Water uptake by particles containing humic materials and mixtures of humic materials with ammonium sulfate

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Abstract

Recent field studies show that a large fraction of the previously uncategorized organic compounds in atmospheric aerosols are polycarboxylic acids resembling the humic materials (HMs) in soil. The presence of these compounds may alter the water uptake and deliquescence characteristics of particles. We have measured the water uptake by pure HM and by mixed HM/ammonium sulfate particles as a function of relative humidity (RH). We find that the water uptake behavior varies with the type, source, and isolation method of the HM. Two of the three pure humic acids (HAs) and the fulvic acid (FA) studied here exhibited very little water uptake up to $\sim 90\%$ RH, while the fourth material, HA from the Fluka chemical company, deliquesced at 70% RH and showed continuous water uptake to $\sim 90\%$ RH. For comparison, water uptake by polyacrylic acids of two chain lengths and by phthalic acid were also measured. These species also took up small amounts of water over the range of RHs studied. Particle size and chain length had very little effect on water uptake. The mixed organic/ammonium sulfate particles took up a reduced amount of water relative to pure ammonium sulfate, with the exception of the Fluka HA. We modeled the water uptake of mixed particles assuming that ammonium sulfate and HM took up water independently, and results are consistent with the measured water uptake by mixed particles.
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1. Introduction

The effects of organics on the chemical and microphysical properties of aerosols are currently a major focus of aerosol research. While hundreds of compounds have been identified in field studies, the chemical composition of as much as 90% of the organic material typically remains unidentified (Saxena and Hildemann, 1996). Using a new nuclear magnetic resonance (^{1}H-NMR) technique, Fuzzi et al. have recently classified $\sim 90\%$ of the organic material in aerosol and fog water samples (Fuzzi et al., 2001). Using the ^{1}H-NMR technique in the

Po Valley in Italy, Decesari et al. identified as much as 40% of the water soluble organic carbon as polycarboxylic acids having molecular structures analogous to humic materials (HMs) (Decesari et al., 2001).

A major component of soil, HMs form through the decomposition of plant and animal materials. Larger HM, humic acids (HAs), form first and eventually break down into smaller fulvic acids (FA). Both humic and FAs exist as a heterogeneous mixture of structures. Specifically, they are polycarboxylic acids which contain aromatic and phenolic functional groups (Diallo et al., 2003). While the specific chemical formulas are unknown, well-characterized reference samples of HMs are available through the International Humic Substance Society (IHSS). The IHSS's collection includes standards obtained from fresh water, mineral soil, and lignite environments.

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Humic-like substances have been found in both rural and urban particulate samples by several research groups (Decesari et al., 2001; Havers et al., 1998; Hildemann et al., 1996; Ketseridis et al., 1976). Possible primary sources include local soil, dead leaves, biomass burning, and soot from automotive exhaust (Decesari et al., 2002; Fuzzi et al., 2002; Mukai and Ambe, 1986). In one study, rural fine tropospheric matter was collected, and the organics closely resembled those obtained by the pyrolysis of natural humic and FAs (Gelencser et al., 2000). Other studies have identified high-molecular-weight and/or humic-like substance in fogwater (Cappiello et al., 2003; Herckes et al., 2002; Krivacsy et al., 2000). There is also evidence that humic-like materials may form in the atmosphere via photo-oxidation of soot and biogenic hydrocarbons (Decesari et al., 2002; Hoffmann et al., 1997). Humic-like materials have even been identified in marine particulate samples over the Atlantic Ocean and in Antarctic snow due to marine aerosol transport (Cini et al., 1996; Simoneit, 1980).

The presence of HMs in atmospheric aerosols may cause the physical properties of the aerosol to be very different than expected for pure sulfate aerosol. This could alter the direct and indirect effects of aerosols on climate as well as visibility. Relative to the numerous field studies, there is a dearth of laboratory studies of the properties of HMs. In one of the few published laboratory studies, HMs have been shown to alter cloud nucleation and growth by changing the surface tension of the aerosol (Facchini et al., 2000). In wet aerosol, cloud, and fog samples, HMs were found to be the most surface active species within the samples, reducing the surface tension to one-third of that of pure water (Facchini et al., 1999, 2000). This reduction in surface tension may lead to an increase in droplet population, through a reduction in the Kelvin effect, and consequently an increase in cloud albedo.

While smaller dicarboxylic acids have been shown to affect the water uptake and deliquescence of ammonium sulfate (Brooks et al., 2002, 2003; Choi and Chan, 2002; Prenni et al., 2003), little is known about the hygroscopicity of polycarboxylic acids, such as humic and fulvic acids. Furthermore, thermo-dynamic modeling of mixed organic/inorganics particles has been conducted (Clegg et al., 2001; Ming and Russell, 2001, 2002), but these models have not been extended to include polycarboxylic acids. To accurately model these acids, more information regarding their physical properties is needed, including water uptake as a function of relative humidity (RH) with respect to water.

