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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. *Page 21655, line 19-20:” One of the major limitations of the H-TDMA comes from most measurements occurring at 90 percent RH. . .” Measurements at constant, for example 90 percent RH have the advantage that they are easy comparable. It is not an instrumental limitation, more a question of the aim and research question one has. Most H-TDMAs have the ability to measure diameter growth factors at a wide range of RH.*

This is a valid point (see also Comment 4 of Reviewer 3). There are different modes of operation of H-TDMAs (e.g. constant RH or scanning RH) to address different scientific objectives. We have revised this section placing more emphasis on the features of these systems. For different applications these features can be either advantages or disadvantages as the comment suggests. We actually believe that because of these

differences the H-TDMA and DAASS are quite complimentary in characterizing the hygroscopicity of ambient PM in sub-saturated conditions.

2. *Page 21656, line 9-10: “Despite the many contributions of H-TDMA measurements, this technique lacks the ability to measure liquid water content of atmospheric particles in their ambient state.” The HTDMA is able to measure the liquid water content of atmospheric particles in their ambient state, even if it is more complicated: measuring humidograms (scanning through an RH range) at sufficiently numerous dry sizes, and with having a separate ambient RH measurement.*

The point that we tried to make here with “ambient state” is that the H-TDMA requires the particles to be dried first before they are humidified. During that initial drying step the particles may change (e.g. effloresce or lose some species or change their morphology). So the H-TDMA measurement starts from an initial particle state that is different than the one existing in the atmosphere. As a result if they are brought back to the atmospheric RH they may reach a different state (e.g., stay in the deliquescence branch of the activation curve). So while the H-TDMA measurements provide valuable information about the hygroscopic properties of atmospheric particles, the calculation of the liquid water concentration of the PM is challenging and has rarely been attempted in the literature. The DAASS can conduct these measurements starting from the atmospheric state of the particles. We have tried to clarify these features and differences of the two systems in the revised paper. These features are useful for different scientific objectives.

3. *Page 21656, line 29 to page 21657 line 2: “Its major advantage is that it measures the aerosol water concentration of the full PM0.5, PM1 or PM10 distribution and does not focus on the behavior of particles of a given size like the H-TDMA.” We would not say, that it is a major advantage, if the measured sizes represent relevant diameter of the size distribution, it is simply a different technique.*

This point also needs some additional clarification. The full DAASS can measure the PM0.5, PM1, or PM10 water every 15-20 minutes (or less for higher aerosol concentrations). A similar measurement with the H-TDMA would require scanning several particle sizes and RH values and would probably require hours. Given that both techniques assume that the sampled particle population does not change (e.g., in chemical composition) during the measurement period, the DAASS has a clear advantage here for the total aerosol water concentration. On the other hand the H-TDMA provides more detailed information (including mixing state) for the selected particle sizes and RH (value or values depending on the operation mode). We have clarified this point in the revised text.

4. *Page 21658, line 2: please give the exact start and end dates of the campaign.*

The overall campaign lasted from May 4 to June 8, 2008. However different instruments were online for slightly different periods of time during FAME-08, which is the reason for the general range given in the overview of the sampling site. For example, the DAASS measurements described in this paper are from May 8-May 28 and the AMS measurements are from May 8-June 5. Details for all the conducted measurements and the corresponding periods are given in Table 1 of Pikridas et al. (2010). We have updated the axes of Figures 5 and 9 with the month and date to add clarity of measurement time frames for the reader. A reference to the FAME-08 overview paper by Pikridas et al. (2010) has been added at this point.

5. *Section 2.2.1: Have you performed any calibration of the instrument with test aerosol? For instance dry and humid ammonium sulphate measurements would be helpful to see the characteristics of the instrument.*

The development and testing of the full DAASS system (including testing with ammonium sulfate) has been described in detail by Stanier et al. (2004). An additional reference to this paper has been included here for the interested reader.

6. *Page 21659, line 22 to Page 21660, line 14. Here, the correction of the integration boundaries is introduced. It is argued that the lower integration limit does not have to be corrected since first, only a small fraction of the particles are present below 15 nm and second, the small particles do not contribute significantly to the total volume. Please be more specific at the first point. How small is this fraction (average, min, max or other statistics like percentiles)? The determination of the upper integration limit is also only correct if this fraction of the small particles is always negligible, since the upper integration limit is searched where the dry total integrated concentration equals the wet one. If there is a significant error in number which is introduced by the not corrected lower integration limit this will introduce an error for the upper integration limit as well. Losses in the drier would case the same kind of problem in the determination of the upper integration limit. Do you have any information on the losses? Please comment on these.*

The characteristics of the aerosol size distribution have been summarized by Pikridas et al. (2010) (see for example Figure 12 of that paper for the average size distributions). The fraction of particles smaller than 15 nm was always less or much less than 1 percent during the study with the exception of a few hours during which nucleation took place. Obviously, with such low number concentrations the contribution to the volume concentration was for all practical purposes equal to zero. This information and a reference to Pikridas et al. (2010) has been added to the revised paper.

