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

A. Middlebrook

Ann.M.Middlebrook@noaa.gov

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This paper presents measurements of aerosol water content from a dry-ambient aerosol size spectrometer (DAASS) and a quadrupole aerosol mass spectrometer (AMS) and shows comparisons of that data with EAIM-II model output.

This appears to be a unique data set where the aerosol is acidic and does not completely dry as shown by the DAASS data. It is expected to have water loss as a function of decreasing relative humidity, as the particles are dried in the AMS sampling line and inlet. Yet, the particles apparently did not "completely dry" in the AMS. This is different from the pure ammonium sulfate particles in the laboratory which were completely dry after crystallization below the ERH. Hence, in the present study there is a linear relationship for this data between AMS particulate water and EAIM-II water.

While the AMS can indicate relative changes in m/z 18 as a function of water content

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in the aerosol (and air), much or all particulate water is lost in the AMS sampling inlet and so the measured water content is not reflective of the actual amount in ambient aerosols (Matthew et al., AS&T, 2008). Additional laboratory experiments not described in that paper demonstrated that the amount of water lost was size dependent, with smaller particles losing more water than larger particles.

Prof. Jimenez's comment about potentially a higher RIE for water is very relevant and may be the reason for the apparent inconsistency between the "right" amount of water detected in the particles and the fact that much of the water should evaporate in the AMS inlet.

Another potential explanation for this discrepancy is mentioned at the bottom of page 21666: "it is possible that the standard fragmentation table employed in this analysis slightly underestimates the water ion signal arising from fragmentation of either hydrated inorganic or oxygenated organic compounds." Acidic sulfate is the largest component of the submicron aerosol in this field study and it can have a significant contribution to m/z 18 due to the retention of water under lower RH by particles, as indicated by the DAASS measurements. However, when sulfate particles are analyzed by the AMS, there is also signal from m/z 18 due to dehydration of sulfuric acid. This effect is included in the fragmentation table. However, the actual relative contribution of m/z 18 to the sulfate fragmentation pattern can be higher than the table value due to variations in the performance of the mass spectrometer, such as more efficient transmission of small ions compared to large ions. Differences in ion transmission efficiency at a function of m/z can be higher when using a quadupole with 8 mm rods instead of 16 mm rods (the former transmits larger ions less efficiently) or by different electron multiplier detector voltages (where higher voltages can lead to higher transmission of smaller ions in the 90-degree turn between the exit of the quadrupole and the multiplier). Note that if the default ratio is used in the calculation of sulfate with the default RIE for sulfate, the correct sulfate mass loading will be calculated. However, any additional signal at m/z 18 will affect the calculation of particulate water.

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To accurately account for the m/z 18 from sulfate in the fragmentation table for this data set, the fragmentation pattern of sulfate must be measured from the difference spectra using dry particles at the same conditions of the field project. In the absence of doing laboratory calibrations, the spectra from the driest conditions of the field study could potentially be useful. The intercept of 0.74 for Fig. 6 indicates that for this sulfate mass loading the contribution of sulfate to the m/z 18 signal is significant. The ratio of the m/z 18 to m/z (48+64) in the AMS mass spectra for the lowest DAASS water concentration should be input into the fragmentation table (as frag_SO3[18]=ratio*frag_sulphate[48],ratio*frag_sulphate[64]) and then the particulate water can be recalculated (but not the sulfate mass loadings because the RIE_SO4 would need to be adjusted for the different fragmentation pattern). It appears that this ratio could be as high as 1.3 for this data, whereas it is 0.67 in the fragmentation table. With the new water calculation, the intercept with the DAASS data in Fig. 6 should be zero.

The correlation of AMS particulate water with the EAMI-II model (shown in Figure 9 and Equation 10) is surprising and it implies the (fraction of water evaporating)x(RIE_water)$\sim$1. However, it gives the impression that the measured AMS particulate water is the same as what is modeled using EAIM-II and that aerosol water content can be quantitatively measured with the AMS. Furthermore, if RIE_water is truly 1, then there would not be any evaporation. This can easily be misinterpreted by a reader as the AMS being an accurate detector for particulate water, if all the careful wording in the text is not read or understood.

It is interesting that for this dataset the water from the AMS is linearly correlated with the amount measured by the DAASS and the predicted amount from EAIM-II. Possibly the fraction of particle water that evaporated was constant if the mass distribution and composition were fairly constant. Perhaps the best way to convey the relationship of the AMS water content to the other data would be to replot the AMS particulate water in "nitrate-equivalent mass" units vs the DAASS (Fig 6) and predicted EAIM-II water

(replacing Fig 9). Then the slope of the second plot indicates the combined fraction evaporated and RIE_water which at this point cannot be separated. Or there could be various lines w/ RIE_water = 1, 2, and 4 that would have slopes indicating how much of the water is evaporating.

Unfortunately, the drying of the aerosol in the AMS sampling inlet, the high acidic sulfate content of this aerosol, and the potentially high contribution of sulfate to m/z 18 all combined to make the interpretation of the AMS data from this field project difficult for particulate water. Understanding how the sulfate fragmentation pattern and RIE_water can vary has been an ongoing subject among some AMS users, yet these details have not been relevant for the determination of sulfate mass. Since both effects only affect particulate water, which is known to partially or completely evaporate in the AMS inlet, there has been limited detailed study of these topics. With the additional complication of the water loss being size dependent, it is very surprising that the AMS particulate water would have a linear relationship with the expected water content. If all of these effects can be convincingly quantified, the AMS could turn out to be useful for understanding the water content of ambient aerosols, at least under some conditions.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 21653, 2010.