Here we report the water uptake properties of HA and FAs obtained from several sources. We have investigated the size dependence of this uptake. We have also studied the water uptake by polyacrylic acids (PAAs), which have structures similar to the basic structure of HAs (Avena et al., 1999), and by phthalic acid, whose structure represents the metal binding sites present in HMs (Gamble et al., 1980). In addition, we report the water uptake by internally mixed particles containing HMs and ammonium sulfate, and test whether aerosol water contents can be predicted using simple thermo-dynamic models.

2. Experimental

The humidified tandem differential mobility analyzer (HTDMA) used here has been described fully elsewhere (Brechtel and Kreidenweis, 2000b) and will be described only briefly here. Particles are generated using a TSI 3076 atomizer and bulk aqueous solutions of pure HM or mixtures of HM and ammonium sulfate, prepared using ultrapure deionized water for dilution (Barnstead NANOpure ultrapure water system). While the FA is completely soluble, the HAs contain some insoluble components even in the dilute solutions (1 g HM per 100 g of ultrapure water) used here. Thus the actual dry weight percent (wt%) HM, i.e. g HM/(g HM + g ammonium sulfate), in the atomized particles had to be experimentally determined as described below. Upon leaving the atomizer, the aerosol is dried by diffusion dryers and dilution with dry air before entering the HTDMA. For all experiments, this produced conditions of $<5\%$ RH at 30°C.

The HTDMA apparatus is maintained at a constant 30°C for all experiments. Particles enter the first DMA (DMA 1) and a near-monodisperse distribution of particles of the desired diameter (50, 100 or 200 nm) are selected. After size selection, the aerosol is humidified by passing it through Perma Pure tubing (model MD-110-48S). A size distribution is then measured for the humidified particles using the second DMA (DMA 2) and a particle counter (TSI model 3010). The sheath flows for the Perma Pure tubing and DMA 2 are operated at the same humidity.

At the start of each experiment, the size distribution entering DMA2 is first measured at $\leqslant 5\%$ RH. For all compositions, the peak of the distribution observed at low relative humidities in DMA 2 was equal to the diameter selected by DMA 1, within known uncertainties, indicating no significant evaporation of particles. Next, the monodisperse aerosol is exposed to increasing RH and the size distribution is monitored with DMA 2. The RH of the DMA 2 sample flow and sheath flow are measured using ROTRONIC hydroclip humidity sensors (type S). The RH measurements are accurate to $\pm 2\%$ RH over the humidity range studied.

Table 1
Weight percent HM in atomized solutions and measured (see text) in particles

Substance	Type	Location of Origin	wt% HM in atomized solutions	Actual wt% HM
Humic acids				
Fluka Chemical	Brown coal	Germany	9	10 ± 1
			50	53 ± 8
Pahokee Peat Reference	Agriculture	Florida Everglades	9	2 ± 0.3
			50	13 ± 2
Leonardite Standard	Natural oxidation of exposed lignite	Gascyoyne Mine, ND	9	2 ± 0.3
			50	13 ± 2
Fulvic acid				
Suwannee River Reference	Plants	Okefenokee Swamp, GA	9	8 ± 1
			50	44 ± 6

3. Results

3.1. Characterization of HMs

Since HMs have no single chemical formula, materials are classified by their origin. The chemical composition may be different for each type, and thus the physical properties may vary as well. We have studied the water uptake characteristics of 3 HAs and 1 FA. The origins of each are listed in Table 1. To isolate the HA, the Fluka chemical company first obtains the HA sodium salt by alkaline digestion. Next the salt is neutralized by adding a hydrochloric acid solution. Finally, the solution is decanted off, and the remaining brown residue is collected. The other three materials studied here were obtained from the IHSS. At IHSS, samples are collected and purified in a procedure very similar to the procedure described above with one additional step. A final cation exchange step is performed to desalt the samples. Thus, in the IHSS samples only the organic acids of the HM remain. This difference in refinement procedure may contribute to the differences in results described below.

3.2. Water uptake by pure HMs

To quantify the amount of water taken up by aerosol we use the hygroscopic growth factor (G). G is calculated as D_{wet}/D_{dry} where D_{wet} is the mean particle diameter at the RH of the measurement and D_{dry} is the diameter of the particle at 5% RH. Particles that do not take up any water have $G = 1$, and particles that do grow have $G > 1$. To determine the mean particle diameter, D_{wet}, the data are fit to a lognormal size distribution at each RH. The precision in measurements has been quantified experimentally. In these experiments, 100 dry particles were produced with DMA 1,

and without conditioning the particle size distribution was measured by DMA 2. We determined that one standard deviation in these measurements was $\pm 1.5\%$ of the diameter. A similar experiment was conducted by Rader and McMurry (1986). They report a $\sim 1\%$ difference in diameter between DMA 1 and DMA 2, which they primarily attributed to an offset in voltages between the 2 instruments. Interestingly, Rader and McMurry state that their experiment results are slightly different than the error they calculated $0.8 \pm 0.2\%$ in the same study. Based on our measured uncertainty of $\pm 1.5\%$ in diameter, the precision in the diameter measurement is $\pm 2.9\%$ at the 95% confidence limit, and the corresponding precision in growth factor is $\pm 4.2\%$ at the 95% confidence limit.