The particle losses for the size range of interest in FAME-08 (practically all the aerosol volume was in the 50-500 nm size range) were less than 5 percent. The number concentrations in the two modes of operation (dry and wet) are continuously compared in the DAASS and the few points where there are significant differences (e.g., due to a temporary local source like a car coming to the site) the measurement is considered invalid. The size dependent losses in the system have been investigated by Stanier et al. (2004). A comment on these has been added.

7. *Page 21660, line 15-18: "If we assume that the aged submicrometer particle population was homogeneous and therefore all the particles have the same growth factor then" What do you mean by the aerosol population being homogenous? Please specify it! Is it that all particles have the same chemical composition? In that case the above statement is not correct. What about the Kelvin effect? Smaller particles grow less. With this equation 4 is also not valid. This effect might be small at 70 percent RH, but still it has to be discussed.*

This assumption is used to support Equation (4). In other words, we assume that the VGF of particles with diameter around 500 nm is the same as the total VGF of the full aerosol population in the submicrometer range. The AMS measurements during FAME-08 showed that there is not a large difference in composition with size (please see Figure 2 of Hildebrandt et al., 2010) and the 500 nm size range is close to the peak of the accumulation mode. Given that this is used to make a first order correction to the water concentration (adjusting the limit of integration) the uncertainty introduced is at most a few percent.

The contribution of the sub-100 nm particles to the aerosol volume and therefore the VGF was less than 5 percent during the study and for the sub-50 nm it was much less than 1 percent. As a result the role of the Kelvin effect in the analysis of our measurements is negligible.

We have added some text discussing the above two points.

8. *Page 21663, line 10-14: "The particles during FAME-08 showed no signs of efflorescence (Fig. 4.). The particles retained as much as 10 percent of their total particulate volume in water at 20 percent RH." This is a very interesting finding. Marine air-masses often arrive to the station, where a high fraction of the particles could be sea-salt. How is it possible that no efflorescence behavior can be observed? Is it not possible that you simply "miss" this behavior by measuring only always at ambient RH? Probably when marine air-masses arrive to the station they are humid as well, so you are however*

above the efflorescence point, and with this you measure always a VGF>1? To find this out we would suggest coloring figure 4 according to the air-masses. Also because in this plot you show a mixture of different aerosol types, and these might show quite different growth behavior.

The explanation here is that our reduced DAASS measurements discussed here focused on particles much smaller than one micrometer (ambient dry sizes of less than 500 nm) where the mass/volume contribution of sea-salt particles is very small. Our focus was on the effect of aged organic aerosol on the hygroscopic behavior of the particles and we tried on purpose to avoid the complications caused by the sea-salt. Please note that the DAASS has observed efflorescence in other applications (for example winter in Pittsburgh, Khlystov et al., 2005) so we do not think that there is any instrument limitation here. However, the suggestion here is good and we do plan in future studies in the same area to use the complete DAASS (with measurements up to 10 micrometers) to investigate the behavior of sea-salt. We have added a couple of sentences to address this interesting point.

9. *Page 21664, line 4-5: please give the value of the correlation coefficient.*

The R^2 is 0.90 for the measurements below 8 micrograms per cubic meter. This has been added to the paper.

10. *Section 3.4: The DAAS and the AMS measured water content was compared to theoretical calculations. Using the theory why don't you try to correct the AMS measured water content to the ambient RH and compare then the two measurements as well?*

The first step in the analysis is the comparison of the predictions of aerosol thermodynamic theory with the AMS measurements. The agreement is encouraging so one could use AIM to calculate the aerosol water content at other RH values including the ambient. Of course in this case one compares once more the AIM model to the DAASS measurements resulting once more in the comparison shown in Figure 7 (there is no additional information gained from the exercise).

For a direct comparison of the DAASS and the AMS, following Comment 8 of Reviewer 1 we have binned the measurements of the two instruments by RH and compared the averages. 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

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

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