

Water content of ambient aerosol during the Pittsburgh Air Quality Study

Andrey Khlystov

Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina, USA

Charles O. Stanier, Satoshi Takahama, and Spyros N. Pandis

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, USA

Received 16 February 2004; revised 4 June 2004; accepted 22 June 2004; published 3 March 2005.

[1] The aerosol water content and volumetric growth factors of fine particulate matter were measured during July–August 2001 and January–June 2002 in an urban park about 6 km from downtown Pittsburgh, Pennsylvania. Most of the aerosol during the study was transported to the region from other areas, and its composition and concentration were characteristic of the regional particulate matter in the northeastern United States. During the summer months the ambient aerosol practically always contained water even when the relative humidity (RH) was as low as 30%. In contrast, during the winter the aerosol was dry below 60% RH. The spring months were characterized by a transitional behavior between these two states. The observed seasonal behavior can be explained by the aerosol acidity. The summer aerosol was acidic and retained water at low RH. The winter aerosol was neutral and became wet when the relative humidity reached the deliquescence point of ammonium nitrate. The observations during July 2001 were compared with the predictions of the thermodynamic Gibbs Free Energy Minimization (GFEMN) model and the aerosol inorganics model (AIM), neglecting the organic aerosol contribution to water absorption. The models under-predicted water concentrations by about 35%, but no clear correlation between organic mass and the excess water was observed. On average, the contribution of the organics to water absorption appeared to be higher during the afternoon hours and when the aerosol was presumably more oxidized.

Citation: Khlystov, A., C. O. Stanier, S. Takahama, and S. N. Pandis (2005), Water content of ambient aerosol during the Pittsburgh Air Quality Study, *J. Geophys. Res.*, 110, D07S10, doi:10.1029/2004JD004651.

1. Introduction

[2] Absorption of water by aerosol particles has a major effect on their physical and chemical properties. Water increases particle size and thus affects its lifetime. The light scattering and, consequently, the visibility reduction and direct climate forcing by the aerosol particles depend strongly on their water content [Ramaswamy, 2001]. The presence of water changes the partitioning of semivolatile species between the gas and aerosol phase and affects the particle composition [Ansari and Pandis, 2000]. In addition, aerosol water provides a medium for heterogeneous chemical reactions in the atmosphere.

[3] The hygroscopic behavior (absorption of water) of aerosol particles exhibits a hysteresis. A dry single-salt particle becomes wet at a certain relative humidity, the so-called deliquescence relative humidity. For example, the deliquescence point of ammonium sulfate at 25°C is at approximately 80% RH [Tang and Munkelwitz, 1994]. After becoming wet, the particle will absorb more water if the relative humidity is increased. If the relative humidity is

then decreased, the particle will release some of the absorbed water to equilibrate with the new conditions. However, if the relative humidity is decreased below the deliquescence point, the particle will not crystallize but it will remain wet until a substantially lower RH, 35–40% for ammonium sulfate. Most other inorganic species present in the ambient aerosol have a similar behavior [Tang, 1997]. Because of the hysteresis effect even for ammonium sulfate particles there is a wide range of relative humidity (40–80%) within which the physical state (dry or wet) of the ambient particles is not known. The crystallization point of the ambient aerosol is also uncertain. It has been shown that the presence of other components such as minerals can affect the crystallization relative humidity [Han *et al.*, 2002; Martin *et al.*, 2001]. Organic compounds may also affect deliquescence and crystallization points of inorganic salts [Choi and Chan, 2002]. All of this leads to uncertainties in predicting aerosol properties that depend on absorbed water, including partitioning of semivolatile compounds and light scattering.

[4] In addition to the uncertainty in the physical state of the particles, there is difficulty in predicting the amount of water that would be present in the aerosol phase at given atmospheric conditions. The difficulty arises from the

multicomponent nature of the aerosol and high concentrations of dissolved species. The role of the organic compounds in water absorption is especially uncertain, with a number of recent investigations reaching differing conclusions regarding the role of organics in water uptake. *Saxena et al.* [1995] reported that organics at a remote continental location increased water absorption by 30% or so at 85% relative humidity, while at an urban location, organics decreased overall water absorption by approximately 30% at 85% RH. *Dick et al.* [2000] reported, for a rural continental site, organics contributed significantly to water uptake at relative humidity below 50% and less significantly at higher relative humidity. In a modeling study, *Ansari and Pandis* [2000] estimated that a high loading (35% by mass) of secondary organic compounds increased water content by about 20% at 50% relative humidity, with smaller effects at higher relative humidity. Laboratory studies by *Cruz and Pandis* [2000] and *Choi and Chan* [2002] have demonstrated that the presence of organic substances in the mixed particles may either reduce or enhance water absorption by inorganic salts.

[5] The hygroscopic aerosol growth is usually studied with humidified tandem differential mobility analyzers (H-TDMAs). H-TDMAs select a narrow size range of particles and subject it to a certain relative humidity, after which the sizes of the grown particles are measured [*Cocker et al.*, 2001; *Rader and McMurry*, 1986; *Swietlicki et al.*, 1999]. The H-TDMA studies show that particles are often externally mixed with respect to their water absorption properties, i.e., there are more hygroscopic and less hygroscopic fractions. The number of fractions and their behavior varies with time, place and size [*Cocker et al.*, 2001]. The H-TDMA studies, however, can provide information on the hygroscopic properties of only a few size classes and they do not measure directly the aerosol water concentration. *Nessler et al.* [2003] have measured aerosol size distributions at ambient and indoor (heated and dry) conditions to investigate size changes due to the hygroscopic growth of the entire size spectrum. The observed shift of the distribution was consistent with the measured growth factors using an H-TDMA. However, due to the heating, considerable losses of particles smaller than 100 nm were observed.

[6] In this study we have used the recently developed dry and ambient aerosol size spectrometer (DAASS) that measures aerosol size distributions at ambient and low (<35% RH) relative humidity conditions without substantial changes in sample temperature [*Stanier et al.*, 2004]. The DAASS provides information on the effect of ambient humidity on the whole size distribution, the volumetric growth factors and the amount of water present in the aerosol phase. Here we report our observations using the DAASS during the Pittsburgh Air Quality Study (PAQS).

2. Experiment

2.1. Sampling Site

[7] The measurements were carried out continuously during July–August 2001 and January–October 2002 at the central monitoring site of the PAQS located in an urban park, approximately 6 km from downtown Pittsburgh, PA. The city is located between the utilities and agricultural sources of the Midwest and the large urban centers of the

eastern United States. Roughly one kilometer of parkland exists between the site and the residential areas in the predominant upwind direction (south and west). The site was several hundred meters from any major sources.

[8] The average $PM_{2.5}$ mass concentration in the summer was $18.2 \mu\text{g}/\text{m}^3$ and $12.2 \mu\text{g}/\text{m}^3$ in the winter. Sulfate was the major aerosol constituent comprising over 45% of the $PM_{2.5}$ mass in the summer and 35% during the winter, while the organic material contributed approximately 20% and ammonium 15–17%. The contribution of nitrate during summer was small (less than 3%). However, during the winter it contributed 15% of $PM_{2.5}$ mass. The crustal material contributed 3–6% to $PM_{2.5}$ mass [*Rees et al.*, 2004].