Ammonium sulfate was used to test the experimental set-up due to its well-known deliquescence relative humidity (DRH). The DRH measured periodically throughout this series of experiments was $77 \pm 2\%$ RH at $30\,^\circ C$. This DRH is slightly below, but within error of the DRH of ammonium sulfate measured in previous studies (Cziczo et al., 1997; Onasch et al., 1999).

Here we present the hygroscopic growth factor as a function of RH for each of the pure HMs. The first material studied was HA from the Fluka chemical company. The hygroscopic growth factors of 50, 100, and 200 nm diameter Fluka HA particles are shown in Fig. 1. As can be seen in the figure, there is a very small amount of water uptake at relative humidities below $\sim 70\%$. Above $\sim 70\%$, there is an abrupt increase in G, indicating that the sample contains a component which deliquesces. This component may be present in naturally occurring HA or may be a product of the Fluka isolation method described above. Over the size range studied, there is no size dependence to the water uptake by Fluka HA. This observation is in contrast to the size
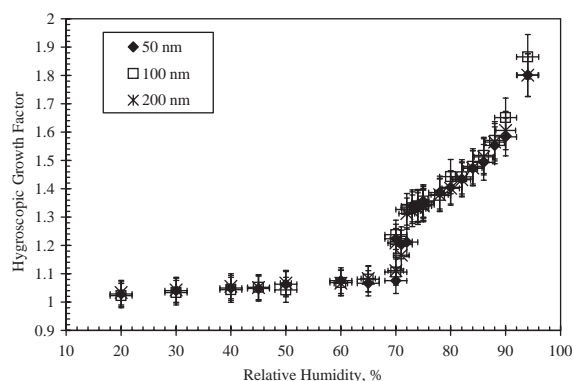
Fig. 1. Water uptake for Fluka HA particles at 30°C. Results for 50, 100, and 200 nm diameter particles are shown in filled diamonds, open squares, and asterisks, respectively.
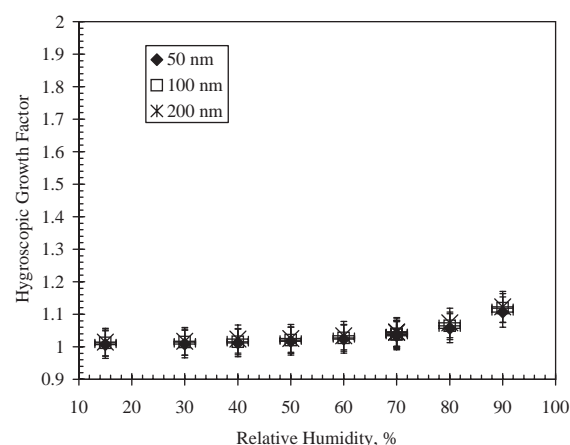

Fig. 2. Water uptake for Pahokee Peat Reference HA particles at 30°C. Results for 50, 100, and 200 nm diameter particles are shown in filled diamonds, open squares, and asterisks, respectively.
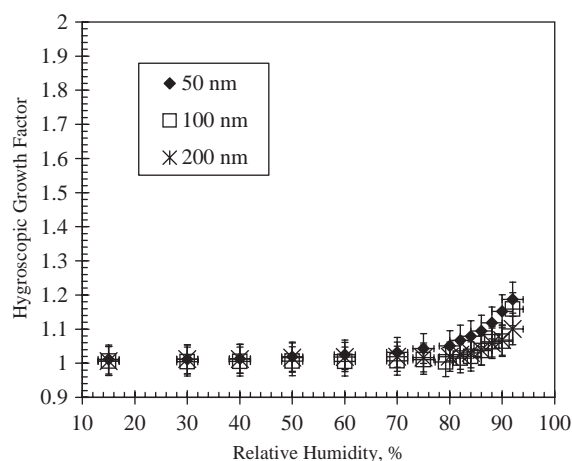

Fig. 3. Water uptake for Leonardite Standard HA particles at 30°C. Results for 50, 100, and 200 nm diameter particles are shown in filled diamonds, open squares, and asterisks, respectively.

dependence expected based on Köhler theory for particles composed of ionic solutions of similar hygroscopicity and to the experimental observations for ammonium sulfate particles (Brechtel and Kreidenweis, 2000a, b). However, both the theoretical and previously measured size dependencies are within the uncertainty in our experiment.

