

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

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*1. This manuscript discusses the possibility of quantifying particulate water content using an aerosol mass spectrometer (AMS). The authors use dry and ambient RH size distribution data to obtain the total particulate water volume. This water volume is then compared to the AMS signal. The water content is also compared to modeled water content calculated from E-AIM II, using the chemical composition from the AMS. Using E-AIM II and recalculating the RH to that inside the measurement container housing the AMS, a linear relationship was found between modeled and measured water concentration. Although the applicability of the result for other AMS instruments and other aerosols is unclear, the authors have presented a methodology that, if applied by other groups, in the long run could prove to be very useful. The manuscript is well written and the methodology and result interpretation are clearly presented. I recommend this paper to be published, after modifications and clarifications described below.*

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We do appreciate the positive comments. We would like to stress though that the main objective of the paper is the measurement and analysis of the water concentration of ambient aerosol in an area with highly aged aerosol. This is achieved by the use of the DAASS measurements, the aerosol composition as measured by traditional filter measurements and the AMS, and the aerosol thermodynamic model E-AIM. The study was not designed to investigate the measurement of water by the AMS. This was an interesting result that we think that is worth-reporting. We do understand that this result has generated a lot of interest given the popularity of the AMS, but it should not be viewed as the main objective of this paper.

*General questions/remarks:*

*2. As stated, it has previously been thought that particulate water evaporates in the AMS, which would make you lose a lot of the water. If this is true (like prof. Jimenez pointed out in a comment), it may be that the chosen RIE for water is too low, and the nice linearity that you obtain may be an effect of a relatively stable aerosol (as Dr. Middlebrook pointed out in another comment). Do you indeed have a fairly stable aerosol or is it very dynamic? If it is dynamic, can you see changes in the correlation slopes? Particle size would strongly influence the mass fraction of particle bound water that is evaporated in the aerodynamic lens. How much did the mass weighted GMD vary in this experiment? This matter needs further discussion in the paper.*

Mensah et al. (J. of Aerosol Science, 42, 11-19, 2011) have very recently reported a RIE of 2 for water in an AMS. Combination of this value of the RIE and our results suggests that approximately half of the water evaporated in our AMS and that this fraction was relatively constant during the measurement period. While the absolute aerosol concentration was quite variable during FAME-08 (see for example Figure 1 of Hildebrandt et al., ACP, 2010 or Figures 6 and 7 of Pikridas et al., ACP, 2010) the shape of the volume/mass aerosol distribution was relatively stable (see Figure 12 of Pikridas et al., ACP, 2010). This is a potential explanation of the surprising agreement of the

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AMS water measurement with the E-AIM predictions. Discussion of this important issue together with the recent Mensah et al. (2011) study has been added to the paper to improve the interpretation of the AMS water measurements.

**3.** *The organic fraction is sometimes used in the calculations, sometime it is not. Although the difference may be negligible when it comes to  $\mu\text{g}/\text{m}^3$ , a large volume fraction of less hygroscopic organics might be very important when it comes to e.g. CCN properties, as it is the mean-value (Petters and Kreidenweis, 2007) in combination with the dry particle size which is the important parameter when it comes to cloud formation. This question is not the focus of the paper, but could be worth to at least mention.*

Our null hypothesis was that the effect of the organic content of the PM had a zero influence on the aerosol water concentration. Therefore in the first simulations (see Figure 7) we neglected the water uptake by organics. This is now mentioned explicitly both in the text and in the corresponding figure caption. In the second test we used a simple parameterization of the water uptake by organics to see if our results were consistent with what is known about the hygroscopicity of SOA. The results are depicted in Figure 8 and suggest, as the reviewer remarks, that the effect is small (around 3 percent increase of the water on average). We agree though that the effect of organics on water uptake by aerosols in sub-saturated and super-saturated conditions can be quite different. We have shown the importance of organics in the CCN concentrations in the same area in Bougiatioti et al. (ACP, 2009). This point is now mentioned in the revised paper together with the corresponding reference.