[9] During the summer, long-range transport was the major secondary aerosol source. For example, concentrations of $PM_{2.5}$ mass, sulfate, ammonium, and organic carbon were measured to be the same within experimental error at six sampling locations in and around Pittsburgh separated by more than 300 km [*Tang et al.*, 2004]. However, less abundant species such as nitrate and elemental carbon were more affected by the local emissions. The contribution of local sources was stronger during winter than in summer.

2.2. DAASS

[10] Measurements of water content of ambient aerosol and its hygroscopic growth were made using a dry and ambient aerosol size spectrometer (DAASS), which is described in detail by *Stanier et al.* [2004]. The DAASS measures alternatively the aerosol size distribution at ambient and at low RH ($18 \pm 5\%$) conditions (referred to as ambient and dried, respectively). A comparison of the dried and ambient distributions provides information on both the amount of absorbed water and the change in aerosol size with RH. The amount of absorbed water can be calculated from the difference in the aerosol volumes at ambient conditions and at the low RH state. The changes in size can be deduced from the mass or number mean diameters, shifts in the position of different modes in the distribution, etc.

[11] The DAASS consists of two SMPS (TSI 3936N25 and TSI 3936L10, TSI Inc.) and an APS system (TSI 3320, TSI Inc.) that measure the aerosol size distribution in the range of 3 nm to 10 μm . The APS and the SMPS data were merged using the algorithm of *Khlystov et al.* [2004]. During the dried measurements the sample flow and the sheath flows of the instruments were directed through a set of nafion driers (Permapure MD-110, Toms River, NJ) such that the relative humidity was reduced below 25% while the temperature remained virtually unchanged. Multichannel dryers (Permapure PD-50T and PD-200T) were used in the sheath lines of the instruments. During the ambient measurements the dryers were bypassed and the aerosol was directed to the instruments at conditions close to the ambient. The switching between the dried and ambient measurements was accomplished by means of computer-controlled 3-way solenoid valves. Four alternating dried and ambient measurements each were made during one hour.

[12] To avoid large deviations from the ambient conditions in temperature and, thus, relative humidity the DAASS was placed in a 3.6 m^3 plywood enclosure on the roof of the central sampling station of the PAQS in Pittsburgh, PA. The

enclosure was actively ventilated with a large 35 m³/min fan. Despite the precautions taken, the temperature of the system was about 4°C higher than the ambient during July 2001. During that time the ambient scans reached only approximately 80% of the ambient relative humidity (e.g., outdoor relative humidity of 95% yielded an ambient channel RH of around 76%). Starting August 2001, the DAASS was modified by placing the DMA columns of the SMPS systems outside the enclosure with fans pulling ambient air over them. This way aerosol classification was done very close to the ambient temperature and the system achieved greater than 90% of ambient relative humidity (e.g., outdoor relative humidity of 95% yielded an ambient channel RH of greater than 86%). The discrepancy in RH was due to the inlet and sheath lines being still inside the enclosure. The RH of the measurements will be used for the reporting of the data and the analysis in the rest of the paper.

[13] During winter, the enclosure was maintained at a minimum temperature of 9°C which was required for the correct operation of the condensation particle counters. This did not significantly affect the final sheath and aerosol relative humidity because the DMA columns were outside the enclosure at (or close to) the outdoor temperature. However, the aerosol flow did pass through the heated enclosure, which exposed the aerosol to a lower than ambient RH. Even though this did not affect the RH of the measurements, it might induce crystallization of aerosol at low RH. For this reason, the lowest RH encountered by the aerosol within the system is taken into account during the analysis of the data.

[14] Uncertainties in the DAASS measurements are described in detail by *Stanier et al.* [2004]. For an accurate determination of the water amount in the aerosol phase it is important that there is no significant bias between the dried and ambient channels of the DAASS. It was shown that no such significant bias exists and the number concentrations of the channels are within 5% of each other. The other sources of error are associated with the differences in temperature between aerosol charging and actual measurements during winter months when the ambient temperature was below 9°C. The magnitude of this error was estimated using the study average size distribution and a composition of 50% ammonium sulfate and 50% organics and other nonhygroscopic aerosols. It was shown that at low ambient RH (around 50%) the volume growth factor is biased positively by about 3%. The maximum error is expected at low temperatures and high relative humidity conditions. For example, in the worst-case scenario, at -5°C and 92% RH, the error in the wet aerosol state is estimated to be 14% [*Stanier et al.*, 2004].

2.3. DAASS Data Reduction and Interpretation

[15] The DAASS data reduction is reported in detail by *Stanier et al.* [2004]. For this work we have calculated the amount of water in the aerosol phase and the volume-based growth factors. These calculations are described briefly below.

[16] The amount of aerosol water can be found from the comparison of integrated dried and ambient aerosol volumes. Assuming volume additivity, the increase in volume between the ambient and the dried measurements is proportional to the mass of absorbed water (the proportionality

factor being the density of liquid water). Consequently, the amount of absorbed water can be calculated as:

$$m_w = \rho_w(V_{wet} - V_{dried}), \quad (1)$$

in which m_w is the mass concentration of water, ρ_w is the density of liquid water, V_{wet} and V_{dried} are, respectively, the ambient and dried integrated volume concentrations. The assumption of volume additivity may introduce a small error, because the actual solution may deviate from ideal. However, the error due to the assumption of additivity is negligibly small [*Dick et al.*, 2000].

[17] When integrating the volume distributions to obtain V_{wet} and V_{dried} , the shift in aerosol size distribution due to the hygroscopic growth needs to be accounted for. This is done by iteration, searching for the size boundaries that satisfy the following criteria:

$$V_{wet} = \frac{\pi}{6} \int_{D_{w1}}^{D_{w2}} D^3 n_{wet}(D) dD, \quad (2)$$

$$V_{dry} = \frac{\pi}{6} \int_{D_{d1}}^{D_{d2}} D^3 n_{dry}(D) dD, \quad (3)$$

$$GF_v = \frac{V_{wet}}{V_{dry}}, \quad (4)$$

$$D_{w2} = D_{d2} \sqrt[3]{GF_v}, \quad (5)$$

in which GF_v is the volumetric growth factor, D is the particle size, $n_{wet}(D)$ and $n_{dry}(D)$ are the number-based ambient and dried size distributions, respectively, subscripts w and d correspond to the ambient and dried integration limits. To simplify calculations the lower integration limits (D_{d1} and D_{w1}) are set to be both equal to 5 nm. A more accurate calculation would require correcting the lower boundaries using equation (5), however, because of the negligible amount of aerosol mass below 10 nm, the error introduced by this simplification is insignificant.

[18] The amount of absorbed water was calculated from the DAASS measurements for the wet size range up to 2.5 μm (i.e., $D_{w2} = 2.5$ μm). This was done to allow a direct comparison of the amount of water to measured PM_{2.5} concentrations of individual chemical species. However, due to the frequent malfunction of the Aerosol Particle Sizer in the DAASS, consistent measurements of water content in the PM_{2.5} range are only available for July and August 2001. For the rest of the study the measurements extended only up to 0.5 μm in diameter (ambient size) and the comparison with PM_{2.5} measurements was not possible.