Fig. 2 shows water uptake by Pahokee Peat Reference HA obtained from IHSS. Uptake studies were again conducted for 50, 100, and 200 nm diameter particles. For the three sizes studied, there is no water uptake observed at RHs below ∼50%. Above 50% RH, there is a very small amount of uptake which increased continuously with increasing RH. However, unlike the Fluka HA, there is no abrupt change in uptake at any RH, indicating that Pahokee Peat HA does not contain significant concentrations of deliquescent materials.

Once again, the uptake behavior for the 50, 100, and 200 nm diameter particles is indistinguishable.

The hygroscopic growth of 50, 100, and 200 nm diameter particles of Leonardite Standard HA obtained from IHSS is shown in Fig. 3. As can be seen in the figure, the 50 nm particles begin to take up water at a lower RH (∼70%) and take up slightly more water at higher RH than the larger particles. These differences are within the experimental uncertainty. The 50 nm particles may have a somewhat different composition, i.e. an insoluble component may be included in particles generated at 100 and 200 nm, but excluded from the more hygroscopic 50 nm diameter particles. Alternatively, the observed initial decrease in growth factor could be attributed to microstructural rearrangement, as described in Mikhailov et al. (2003). Specifically, partial dissolution of the crystal surface may cause irregularly shaped particles to become near-spherical. While the mass equivalent diameter remains unchanged, the mobility equivalent diameter and hygroscopic growth factor are reduced. Mikhailov et al. calculated that the reduction in growth factor they observed is roughly equivalent to the calculated change from a cubic to spherical structure. Furthermore, it is possible for morphology effects to be more pronounced in the larger particles, as observed by Mikhailov et al. in the cases of 100 and 200 nm NaCl particles. In these cases, the irregular dry particles have equivalent diameters smaller than 100 or 200 nm, resulting in an underestimation of *G*. This may explain why we observed lower apparent values of *G* for the 100 and 200 nm Leonardite HA particles than for the 50 nm particles.

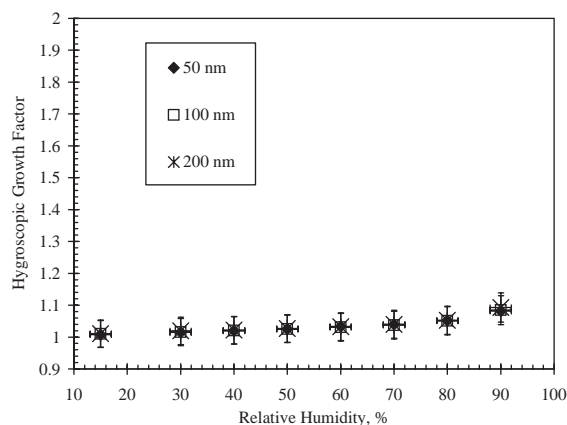We also studied the water uptake behavior of FA obtained from IHSS, collected from the Suwannee River

Fig. 4. Water uptake for Suwannee River Reference FA particles at 30°C. Results for 50, 100, and 200 nm diameter particles are shown in filled diamonds, open squares, and asterisks, respectively.
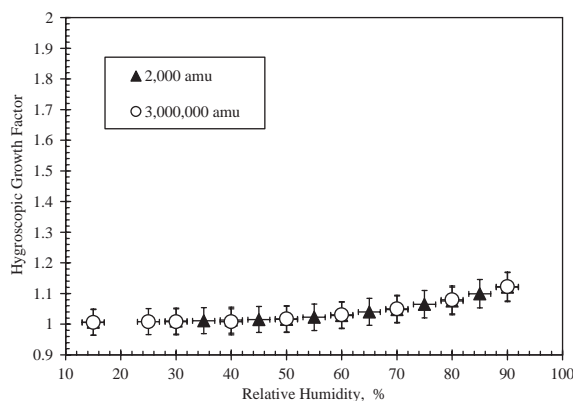

Fig. 5. Water uptake for 100 nm PAA particles at 30°C. Results for PAA with molecular weights of 2000 amu and 3,000,000 amu are shown as filled triangles and open circles, respectively.

in the Okefenokee Swamp in Georgia. This FA was purified in the same way as the IHSS HAs. The hygroscopic growth factor of the FA is shown in Fig. 4. The FA takes up a minimal amount of water over the range of RH studied (up to and including 90% RH). As in the Pahokee Peat HA, there is no evidence of size dependence within the 50–200 nm size range.

3.3. Water uptake by representative species

While the molecular structure of HA is not known in detail, several models have been proposed. Avena et al. found that the volume and structure of HA are similar to flexible synthetic PAAs (Avena et al., 1999). For comparison, we next investigated the water uptake capabilities of two PAAs. PAAs are long flexible chain polymers with a basic unit structure comprised of a carboxylic acid bonded to the saturated carbon backbone. There is one CH_2 in the chain between each basic unit. Synthetically produced PAAs with a range of molecular weights were obtained from Sigma-Aldrich. We investigated the water uptake characteristics of two PAAs with average molecular weights of 2000 amu and 3,000,000 amu, which correspond to ~ 30 and $\sim 44,000$ basic units, respectively. The hygroscopic growth of monodisperse 100 nm particles of each PAA is shown in Fig. 5. As can be seen, each of these took up very little water for the humidity range studied, with chain length having no effect on water uptake. Quantitatively, the water uptake by the PAAs is very similar to the uptake by the Pahokee Peat Reference HA, the Leonardite Standard HA, and the Suwannee River FA.

