filled with granular activated carbon and a high efficiency particulate air filter. The silica gel dryer reduces the humidity even further after the heatless dryer and the final HEPA filter ensures particle-free air. This air is passed counter current to the aerosol stream in a

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Permapure dryer. The Nafion membrane selectively removes 90 percent of the water, while retaining most of the other compounds in the aerosol stream. Our laboratory tests did not show a loss of organics or nitrate due to the Nafion dryers. A brief summary has been added to the revised paper.

7. *"If we assume that the aged submicrometer particle population was homogeneous and therefore all the particles have the same growth factor then:" Regarding this and other assumptions some uncertainty analysis should be presented. Assumption of volume additivity in eqn. 5. Assumption about no (negligible) water less than 10 percent RH even at low acidity ratio. Assumption of ammonium sulfate density in spite of variable acidity ratio.*

A detailed uncertainty analysis for the effect of the aerosol mixing state on the calculated aerosol water concentration is a demanding task because there are a lot of scenarios to be explored (too many potential states exist between the two extremes of external and internal mixing). However, the problem can be simplified because this assumption is used just to determine the upper limit of integration in the dried aerosol distribution D_{d2} (see equations 1, 3 and 4). The sensitivity of the measured aerosol water concentration to this diameter has been explored by Stanier et al. (2004) in their paper describing the DAASS development and data analysis. These authors concluded that for an externally mixed population the growth factor in equations (3) and (4) is approximately the volume-weighted average growth factor of the various externally mixed aerosol subpopulations. Simulations with log-normal externally mixed aerosol modes of different hygroscopicities show that the growth factor calculated by Equations (3) and (4) may be biased low under this circumstance. This error is expected to be small (a few percent at most) for the conditions of FAME-08 where the deviations from the internally mixed state (as indicated from the AMS size distributions) are small (Hildebrandt et al., 2010). This discussion has been added to the revised paper.

The effect of the water additivity assumption on the calculation of aerosol water con-

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centration is easy to quantify through equation (5). Any deviation from ideality will introduce the same error in the water. For these aerosol systems where the aerosol water is determined mainly by the uptake of water by the sulfate salts the deviations are expected to be a few percent resulting in similar uncertainties. Finally, the maximum aerosol water at a RH of 10 percent is approximately 2 percent of the sulfate concentration. The average sulfate concentration during FAME-08 was 3 micrograms per cubic meter, so the average effect of this assumption should be less than 0.06 micrograms per cubic meter. The uncertainty introduced by using a constant ammonium sulfate density is related to the difference between the ammonium sulfate and bisulfate densities (1.77 versus 1.78 grams per cubic centimeter) so it is much less than 1 percent for all cases.

We have added a paragraph summarizing the effects of the above sources of uncertainty in the DAASS water measurements.

8. *"The sampling lines leading to the Q-AMS were sufficiently long for the sample to come into equilibrium with the room temperature, altering the RH from ambient conditions. This may explain some of the observed disagreement at high water content, as water content versus RH is exponential in nature. We will explore this in a subsequent section using thermodynamic theory." Given the lab temperature of "around 25 deg. C, the humidity around the aerosol at the inlet to the AMS could have been above or below the ambient RH and as mentioned may explain much of the discrepancy. I do not see a further exploration of this possible artifact in the text. Somehow the AMS and DAASS data should be sorted to get reasonably equivalent or known RH conditions.*

We followed the reviewer's suggestion and averaged the DAASS and AMS water measurements for the same RH conditions (we used 5 RH bins). Even if these correspond to different time periods they were very well correlated:

(AMS Water) = 0.79 (DAASS Water) – 0.39 μg m^{-3} with R^2 =0.95

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The use of the same RH, as expected, does improve significantly the correlation. This analysis has been added to the revised paper.

9. *"The particles during FAME-08 showed no signs of efflorescence (Fig. 4)." Strictly speaking, since this is a plot of volume growth factor vs. atmospheric RH over a long time period rather than a scan of growth factor vs. RH for a nearly constant aerosol composition over a shorter period, observation of efflorescence is not likely to be possible. Equally well, a lack of efflorescence may be due to the acidity of the aerosol or there could be efflorescence in the data but hidden by the variability (data scatter) over the longer time.*

The data points in this plot represent one hour of averaging. Every 20 minutes a data point of VGF was collected. Due to the relative stability of the air masses we believe this is a short enough time period to see efflorescence if it was persistent. We did not have a problem seeing efflorescence with the same set up in different environments (Khlystov et al., 2005). The role of the acidity is noted in the text. We have added some text to discuss this point.

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