2.4. Complementary Measurements

[19] The amount of absorbed water as a function of ambient RH was related to the amount of water-soluble inorganic constituents and the amount of organic matter present in the PM_{2.5} aerosol. These aerosol constituents were measured in parallel to and at the same location as the

DAASS measurements. The measurements of chemical constituents are described by Wittig *et al.* [2004]. Aerosol sulfate and nitrate were measured with a denuder filter-pack system and at a higher time resolution with Rupprecht and Patashnick (R&P) models 8400S and 8400N (R&P Co., Albany, NY). The $PM_{2.5}$ aerosol nitrate and ammonium and the gas phase nitric acid and ammonia were measured with a steam sampler [Khlystov *et al.*, 1995]. Organic and elemental carbon content in the aerosol was measured with a denuder-filter pack system described by Subramanian *et al.* [2004] and at a higher frequency with a Sunset Labs in situ analyzer (Sunset Labs Co., Portland, Oregon). In addition to the measurements of the aerosol chemical composition, $PM_{2.5}$ aerosol mass was measured with a TEOM (Model 1400a, R&P Co, Albany, NY) that was operated at 30°C and with a naphion dryer to minimize losses of volatile material.

[20] Data from the different instruments were combined to form a best estimate of the corresponding concentration [Takahama *et al.*, 2004]. The instruments measuring the same component were intercompared and the outliers identified. After the outliers were removed, the high time resolution data were corrected such that their average over a sampling period produced the same value as the filter pack measurements. This was done because the denuder filter-pack techniques are generally considered to be the reference for newer and less widely tested high time resolution methods.

2.5. Estimation of Water Absorption by Organic Aerosol Fraction

[21] The observations during July 2001 (as a representative month for summer) were compared to the predictions of the thermodynamic models GFEMN [Ansari and Pandis, 1999] and AIM (<http://mae.ucdavis.edu/wexler/aim>) [Clegg *et al.*, 1998] in order to estimate the contribution of organic material to water absorption. Because $PM_{2.5}$ water content data are not available for months after August 2001, a direct comparison with $PM_{2.5}$ chemical data was only possible for the summer months and the modeling was limited to July 2001 only.

[22] The GFEMN and AIM models calculated the amount of aerosol bound water based on the measured relative humidity and the $PM_{2.5}$ aerosol concentrations of sulfate, nitrate and ammonium. The contributions of chloride and sodium to water absorption were neglected, because the concentrations of these compounds were negligible in comparison to the other components. Both models assumed that organic compounds do not contribute to water absorption. Thus any difference between the observations and the model predictions may be an indication of the influence of organics on the absorption of water.

[23] The models assumed that the aerosol is dry during the low RH measurement of the DAASS. The neutral aerosol, composed mostly of ammonium sulfate is expected to crystallize at the RH of the dried measurements, which did not exceed 25% RH. Only when the aerosol is acidic, i.e., contains ammonium bisulfate, the assumption may not be justified. However, even on those occasions the amount of water in the aerosol at the RH of dried measurements is expected to be small. For this reason, the amount of water in the aerosol during the dried measurements was assumed to

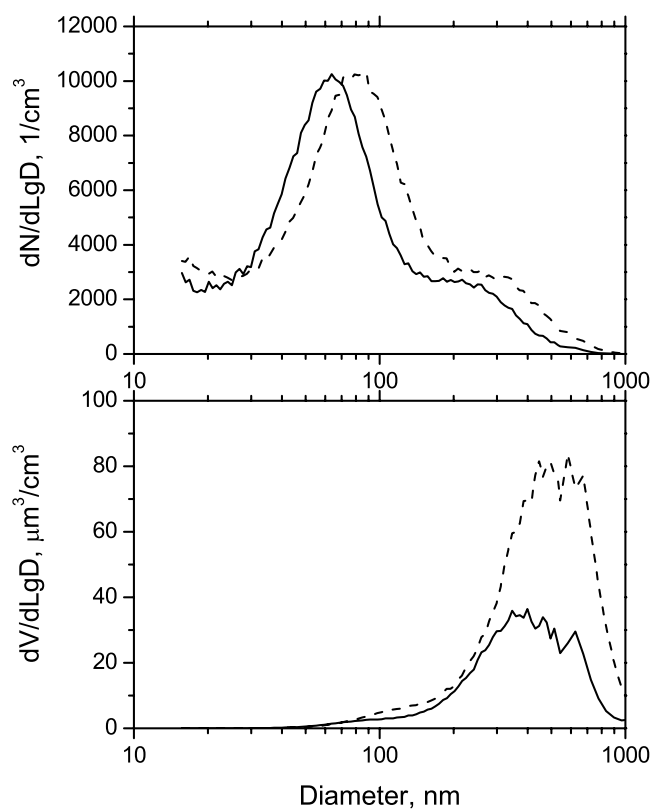


Figure 1. An example of the effect of relative humidity on the ambient aerosol size distribution measured on 1 July 2001 0130 EST, 73% RH. The solid lines represent the dried distributions, and the dashed lines are for the wet distributions.

be negligible. In addition, there is no reliable data available for the activities of aerosol components in water solution below 30% RH to accurately model the water content at such a low RH.

[24] A Latin hypercube sampling (LHS) routine [McKay, 1988] was used to estimate the uncertainty in the model output due to the uncertainties in the input variables (RH, ammonia, nitrate and sulfate). Owing to the computational intensity of the LHS routine the uncertainty of the model output was assessed only with the GFEMN. Normal distributions were chosen for the input variables, with coefficient of variation of 0.15 for sulfate, nitrate and ammonia, and 5% for RH. To avoid generating artificial correlations among the different input variables and to allow the statistics (e.g., mean and variance) of the output distribution to converge, a sampling size of 200 was selected. Thus for each input point the model simulated 200 possible scenarios according to the Latin hypercube sampling. These 200 points were then used to calculate the mean and the standard deviation, the latter being a measure of the model uncertainty due to the uncertainty in the input variables.

3. Results and Discussion

3.1. Aerosol Water Content

[25] The effect of relative humidity on the aerosol size distribution is shown in Figure 1. The number concentration

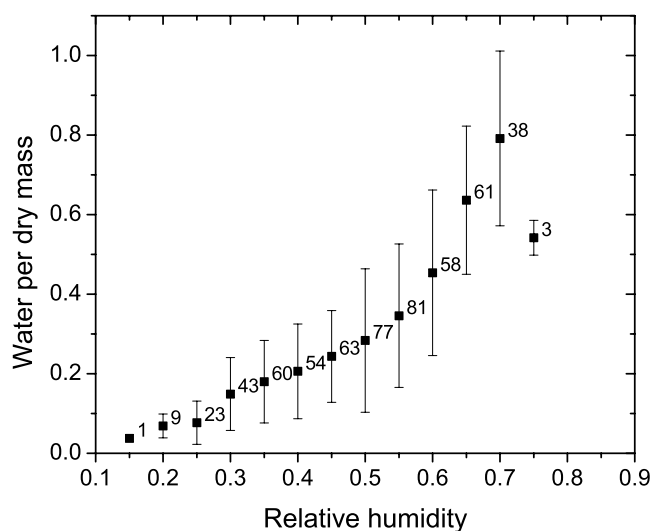


Figure 2. Mass of $PM_{2.5}$ aerosol bound water per $PM_{2.5}$ dry aerosol mass as a function of relative humidity during July 2001. The error bars indicate the standard deviation, and the labels show the number of observations per each point.

is preserved as well as the shape of the distribution. However, the wet distribution is shifted to larger sizes relatively to the dry distribution due to the hygroscopic growth of particles. The volume size distributions, shown on the lower panel of Figure 1, indicate that the volume concentration of the wet aerosol is larger than that of the dried aerosol, the difference being the amount of absorbed water, i.e., the aerosol water content.