In addition, metal binding sites such as salicylic acid and phthalic acid have been identified in HAs (Gamble et al., 1980). For comparison, we also investigated the
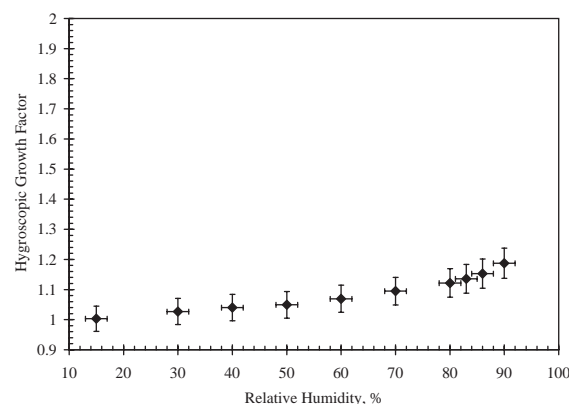

Fig. 6. Water uptake for 100 nm phthalic acid particles at 30°C.

water uptake by 100 nm phthalic acid particles (Fig. 6). The phthalic acid particles took up slightly more water than the other species studied, with the exception of the Fluka HA. However, overall this uptake was very similar to the HMs. It is likely that within the humic structure, some water is taken up both by the chain itself and by the phthalic acid binding sites.

3.4. Water uptake by mixed HM/ammonium sulfate aerosol

Next we studied water uptake by particles of mixed HM/ammonium sulfate compositions. For these studies, solutions of 50 wt% and 9 wt% HM with ammonium sulfate were atomized with constant stirring. While the FA is water soluble, the HAs studied here are not completely soluble. An additional complication is that some of the insoluble material may be atomized as well.

Thus, the composition of the particles may be different than in the atomized solution.

To determine the atomizing efficiency and the actual dry wt% HM, we conducted 2 additional measurements for each mixture. First, solutions identical to those used for the HTDMA experiment were atomized under the experimental conditions and collected in glass vials for ∼8 h. Next, 5 ml of distilled water were added to each vial. Separate measurements were made to determine the carbon and ammonium sulfate content in the resulting solutions. Carbon content (grams C ml^{-1} solution) was measured using a Shimadzu 5000A total organic carbon (TOC) analyzer. The TOC analyzer measures the total carbon (organic + inorganic) in the sample. The dry wt% carbon in each HM was obtained from the supplier. The concentration of HM is calculated as follows:

$$
\begin{array}{ccc}
& \text{from TOC} & \text{from elemental analysis} \\
\text{g HA ml}^{-1} = & (\text{g C ml}^{-1}) \quad \times & (\text{g HM gC}^{-1}).
\end{array}
$$
(1)

To quantify the ammonium sulfate in the sample, we used a Dionex CD20 ion chromatography (IC) system to separate the components and to quantify the sulfate in each sample. Assuming all sulfate present is in the stoichiometric proportions of ammonium sulfate, we calculate the concentration of ammonium sulfate (grams $(NH_4)_2SO_4$)/ml solution). Next we ratio the HM concentration to the total concentration of $(NH_4)_2SO_4$ and HM to obtain the actual dry wt% HM in the solutions studied here, assuming there is uniformity in actual composition among different particle sizes. The results are summarized in Table 1. Listed next to the solution wt% are the actual values as determined here. Errors based on the combined uncertainties in these three measurements used to compute actual wt% are ±14%.

We next test whether the water uptake by the mixed HM/ammonium sulfate particles can be predicted based on the measured properties of the single components. We use the following expression to model the hygroscopic growth factor of the HM, G_O, as a function of RH for the pure HMs (Dick et al., 2000):

$$
G_O = \left[1 + (a + b(\text{RH}*0.01) + c(\text{RH}*0.01)^2) * \frac{\text{RH}}{100 - \text{RH}} \right]^{1/3}.
$$
(2)

Fit parameters for 100 nm particles of each composition are shown in Table 2. Since this expression is intended for continuous uptake curve behavior, this expression does not represent the data well over the full range of RH for particles which do not exhibit continuous uptake. For this reason, the expression given by Eq. (2) is not appropriate for the Fluka and Leonardite HA cases. Instead, we use experimental

Table 2
Fit parameters for hygroscopic growth factor by 100 nm particles in Eq. (2)

Composition	a	b	c
Humic acids			
Fluka Chemical	−0.88856	3.2694	−2.0499
Pahokee Peat Reference	0.13873	−0.18862	0.09398
Leonardite Standard	0.32298	−0.98088	0.73224
Fulvic acid			
Suwannee River Reference	0.18593	−0.26648	0.10447
Other compounds			
Polyacrylic acid (2000 MW)	−0.03719	0.34295	−0.25686
Polyacrylic acid (3,000,000 MW)	−0.03507	0.33969	−0.27628
Phthalic acid	0.14911	0.16643	−0.27715

values taken at each RH as inputs into the equation below, rather than the fit described here.