**4.** *Would it be possible to correct the VGF to the ambient distribution by recalculating using Köhler theory? In figure 2 it looks like there is a difference of a few percent between DAASS-RH and ambient RH. How large is this potential error?*

Given the good agreement of the thermodynamic model used in this study the water concentration and the corresponding VGF can be easily recalculated at the ambient  
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RH or any other RH. This calculation was actually performed for the indoor RH and the comparison with the AMS measurement (please see Figure 9). The difference in this case is related to the slope of the growth curve of sulfate salts and increases as the RH increases. It is very small for low RH values (a few percent) and increases to 10-20 percent at the highest RH values of the study. We would not describe this difference as an error given that our whole analysis is based on the appropriate RH. For example, using the ambient RH would not change Figure 8 appreciably (it would just shift the data a few percent along the direction of the curve). It would however increase the absolute water concentration. This point is made now in the revised paper.

**5.** *The modeled water content from the E-AIM model is lower for the recalculated RH than from the ambient RH (at least looking at the scale of the axis), which would imply that the temperature at the point of the AMS measurement was higher than the ambient temperature. Is this correct?*

This is correct for most of the study. The average temperature inside the isobox, where the Q-AMS and the other instrumentation (SMPS systems, thermodenuder, gas-monitors, aethalometer, filter sampler) used in the study was located was on average 29 C while the average ambient temperature was 19 C. This temperature increase (despite the use of air conditioning) was due to the 10 pumps and the rest of the instrumentation operating inside a rather small room. Additional information about the indoor and outdoor temperatures has been added to the revised paper.

*Details:*

**6.** *The Q-AMS instrument is introduced late in the abstract, after discussing results from E-AIM. It should be presented before results from the instruments are discussed.*

This was done intentionally given that the AMS is a secondary instrument for the purposes of this study (see also our response to Comment 1 above). We do prefer to introduce it in the end of the abstract.

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7. Page 21654: Particle lifetime is mentioned twice (row 21 and 26) in a repetitive way.

Corrected.

8. Page 21655, Row 16: Reference should be Nilsson et al., 2009.

Corrected as described.

9. Page 21655, rows 26-28: Was it Choi and Chan (2002) who said that non-neutralized sulphate aerosols could be correlated to lack of efflorescence? Or should there be another reference here?

There have been a number of studies regarding the efflorescence (or lack thereof) of inorganic salts. A very good review has been provided by Martin (Chem. Rev., 2000) and has been added to the text at this point.

10. Page 21656, row 1: This sentence needs rephrasing. Can you define "hygroscopic"? It is true that kappa values of organics have been found to vary significantly (see e.g. Jimenez et al. 2009), but what do you mean by affecting the water uptake "negatively"? As long as the organic fraction of the particle is not completely hydrophobic, it will contribute to the water uptake. However, the organic part can both increase and decrease the hygroscopic growth factor (GF) of the particle; this all depends on what the rest of the particle consists of. Please clarify what you mean here.

We have clarified in this point the potential range of effects that organics may have on the water uptake of the ambient particles and inorganic salts. The negative effect here means diminishing water absorption of the inorganic salts. The existence of organics can in some cases decrease the water uptake of these salts due to non-ideal interactions of the corresponding molecules and ions in the aqueous solution (Saxena et al., 1995; Cruz and Pandis, 2000).

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11. Page 21656, row 5: As I understand it, this was a pure HULIS-measurement, and does not mean this is the GF for the entire organic fraction. Maybe this is not so relevant for this study.

This is correct. Due to one reviewer's request for a shorter introduction and the lower relevance of this study to the current work the reference has been removed.

12. Page 21656, row 6. I prefer "hygroscopic" instead of "hydrophilic", since it is to my knowledge the term most commonly used.

Changed for precision. Beyond the common usage hygroscopic means readily absorbing moisture as compared to hydrophilic which indicates an affinity for absorbing or dissolving in water.