[26] The aerosol water content shows a strong dependence on the ambient relative humidity. Figure 2 shows average ratios of $PM_{2.5}$ aerosol bound water to the dry mass of $PM_{2.5}$ aerosol measured with the TEOM during July 2001. At 70% RH approximately half of the ambient aerosol mass was composed of water. The point at 75% RH does not follow the overall trend because it represents only 3 observations during which the aerosol contained a relatively small fraction of water-soluble material (sulfate comprised 20% of the aerosol mass as compared to the average of 40%). Figure 2 also shows that in July 2001 aerosol contained water even at a relative humidity as low as 30%, at which point water constituted, on average, about 15% of the wet aerosol mass. As will be shown below, the presence of water at low relative humidities is characteristic of summer aerosol in the Pittsburgh area.

[27] The volume-based growth factors, GF_v , (the aerosol volume at ambient conditions divided by the volume at low RH) as a function of ambient RH during different months of the study are shown in Figure 3. A growth factor larger than one indicates that aerosol contains water. The aerosol was found to always contain water when the relative humidity is above 60%. However, the aerosol water content below 60% RH exhibits a seasonal behavior. The volume growth factors for summer months were practically always above one indicating that the aerosol contained water. Thus the summertime aerosol in the Pittsburgh area may be assumed to be always wet. During winter months, however, the volume

ratios at RH below about 60% did not differ from unity within experimental error most of the time (90% of observations), indicating absence of aerosol bound water. The spring months show a transitional behavior: the fraction of observations when the GF_v is higher than 1 below 55% RH progressively increases from March to May (Figure 4).

3.2. Aerosol Crystallization and Aerosol Acidity

[28] The seasonal behavior of the presence of aerosol-bound water below 60% RH follows that of the aerosol acidity in the Pittsburgh area. The average ammonium to sulfate ratio (moles ammonium to moles sulfate) in summer is 1.4 which corresponds to an approximately equal mixture of ammonium sulfate, $(NH_4)_2SO_4$, and ammonium bisulfate, $(NH_4)HSO_4$ [Rees *et al.*, 2004]. The ammonium bisulfate crystallizes at 0–22% RH [Tang and Munkelwitz, 1994]. Such low relative humidities did not occur during the study to induce crystallization. However, the ambient RH often exceeds its deliquescence point, 40% [Tang and Munkelwitz, 1994]. Even if the ambient RH at the ground level is lower than 40%, the deliquescence point of ammonium bisulfate may be reached at the upper layers of the boundary layer. Thus the particles during their lifetime (a few days) have multiple chances to become hydrated. In contrast to summer, the ammonium to sulfate mole equivalent ratio in winter is higher than 2 indicating that all of sulfate is neutralized by ammonium. The ratio is higher than 2 because some of ammonium is bound to nitrate forming ammonium nitrate. Sulfate is thus in the form of ammonium sulfate that crystallizes at about 40% RH, which is frequently encountered during the daytime in the mixed boundary layer. Spring months exhibit a transitional behavior as the aerosol becomes progressively more acidic.

[29] The monthly average aerosol acidity is not representative for all observation points: the aerosol was not always acidic and there were periods when it was neutral. However, it appears that most periods of low RH (below 40%) are associated with acidic conditions. For illustration purposes we consider one week in July 2001. Figure 5 shows the ambient RH, the GF_v and the periods during which the aerosol was acidic (i.e., had anion to cation mol-equivalent ratio larger than one). During the periods when the RH was close or below 40% (in the afternoon hours of most days), the aerosol was acidic and thus was able to retain some water ($GF_v > 1$). The only period when the aerosol appears to crystallize ($GF_v \sim 1$) was on 13 July, when the RH decreased from 90% to around 40% and the aerosol was neutral.

3.3. Error Analysis

[30] The consistent presence of water ($GF_v > 1$) during the summer could be a result of a loss of semivolatile aerosol components during the drying process. Even though the temperature is kept close to the ambient, a lower RH may cause evaporation of a volatile species, such as ammonium nitrate. The dried volume concentration will be then biased low relatively to the wet measurements, and the GF_v will be thus above 1. This problem, however, should be small during the summer months, as the ammonium nitrate content was only 3% of the total $PM_{2.5}$ mass on average. The loss of semivolatile organic material, on the other hand is hard to quantify, because the volatile fraction