Next we assume that the water content for each of the components can be treated independently, i.e. the Zdanovskii, Stokes, and Robinson (ZSR) assumption, and that the volumes are additive (Seinfeld and Pandis, 1998). We calculate the hygroscopic growth factor of the mixed particles, G_M, according to the following expression:

$$
G_M = (\varepsilon_O G_O^3 + \varepsilon_{IN} G_{IN}^3)^{1/3},
$$
(3)

where G_O is the hygroscopic growth factor of 100 nm organic particles, G_{IN} the hygroscopic growth factor of 100-nm inorganic particles, ε_O the organic volume fraction, and ε_{IN} the inorganic volume fraction.

This expression has been used by others to model the behavior of particles of mixed composition (Cruz and Pandis, 2000; Prenni et al., 2003). To determine the volume fractions, we first convert our mass ratio to a volume ratio. Here densities of 1.8, 0.8, and 1.06 g cm^{-3}, based on bulk density measurements, were used for the ammonium sulfate, the HMs, and the PAAs, respectively (Yates III and Wandruszka, 1999).

The water uptake of internally mixed 100 nm particles containing 10 and 53 wt% Fluka HA is shown in Fig. 7. For comparison the predicted behavior of 100 nm ammonium sulfate particles following Köhler theory, using solution property data from DeMott et al. (1994) and water activity from Clegg et al. (1998), and for mixed particles of each wt% HM, following Eq. (3), are also shown in the figure. Recall that Eq. (2) cannot be used to determine G_O for the Fluka HA case. In this case, we relay on data obtained in the pure Fluka HA experiment for inputs of G_O as a function of RH. We also assume that the deliquescence of each of the components was assumed to remain unchanged in the mixture. As can be seen in the figure, adding Fluka HA
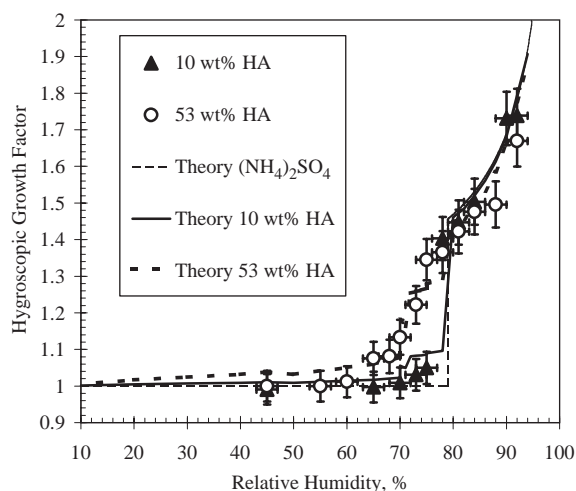
Fig. 7. Water uptake for 100 nm Fluka HA/$(NH_4)_2SO_4$ particles at 30°C. Results for particles containing 10 and 53 wt% HM are shown as filled triangles and open circles. The uptake predicted from theory for pure ammonium sulfate, 10 wt%, and 53 wt% HM are shown as long-dashed, solid, and short-dashed lines, respectively.

Fig. 8. Water uptake for 100 nm Pahokee Peat Reference HA/$(NH_4)_2SO_4$ particles at 30°C. Results for particles containing 2 and 13 wt% HM are shown as filled triangles and open circles. The uptake predicted from theory for pure ammonium sulfate, 2 wt%, and 13 wt% HM are shown as long-dashed, solid, and short-dashed lines, respectively.

causes the particles to begin to take up water at a lower RH, 60–65% RH, than ammonium sulfate particles do. The 53 wt% Fluka HA takes up water in two distinct steps. We attribute the first deliquescence step at 65% RH to a component of the HA and the second step at ~78% RH to the ammonium sulfate. Similar dual step-wise increases in RH have been observed at 69% and 80% RH by Tang et al. for particles composed of sulfuric acid and ammonium sulfate (Tang et al., 1978). In that experiment, the authors concluded that the acid reacted with some of the ammonium sulfate, forming letovicite, $(NH_4)_3H(SO_4)_2$. While no sulfuric acid is introduced in the isolation process of Fluka HA, hydrochloric acid is used. The HCl may convert some of the ammonium sulfate to letovicite in a similar fashion. Alternatively, a component of the naturally occurring HA may independently deliquesce at 70% RH, as observed in the pure HA experiment. The modeled water uptake agrees with the observed behavior within experimental error. This confirms that the behavior of these mixed particles can be adequately predicted based on the hygroscopicity of the individual components.