13. Page 21656, row 28. "increased water uptake". Same as point 5), do you mean that the organic fraction was not completely hydrophobic?

Yes, the aerosol in this study in the middle of an urban area was not completely hydrophobic (a significant fraction depending on the season was secondary). This point has been clarified.

14. Page 21658, row 3: "EUSARRI". Should be "EUCAARI".

The typo has been corrected.

15. Page 21661, row 17: What does "flash-vaporize" mean?

This now reads "quickly" to reduce any confusion from the flash-vaporize terminology. In short, the particles must vaporize in a short time frame upon contact with the AMS heater. Species with slow vaporization times will not be measured correctly.

16. Page 21662, row 1: "with". Should be "in", right?

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Changed to "in".

**17.** *Page 21662, row 4: If you use pToF spectra you have the same results but size resolved. Why don't you present or discuss these data in the paper? Is it really this easy to separate the signals? it seems like it since you have this nice linear relationship, but if you have vaporization in the AMS during the particles lifetime before it hits the heater, I guess this would give a somewhat smeared signal?*

The gas-phase water can be separated from the particle-phase water because they appear at different times in the signal. It is possible to have a smeared signal, but in the FAME-08 the particles were mostly composed of ammonium and sulfate, which vaporize very rapidly on the 600 C heater. The pToF data at these concentration levels tends to be noisy and has been heavily averaged by relative humidity for this analysis. Therefore its use at least in this study is problematic. However, this is a good suggestion for future work focusing on the AMS water.

**18.** *Page 21662, row 3: "H<sub>2</sub>O+/N<sub>2</sub><sup>+</sup> scales with absolute humidity". For non AMS users this is not obvious. Is there a reference for this, or did you do some measurements to confirm this?*

The corresponding reference is Hildebrandt et al. (2010) and was mentioned in line 8. This is based on the fact that the nitrogen signal will be nearly constant, whereas if the absolute humidity is higher there will be more water in the air so the water signal will be higher.

**19.** *Page 21663, row 11. These 10 percent of water is assuming that the aerosol is completely dry at 12 percent RH (or whatever your dry measurement RH is) right? So the water content could be slightly higher than 10 percent, given that you have a small GF also at your dry conditions?*

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This is correct. We dried the particles as much as possible and then the water content is taken to be the ambient measurement of mass minus the dried measurement of mass. Since the relative humidity of the dry particles was not zero they may still maintain a small amount of water. Based on thermodynamic calculations at RH less than 10 percent the remaining water concentration (if any) should be less than 2 percent of the sulfate concentration. This is also discussed in our response to Comment 7 of Reviewer 1. A sentence has been added describing the uncertainty introduced by this simplification.

**20.** *Page 21666, row 11. "same chemical composition information as before". Does this mean with or without the organic fraction?*

The uptake from organics is not considered in this E-AIM analysis. The text has been updated to clarify this.

**21.** *Page 21666, row 13. "the agreement is striking". A bit too "expressive" for my taste. Try to keep the text as formal as possible.*

This has been changed to read "the agreement is very good."

**22.** *Fig 1. I thought that you used closed loop for the DAASS measurements (except when switching between dry and humid). My point is that if you have a pump for the Exhaust in the schematics, there should also be one in the DMA loop.*

It is correct that a closed loop was used for sampling the ambient and dried measurements. The pump with the exhaust was used during the open loop period of time called the "vent cycle". This pump was an external pump to support the rapid air exchange. There are, of course, internal blowers in the SMPS (not shown in the figure) that are simply left in the box for all of the SMPS with long DMA components standard to a TSI model. This is now mentioned in the figure caption.

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**23.** *Fig 2. Write "Time" on the x-axis.*

Added.

**24.** *Fig 4. Relative humidity is commonly described in percent.*

Changed to percent.

**25.** *Fig 8. Same as fig 4. Changed to percent.*

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