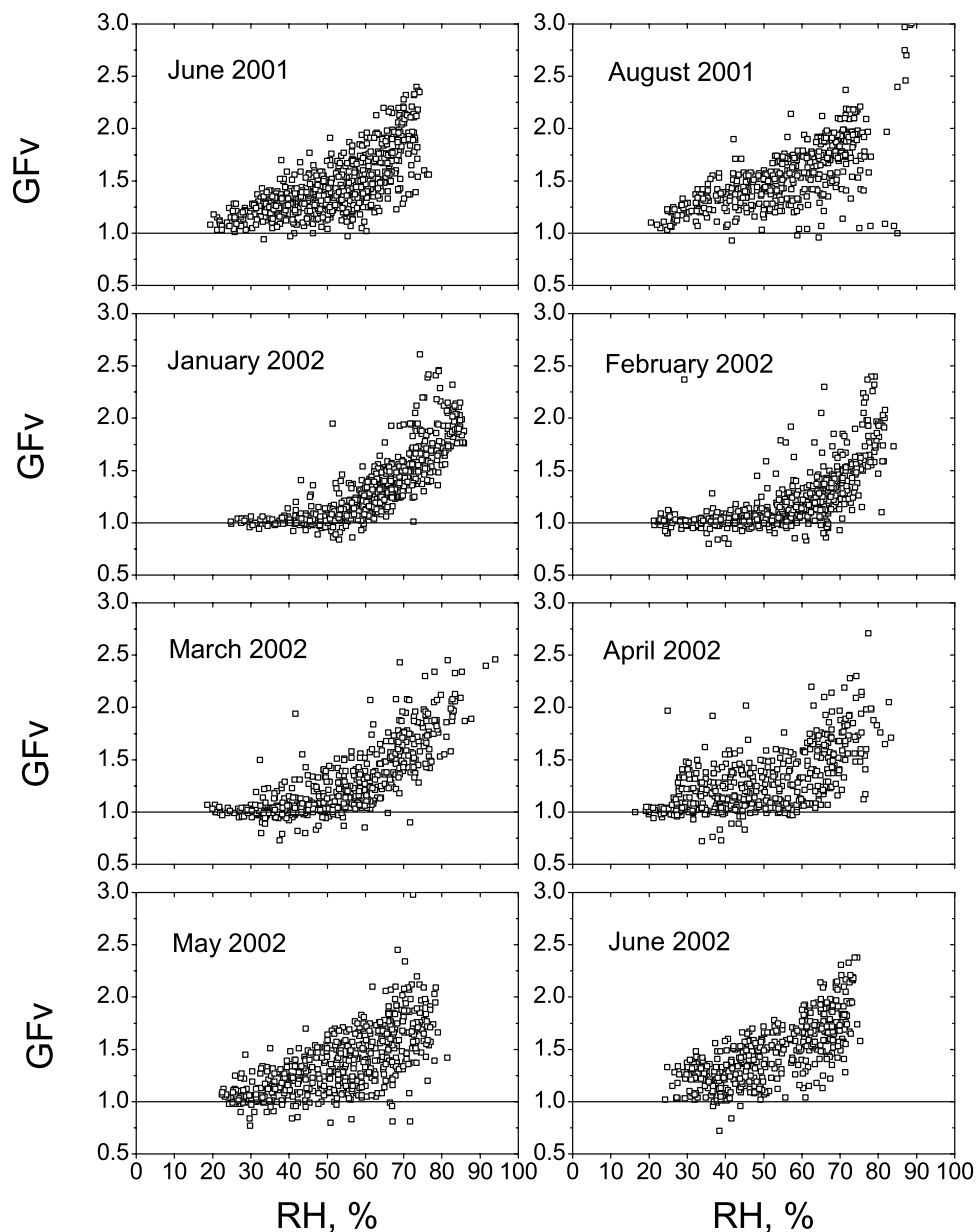


Figure 3. Measured volume growth factors during different months of the study. Each point corresponds to a one-hour average of the growth factors.

of organic aerosol and organic aerosol and its volatility as a function of RH are not known. On the other hand, measurements during the winter indicate that the dried and wet volumes are identical within the experimental error, if the ambient RH is below 60%. If the drying process had a large effect on the growth measurements, the winter measurements would have been biased too. Further, the “dry” DAASS data agree very well with the TEOM $PM_{2.5}$ mass data when the measured volume is translated to mass using a density based on the aerosol chemical composition [Stanier *et al.*, 2004]. If there was a substantial loss of semivolatile material, the DAASS would have been biased low relatively to the TEOM, which was not the case. Consequently, the effect of evaporation of semivolatile material during the drying process is expected to be negligible in our summer measurements.

[31] In winter months during periods when the temperature was below 9°C the aerosol passed through a heated enclosure before it was re-equilibrated to the ambient RH at which the measurements were done (see experimental section). If the aerosol crystallizes during the passage through the heated section (where the relative humidity is accordingly low) it would remain dry even after re-equilibration, unless the ambient RH is above the deliquescence point of the aerosol. This possibility was investigated by examining the growth factors during periods when the ambient RH was below 60% (assuming that this is the deliquescence point) while the RH in the heated section was above 40% (i.e., ammonium sulfate and nitrate should not crystallize). It was found that even at these conditions the aerosol was dry, i.e., ambient aerosol was dry if the ambient RH is below 60%. Likewise, on a few occasions when the ambient RH was around 50%

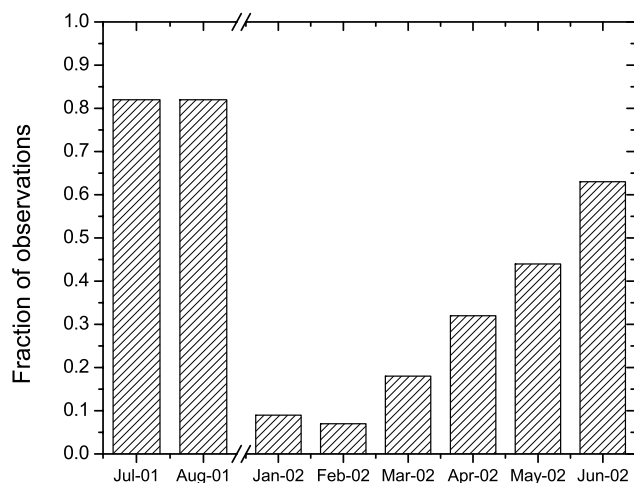


Figure 4. Fraction of observations below 55% RH when the GF was larger than 1.15; i.e., aerosol had a substantial amount of water.

and the heated section RH was below 40%, the growth factor was around 1.1 indicating again that the aerosol was not crystallizing.

[32] Another possible problem associated with the heated section during cold periods is evaporation of ammonium nitrate aerosol. Even though the system is re-equilibrated back to the original temperature, some of the nitric acid vapor may be lost to the walls leading to a loss of ammonium nitrate. The effect of the evaporative loss of ammonium nitrate on the growth factor measurements was assessed using the average aerosol chemical composition during January 2002. Even if all ammonium nitrate was lost in the heated section, the measured volume growth factor would be underestimated by about 10% at RH between 60% and 90% RH. This number represents the worst-case scenario and the actual underestimation should be even lower.

3.4. Comparison With the Thermodynamic Models

[33] The observations with the DAASS during July 2001 were compared to simulations using the thermodynamic

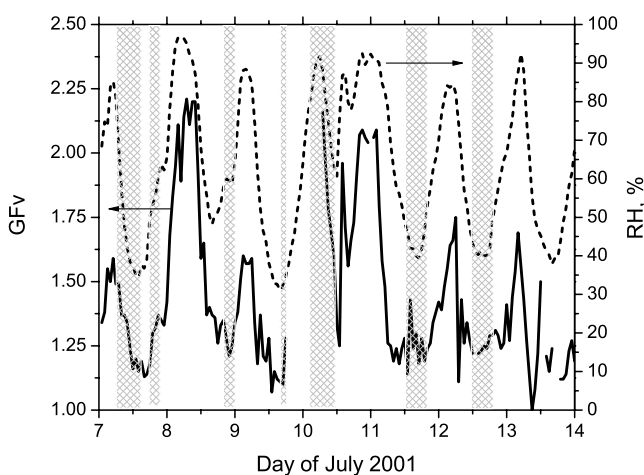


Figure 5. Detailed examination of the effect of aerosol acidity on water retention during summer months. (Solid line, GFv; dotted line, RH; shaded areas, periods when aerosol was acidic).

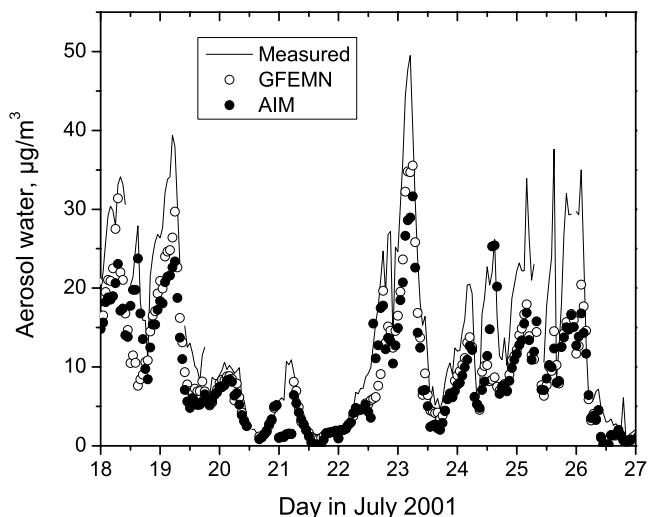


Figure 6. An example of time series of the observed and modeled aerosol water content during a period in July 2001.

models GFEMN [Ansari and Pandis, 1999] and AIM [Clegg et al., 1998] to estimate the contribution of organic aerosol to water absorption. Because the models assume that the organic aerosol does not participate in water absorption, the difference between the observations and the model predictions can be used as a measure of the absorption by organic compounds. The comparison with the models was limited to July 2001 only, because measurements of $PM_{2.5}$ water concentration were not available after August 2001.