Above the deliquescent point of ammonium sulfate, ~77% RH at 30°C, the 53 wt% mixed aerosol exhibits hygroscopic growth which is the same as the predicted growth for ammonium sulfate, within experimental error. This results since the hygroscopic growth of the HA at high RH is similar to that of ammonium sulfate. The predicted uptake for both compositions agrees with the experimentally observed uptake at all RHs.
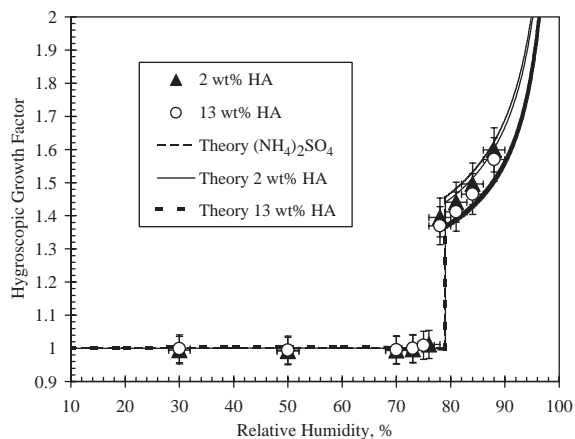
In Fig. 8, the measured and predicted water uptake by 100 nm particles containing 2 and 13 wt% Pahokee Peat HA with ammonium sulfate is shown. As can be seen, adding up to 13 wt% Pahokee Peat HA slightly reduces the water uptake above the deliquescence RH of ammonium sulfate. While the measured uptake by 13 wt% HA is slightly higher than predicted, predictions and measurements agree within error for both mixed compositions.

The water uptake by 100 nm particles containing 2 and 13 wt% Leonardite Standard HA with ammonium sulfate is shown in Fig. 9. Experimentally measured G_Os for the HA were used as inputs into Eq. (3) here, instead of the fit from Eq. (2). In the mixed particles, the presence of the HA causes a small amount of water uptake prior to 80% RH. The G_O at ≥80% RH was slightly reduced by the HA, relative to pure ammonium sulfate. Again, the predicted water uptake agrees with the experimental data within error.

Finally, the water uptake for 100 nm Suwannee River Reference FA/ammonium sulfate particles is shown in Fig. 10. The compositions studied here were 8 and 44 wt% FA. The 44 wt% FA sample was generated by atomizing a 50 wt% solution. Interestingly, in the 44 wt% FA experiment, at RHs just prior to deliquescence, i.e. RH = 70–80%, the hygroscopic growth factor was <1. This was repeated in three separate experiments on three separate days, with reproducible results. While this reduction in the hygroscopic growth factor was reproducible, G was consistent with 1 within error. As discussed with regard to the Leonardite HA results above, this initial decrease in growth factor may be attributed to microstructural rearrangement upon
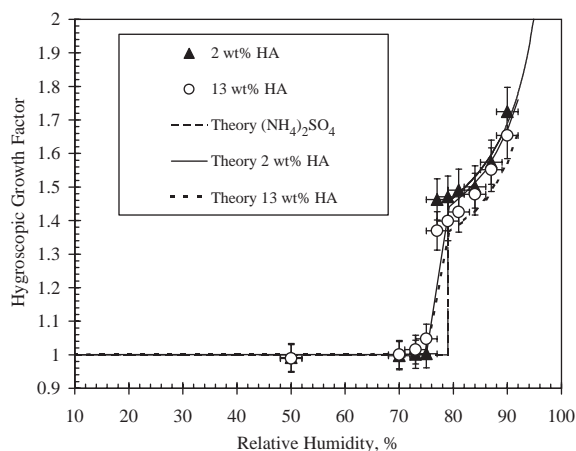
Fig. 9. Water uptake for 100 nm Leonardite Standard HA/$(NH_4)_2SO_4$ particles at 30°C. Results for particles containing 2 and 13 wt% HM are shown as filled triangles and open circles. The uptake predicted from theory for pure ammonium sulfate, 2 wt% and 13 wt% HM are shown as long-dashed, solid, and short-dashed lines, respectively.
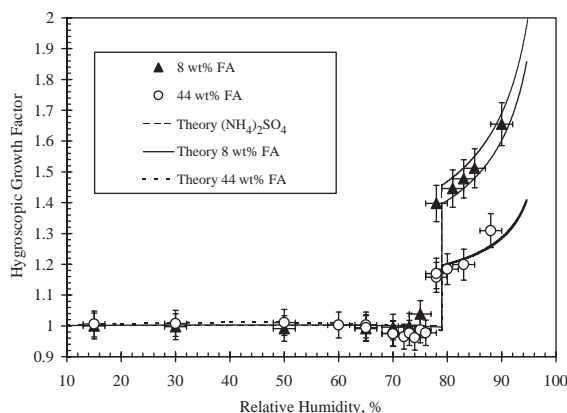

Fig. 10. Water uptake for 100 nm Suwannee River Reference FA/$(NH_4)_2SO_4$ particles at 30°C. Results for particles containing 8 and 44 wt% HM are shown as filled triangles and open circles. The uptake predicted from theory for pure ammonium sulfate, 8 wt%, and 44 wt% HM are shown as long-dashed, solid, and short-dashed lines, respectively.

addition of water. The predicted and experimental Gs agree within error with one exception. The outlying data point taken at 90% RH for the 44 wt% sample is higher than theoretically predicted.