[34] Figure 6 shows an example of time series of the observed and modeled aerosol water content. The models follow the observations, though they often underestimate the water content, which is clear from Figures 7 and 8.

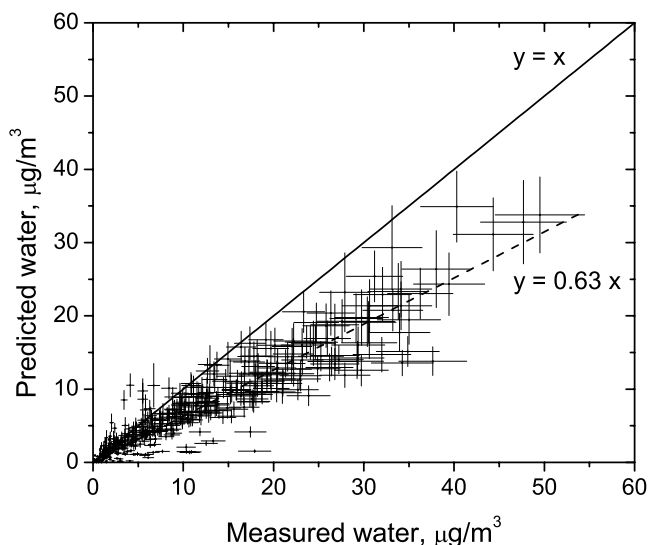


Figure 7. Comparison of the observed and predicted hourly average water concentrations for July 2001. The GFEMN model neglects the organic component contribution to the aerosol water content. The Y-error bars correspond to the standard deviation from the 200 Latin hypercube simulations. The X-error bars represent the measurement uncertainty of the DAASS. A linear regression curve is also shown.

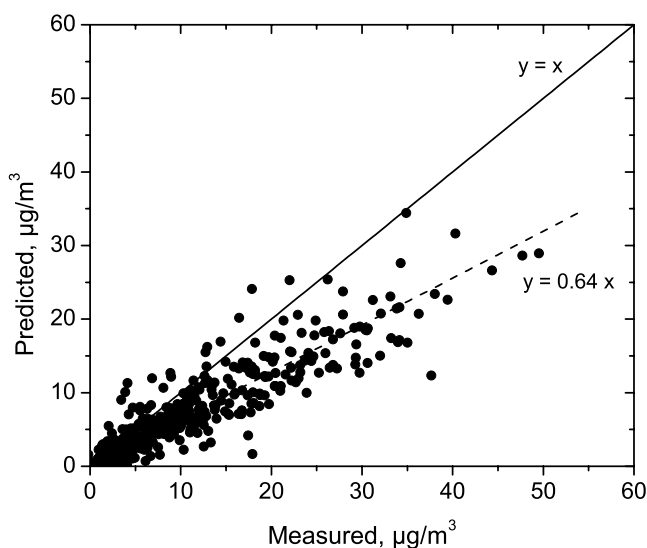


Figure 8. Comparison of the observed hourly average water concentrations and predicted by the AIM model for July 2001.

Figure 7 shows a point-by-point comparison of the aerosol water content during July 2001 observed with the DAASS and predicted with the GFEMN. The model underestimates the water content on average by 37%. Even though this underestimation is not substantially larger than the measurement and modeling uncertainties, it is statistically significant given the number of observations (554). The AIM runs yielded qualitatively similar results to the GFEMN simulations (Figure 8), underestimating the water content, on average, by 36% (Figure 8).

[35] *Cabada et al.* [2004] modeled light scattering by ambient aerosol during the PAQS using a model developed by [Pilinis, 1989] that calculates the light scattering based on the inorganic concentration data and thermodynamic modeling of water absorption by the aerosol. Similarly to our observations, the model under-predicted the measured scattering coefficient during July 2001. When the water content measured with the DAASS was used to calculate the light scattering, the predictions agreed with the observations. This agreement with independent measurements using an integrating nephelometer suggests that the water content measured with the DAASS is accurate. It also shows that modeling of aerosol water content based only on inorganic aerosol concentrations under-estimates water concentration.

3.5. Model Under-Prediction and Organic Aerosol

[36] Because the GFEMN and AIM assumed no contribution to water absorption by organic material in the aerosol, the observed underestimation may be an indication of absorption of water by the organics. However, we have found no clear correlation between the organic mass and the under-prediction by the models (Figure 9). For this comparison the excess water was scaled with $RH/(1-RH)$ to exclude the large effect of relative humidity on water absorption [Hanel, 1979]. This factor follows from the Raoult's law, which states that the equilibrium RH of a solution droplet is equal to the molar fraction of water in the solution. From this follows that the ratio of the absorbed

water to the dissolved mass is proportional to the factor $RH/(1-RH)$.

[37] *Dick et al.* [2000] in their study conducted in the Great Smoky Mountain National Park have found a good correlation between the excess water (measured minus predicted) and organic carbon concentration, if the inorganic fraction of the aerosol was assumed to be crystalline and all the water absorption was due to the organic aerosol when the RH was below 80%. The water absorbed per unit organic mass was within the range expected for dicarboxylic acids. However, no such relationship was found in our study, if the inorganic aerosol is assumed to be crystalline below 80% RH. Also, if only organic matter is assumed to contribute to water absorption below 80% RH, it would have to have unrealistically high water absorption per unit organic mass, on average 4 times higher than that of pure ammonium sulfate. Thus the assumption that inorganic salts are dissolved below 80% RH is more realistic for our study.

[38] A possible explanation for the lack of correlation between the excess water and organic concentration is that the contribution of organics to water absorption is not constant and may change with time. For example, photochemical activity during the day may increase the fraction of water-soluble organics. This possibility was investigated by calculating the diurnal profile of the ratio of the excess water (under-prediction by the model) to the organic carbon (OC) mass (Figure 10). The excess water scaled with $RH/(1-RH)$

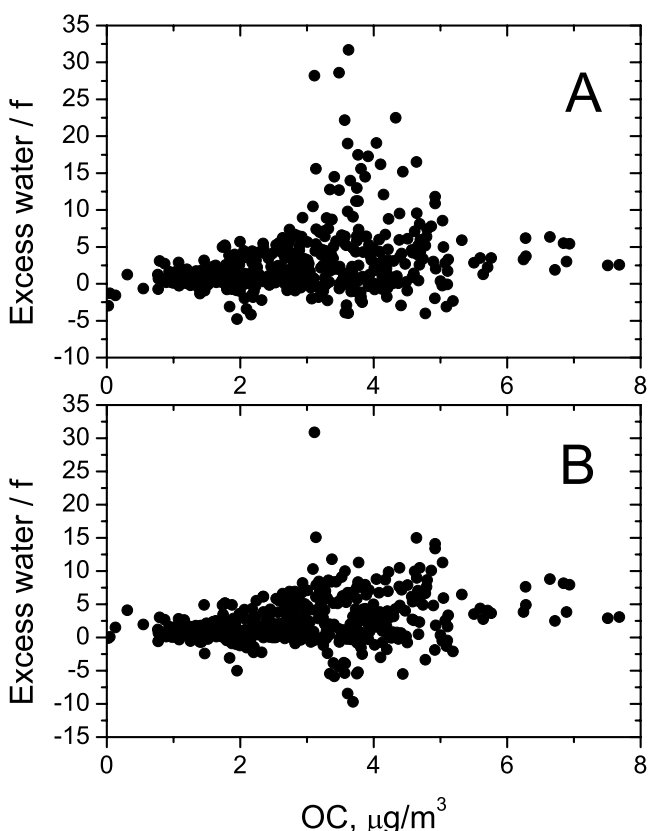


Figure 9. Water deficit versus the concentration of organic carbon. To remove the effect of relative humidity, the excess water was scaled with $f = RH/(1-RH)$: (a) using GFEMN predictions and (b) using AIM predictions.