For comparison, mixed particles containing 9 and 50 wt% PAA with ammonium sulfate were also studied (Fig. 11). Here we considered only the 2000 amu PAA, as a molecular weight of 2000 amu is more representative of the size of HAs. We see that the inclusion of 50% by weight PAA reduced $G - 1$ by $\sim 50\%$ relative to pure ammonium sulfate.
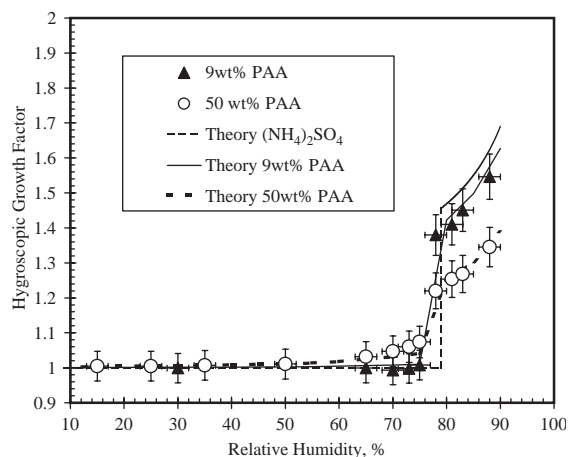

Fig. 11. Water uptake for 100 nm diameter PAA/$(NH_4)_2SO_4$ particles at 30°C. Results for particles containing 9 and 50 wt% PAA are shown as filled triangles and open circles. The uptake predicted from theory for pure ammonium sulfate, 9 wt%, and 50 wt% PAA are shown as long-dashed, solid, and short-dashed lines, respectively.

4. Summary and conclusion

In summary, the hygroscopicity of all investigated IHSS samples is similar, while the sample obtained from Fluka is distinctly more hygroscopic, comparable to ammonium sulfate. The low water uptake observed in the IHSS cases is comparable to phthalic acid and the PAAs. Interestingly, the amount of water taken up here is significantly less than the uptake by soluble dicarboxylic acids (Prenni et al., 2001), although like the dicarboxylic acids, growth was a continuous function of RH. The IHSS samples contain only the organic acid component of naturally occurring materials. We conclude that the polycarboxylic acids found in HMs are not very hygroscopic. In contrast, the Fluka HA exhibits an abrupt deliquescence point at 70% RH, suggesting that the presence of a salt, such as HA sodium salt. Also, the Fluka sample takes up much more water than the other samples at 70–80% RH. While these differences may be attributed to properties of the naturally occurring materials due to differences in the origin of the source materials, it is most likely that the differences may arise due to different isolation methods, i.e. the IHSS isolation procedure includes a desalting step whereas the Fluka procedure does not. From this comparison, we conclude that it is imperative that the isolation method of the material must be considered when the effects of HMs on atmospheric aerosols are considered.

For the pure HMs studied, no size dependence was observed, with one exception, the Leonardite Standard HA. The 50 nm Leonard HA particles began to take up water at a lower RH and took up more water at higher

RH than the 100 and 200 nm particles. This suggests that in the Leonardite case, composition may have varied with particle size generated in these experiments or that size dependent changes in morphology may occur as the RH is increased. In the other cases, the lack of size dependence in the hygroscopic growth data may indicate that the surface tension of the solutions is much less than that of pure water or aqueous sulfate solutions. Measurements of the surface tension and composition of single particles of various sizes would be helpful in understanding these results.

The behavior of the mixed HM/ammonium sulfate samples also varies greatly with the isolation method of the material. For mixed ammonium sulfate/IHSS-derived humic particles, G was significantly reduced relative to pure ammonium sulfate. In contrast the addition of 53 wt% Fluka HA to ammonium sulfate caused some water uptake at a lower RH, 60–65%, than pure sulfate. The model prediction for 53 wt% Fluka HA/ammonium sulfate showed uptake at 65–70% RH and further uptake at 80% RH. The uptake above 80% RH was nearly identical to the uptake by pure ammonium sulfate particles. In all cases, the experimental and predicted behaviors agreed reasonably well which suggests that the ZSR relation may be sufficient for present modeling purposes.

Overall, we have shown that the presence of HMs affects the water uptake by atmospheric aerosols. The results vary with the type of HM investigated. Further investigation is necessary to determine the cause of these differences. In the future, care must be taken in comparing results from laboratory studies of HMs of different type, location of origin, and isolation method.

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