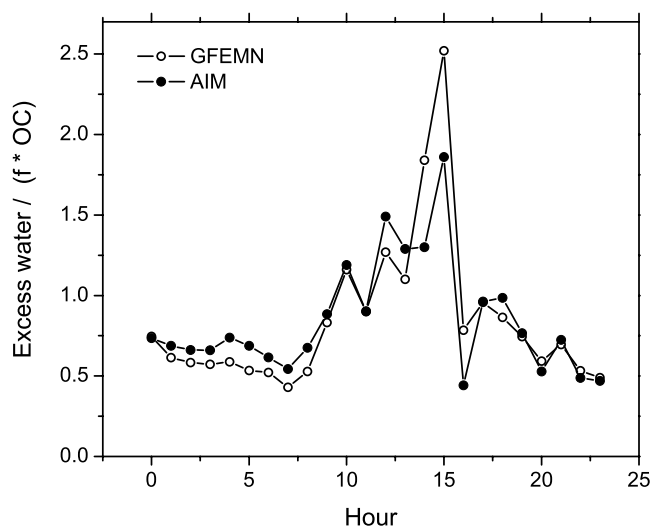


Figure 10. Diurnal profile of the excess water per OC mass. The excess water was scaled with $f = RH/(1-RH)$ to account for the effect of relative humidity.

(1-RH) per unit carbon mass shows, on average, higher values during the afternoon hours. These observations suggest that during afternoon hours organic compounds contribute more to water absorption and that absorption by the organics can explain the “excess” water. However, it should be noted, that during the afternoon the absorption of water per unit organic mass is quite high, being close to that of pure dicarboxylic acids. Even though this cannot be ruled out, because no data is available for the concentration of these acids during our measurements, it is quite improbable that all of the organic mass was composed of these compounds.

[39] The following observations offer a different explanation for the discrepancy between the models and the observations. It was found that the excess water scaled with $RH/(1-RH)$ correlates with $PM_{2.5}$ sulfate concentration stronger than with most of the other parameter measured during the study (Table 1). Concentrations of $PM_{2.5}$ water, mass and sulfate strongly correlate with each other and thus show similar correlation coefficients with the scaled excess water. Given the fact that sulfate concentration in our study was measured with 4 different instruments/methods and that the concentrations measured at the central cite agreed within the experimental error with those measured at the other sites in and around the city, this correlation is not due to a bias in sulfate measurements. A more probable explanation is that the absorption of water by sulfate is enhanced by other substances, organics in particular. *Cruz and Pandis* [2000] have shown in a laboratory study that organic compounds can enhance water absorption by ammonium sulfate by a factor of 2–3 relatively to the absorption by the pure salt. If we assume that the organics do not contribute to water absorption, but enhance that of inorganic salts, the enhancement factor in our study is on average 1.5. It should be noted, that *Cruz and Pandis* [2000] observed the enhancement of absorption at aerosol organic content above 50% and did not observe a noticeable enhancement when the aerosol organic content was close that of our study (on average 20%). It is possible though that organic compounds

in ambient aerosol, which were not tested in the study by *Cruz and Pandis* [2000], enhance water absorption even at lower organic content. However, whether this is the case remains to be resolved.

[40] Modeling of water absorption by atmospheric organic aerosol is extremely difficult due to the complexity of the organic chemical composition confounded by the lack of thermodynamic data and models applicable to organic compounds of various structures and their mixtures. Several attempts have been made to use semiempirical models to predict water absorption by organics using information on the functional organic groups [*Ansari and Pandis*, 2000; *Clegg et al.*, 2001; *Griffin et al.*, 2003; *Ming and Russell*, 2002; *Pividal and Sandler*, 1990]. Unfortunately, no information on functional groups of organic compounds in ambient aerosol is available in our study. Therefore we could not test this approach. Thermodynamic interactions between organic components and inorganic salts in atmospheric aerosol are even less understood. Our data indicate that the observed discrepancy between the models and the observations is unlikely to be explained solely by the contribution of organics, thus suggesting that organic material was changing the activity coefficients of inorganic salts. Analysis of such interactions is beyond the scope of this work. However, our results indicate the apparent importance of such interactions in ambient aerosol.

4. Conclusions

[41] The hygroscopic behavior of ambient aerosol in Pittsburgh exhibits a seasonal behavior. During summer months the aerosol always contained water, even when the relative humidity was as low as 30% at which point water contributed on average about 15% the aerosol mass. In contrast to summer, winter aerosol was generally dry below 60% RH. The spring months showed a transitional behavior. The seasonal behavior of aerosol water content follows that of the aerosol acidity. In summer ammonium bisulfate present in the particles retains water even at RH below 40%, preventing the aerosol from drying. In contrast, the winter aerosol is neutral and has a chance to crystallize at ambient conditions. Aerosol in winter became wet only when the relative humidity reached the deliquescence point of ammonium nitrate.

Table 1. Correlation Coefficients Between the Excess Water Scaled With $RH/(1-RH)$ and Other Variables Measured During July 2001

Component	Correlation Coefficient
PM water	0.70
$PM_{2.5}$ mass	0.67
Sulfate	0.64
Ammonium	0.38
RH	0.29
OC	0.28
Total nitrate	0.24
Temperature	0.22
O_3	0.04
$PM_{2.5}$ nitrate	0.04
NO_x	0.02
SO_2	-0.03
NO	-0.05
CO	-0.10

[42] The observations during July 2001 were compared with the predictions of the thermodynamic models GFEMN and AIM assuming no contribution of the organic aerosol to water absorption. The models under-predicted water concentrations by about 35%. This indicates the magnitude of the possible contribution of organic material to water absorption in July 2001. However, no clear correlation between organic mass and the excess water was observed, which is probably due to a variable nature of the organic aerosol. On average, the contribution of the organics to water absorption appeared to be higher during the afternoon hours. However, this work supports the hypothesis that water absorption by sulfate is influenced by the organics, in addition to the absorption of water by organics themselves.

[43] **Acknowledgments.** The particulate matter measurements were conducted as part of the Pittsburgh Air Quality Study, which was supported by U.S. Environmental Protection Agency (EPA) under contract R82806101 and by the U.S. Department of Energy National Energy Technology Laboratory under contract DE-FC26-01NT41017. This research was supported by NSF ATM-336296.

References

- Ansari, A. S., and S. N. Pandis (1999), Prediction of multicomponent inorganic atmospheric aerosol behavior, *Atmos. Environ.*, *33*(5), 745–757.
- Ansari, A. S., and S. N. Pandis (2000), Water absorption by secondary organic aerosol and its effect on inorganic aerosol behavior, *Environ. Sci. Technol.*, *34*(1), 71–77.
- Cabada, J. C., A. Khlystov, A. E. Wittig, C. Pilinis, and S. N. Pandis (2004), Light scattering by fine particles during the Pittsburgh Air Quality Study: Measurements and modeling, *J. Geophys. Res.*, *109*, D16S03, doi:10.1029/2003JD004155.
- Choi, M. Y., and C. K. Chan (2002), The effects of organic species on the hygroscopic behaviors of inorganic aerosols, *Environ. Sci. Technol.*, *36*(11), 2422–2428.
- Clegg, S. L., P. Brimblecombe, and A. S. Wexler (1998), Thermodynamic model of the system $H^+ - NH_4^+ - SO_4^{2-} - NO_3^- - H_2O$ at tropospheric temperatures, *J. Phys. Chem. A*, *102*(12), 2137–2154.
- Clegg, S. L., J. H. Seinfeld, and P. Brimblecombe (2001), Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds, *J. Aerosol Sci.*, *32*(6), 713–738.
- Cocker, D. R., N. E. Whitlock, R. C. Flagan, and J. H. Seinfeld (2001), Hygroscopic properties of Pasadena, California aerosol, *Aerosol Sci. Technol.*, *35*(2), 637–647.
- Cruz, C. N., and S. N. Pandis (2000), Deliquescence and hygroscopic growth of mixed inorganic-organic atmospheric aerosol, *Environ. Sci. Technol.*, *34*(20), 4313–4319.
- Dick, W. D., P. Saxena, and P. H. McMurry (2000), Estimation of water uptake by organic compounds in submicron aerosols measured during the Southeastern Aerosol and Visibility Study, *J. Geophys. Res.*, *105*(D1), 1471–1479.
- Griffin, R. J., K. Nguyen, D. Dabdub, and J. H. Seinfeld (2003), A coupled hydrophobic-hydrophilic model for predicting secondary organic aerosol formation, *J. Atmos. Chem.*, *44*(2), 171–190.
- Han, J., H. Hung, and S. T. Martin (2002), Size effect of hematite and corundum inclusions on the efflorescence relative humidities of aqueous ammonium nitrate particles, *J. Geophys. Res.*, *107*(D10), 4086, doi:10.1029/2001JD001054.
- Hanel, G. (1979), The properties of atmospheric aerosol particles as functions of the relative humidity at thermodynamic equilibrium with the surrounding moist air, *Adv. Geophys.*, *19*, 73–188.
- Khlystov, A., G. P. Wyers, and J. Slanina (1995), The steam-jet aerosol collector, *Atmos. Environ.*, *29*(17), 2229–2234.
- Khlystov, A., C. Stanier, and S. N. Pandis (2004), An algorithm for combining electrical mobility and aerodynamic size distributions data when measuring ambient aerosol, *Aerosol Sci. Technol.*, *38*, suppl. 1, 229–238.
- Martin, S. T., J. H. Han, and H. M. Hung (2001), The size effect of hematite and corundum inclusions on the efflorescence relative humidities of aqueous ammonium sulfate particles, *Geophys. Res. Lett.*, *28*(13), 2601–2604.
- McKay, M. D. (1988), Sensitivity and uncertainty analysis using a statistical sample of input values, in *Uncertainty Analysis*, edited by Y. Ronen, pp. 145–186, CRC Press, Boca Raton, Fla.
- Ming, Y., and L. M. Russell (2002), Thermodynamic equilibrium of organic-electrolyte mixtures in aerosol particles, *AIChE J.*, *48*(6), 1331–1348.
- Nessler, R., N. Bukowiecki, S. Henning, E. Weingartner, B. Calpini, and U. Baltensperger (2003), Simultaneous dry and ambient measurements of aerosol size distributions at the Jungfraujoch, *Tellus, Ser. B*, *55*(3), 808–819.
- Pilinis, C. (1989), Numerical simulation of visibility degradation due to particulate matter: Model development and evaluation, *J. Geophys. Res.*, *94*(D7), 9937–9946.
- Pividal, K. A., and S. I. Sandler (1990), Neighbor effects on the group contribution method—Infinite dilution activity-coefficients of binary-systems containing primary amines and alcohols, *J. Chem. Eng. Data*, *35*(1), 53–60.
- Rader, D. J., and P. H. McMurry (1986), Application of the tandem differential mobility analyzer to studies of droplet growth or evaporation, *J. Aerosol Sci.*, *17*(5), 771–787.
- Ramaswamy, V. (2001), Radiative forcing of climate change, in *Climate Change 2001, Scientific Basis: Contribution of the Working Group 1 to the Third Assessment Report of the IPCC*, edited by J. T. Houghton et al., Cambridge Univ. Press, New York.
- Rees, S. L., A. L. Robinson, A. Khlystov, C. O. Stanier, and S. N. Pandis (2004), Mass balance closure and the Federal Reference Method for PM_{2.5} in Pittsburgh, Pennsylvania, *Atmos. Environ.*, *38*(20), 3305–3318.
- Saxena, P., L. M. Hildemann, P. H. McMurry, and J. H. Seinfeld (1995), Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, *100*(D9), 18,755–18,770.
- Stanier, C. O., A. Khlystov, W. R. Chan, M. Mandiro, and S. N. Pandis (2004), A method for the in-situ measurement of aerosol water content of ambient aerosols: The Dry-Ambient Aerosol Size Spectrometer (DAASS), *Aerosol Sci. Technol.*, *38*, suppl. 1, 215–228.
- Subramanian, R., A. Y. Khlystov, J. C. Cabada, and A. L. Robinson (2004), Positive and negative artifacts in particulate organic carbon measurements with denuded and undenuded sampler configurations, *Aerosol Sci. Technol.*, *38*, suppl. 1, 27–48.
- Swietlicki, E., et al. (1999), A closure study of sub-micrometer aerosol particle hygroscopic behaviour, *Atmos. Res.*, *50*(3–4), 205–240.
- Takahama, S., A. E. Wittig, D. V. Vayenas, C. I. Davidson, and S. N. Pandis (2004), Modeling the diurnal variation of nitrate during the Pittsburgh Air Quality Study, *J. Geophys. Res.*, *109*, D16S06, doi:10.1029/2003JD004149.
- Tang, I. N. (1997), Thermodynamic and optical properties of mixed-salt aerosols of atmospheric importance, *J. Geophys. Res.*, *102*(D2), 1883–1893.
- Tang, I. N., and H. R. Munkelwitz (1994), Water activities, densities, and refractive-indexes of aqueous sulfates and sodium-nitrate droplets of atmospheric importance, *J. Geophys. Res.*, *99*(D9), 18,801–18,808.
- Tang, W., T. Raymond, B. Wittig, C. Davidson, S. Pandis, L. Robinson, and K. Crist (2004), Spatial variations of PM_{2.5} during the Pittsburgh Air Quality Study, *Aerosol Sci. Technol.*, *38*, suppl. 2, 80–90.
- Wittig, B., N. Anderson, A. Y. Khlystov, S. N. Pandis, C. Davidson, and A. L. Robinson (2004), Pittsburgh Air Quality Study overview and preliminary scientific findings, *Atmos. Environ.*, *38*(20), 3107–3125.

A. Khlystov, Department of Civil and Environmental Engineering, Duke University, Durham, NC 27708, USA.

S. N. Pandis, C. O. Stanier, and S. Takahama, Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA. (spyros@andrew.cmu.edu)