Hygroscopicity and volatility of 4–10 nm particles during summertime atmospheric nucleation events in urban Atlanta

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[1] Continuous measurements of hygroscopicity and volatility of atmospheric aerosol particles of 4–10 nm diameter were conducted with a nanometer tandem differential mobility analyzer (Nano TDMA) during the Aerosol Nucleation and Real-time Characterization Experiment (ANARChE), which took place in Atlanta in July and August 2002. In the Nano TDMA measurements, particles were exposed to either a high humidity (~90% RH) or an elevated temperature (~100°C) downstream of the first differential mobility analyzer (DMA) and were then resized by the second DMA to determine the change in size due to water uptake or evaporation. There were several days when nucleation occurred and high concentrations of sub-20 nm particles were observed, and during those events, particles of 4–10 nm diameter were very hygroscopic and nonvolatile. These observations, together with parallel Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) measurements of sub-20 nm particle composition, suggest that the particles were mostly composed of ammoniated sulfates. This finding strongly supports the hypothesis that the nucleation and subsequent growth of nanoparticles were driven by reactions involving sulfuric acid and ammonia during this study.


1. Introduction

[2] Recent studies have shown that a large number of very fine particles are present in the atmosphere, and that many of them are produced by nucleation from the gas phase. As summarized in a recent review [Kulmala et al., 2004], nucleation has been observed at various locations including the continental boundary layer, polluted urban areas, industrial plumes, the outflows of convective clouds, and over exposed tidal zones. Because of the ubiquitous presence and large numbers of particles thus formed, nucleation may influence global climate through its effect on the concentrations of cloud condensation nuclei (CCN) which affect the optical properties of clouds and therefore the Earth’s radiative balance. Nucleation may also alter aerosol size distributions, thereby affecting the direct radiative effects of aerosols. To evaluate the global impact of atmospheric nucleation, models that predict the locations, frequency, and magnitudes of nucleation are required. There have been several nucleation mechanisms proposed, which include the binary nucleation of sulfuric acid and water [Kulmala and Laaksonen, 1990; Noppel et al., 2002; Vehkamäki et al., 2002], ternary nucleation of sulfuric acid, water, and ammonia [Weber et al., 1997; Kulmala et al., 2000; Napari et al., 2002], and ion-induced nucleation that involves cluster ions of sulfuric acid and water [Yu and Turco, 2001; Lee et al., 2003; Lovejoy et al., 2004]. Recently, a mechanism that involves oxidation of organic iodine species [Jimenez et al., 2003] was also proposed. While direct measurement of the chemical composition of nuclei (ca. 1 nm) would provide insight into nucleation mechanisms, current technology is not capable of such measurements. Therefore our best effort at this point is to infer the mechanism and involved species from the chemical composition of particles that grow to measurable sizes.

[3] We completed an intensive field study of nucleation in Atlanta in July and August, 2002 where nucleation occurs frequently in summer [Woo et al., 2001]. In this study, the Aerosol Nucleation and Real-time Characterization Experiment (ANARChE), we deployed for the first time two instruments to obtain information about the chemical composition of freshly nucleated particles. One was the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) [Voisin et al., 2003; Smith et al., 2004] which determined the chemical composition of sub-20 nm particles. The other was a nanometer tandem
differential mobility analyzer (Nano TDMA) for providing indirect chemical information through measurements of hygroscopicity and volatility [Rader and McMurry, 1986; McMurry and Stolzenburg, 1989; Orsini et al., 1999; Philippin et al., 2004]. In this paper, we present results obtained by the Nano TDMA measurements during the ANARChE study. Results taken by the TDCIMS are given in a separate paper [Smith et al., 2005].

[4] While the information obtained with the TDMA technique does not directly identify the chemical composition of particles, we used this method since it provided crucial supplemental information to the chemical data obtained with the TDCIMS. It also provided a more comprehensive data set by carrying out measurements continuously with higher time resolutions, and for particles of smaller sizes and lower concentrations than was possible using the TDCIMS. The TDMA technique has been frequently used to study the hygroscopicity and volatility of atmospheric particles. This work includes several recent TDMA measurements of the hygroscopicity of sub-20 nm particles associated with nucleation events [Hämeri et al., 2001; Väkevä et al., 2002a, 2002b]. Volatility measurements by the TDMA technique have proved to be effective in determining vapor pressures of volatile components and mixing states of nanoparticles in diesel exhaust [Sakurai et al., 2003a, 2003b], but have not been applied to atmospheric nucleation mode particles. In the ANARChE study, both hygroscopicity and volatility measurements were applied to freshly nucleated atmospheric particles to maximize the information obtained about the chemical composition of those particles.

2. Experiment

[5] The ANARChE study took place at the Jefferson Street sampling site in urban Atlanta. This site was previously used for the 1999 Atlanta Supersite study [Solomon et al., 2003] and for continuous measurements of particle size distributions over a 24-month period as part of EPRI’s ARIES project [Woo et al., 2001]. TDMA measurements were carried out during the study from 10 August 2002 till 30 August 2002.

[6] Measurements on particles reported in this paper were made with two instrument systems: a suite of instruments for measuring continuously the particle size distribution (PSD) from 3 nm to 2 μm with a 5-min resolution, and a TDMA for measuring hygroscopicity and hygroscopicity of nucleation mode particles of 4–10 nm diameter. The PSD system was similar to that used in the St. Louis-Midwest Supersite study [Shi, 2003]. Briefly, the system consisted of (1) a Nanometer Scanning Mobility Particle Sizer (Nano SMPS) for the 3–30 nm size range (TSI 3085 Nanometer Differential Mobility Analyzer (DMA) [Chen et al., 1997]; TSI 3025 Ultrafine Condensation Particle Counter (UCPC) [Stolzenburg and McMurry, 1991]), (2) a Long SMPS for 20–250 nm particles (DMA similar in design to the TSI model 3071 [Knutson and Whitby, 1975]; TSI 3010 Condensation Particle Counter (CPC)), and (3) an optical particle counter for 100–2000 nm particles (Particle Measuring Systems Lasair model 1002). The SMPSs were operated with Po-210 bipolar chargers, home-built flow controllers, and commercial programmable high-voltage power supplies run in the scanning mode [Wang and Flagan, 1990].

[7] The Nano TDMA was the instrument system used previously for studying diesel nanoparticles [Sakurai et al., 2003a, 2003b], with the addition of RH conditioning for hygroscopicity measurements. A schematic of the Nano TDMA is given in Figure 1. Particles first passed through a Po-210 bipolar charger and entered into the first DMA (DMA1 in Figure 1), which was used to select monodisperse particles. This aerosol then entered either an RH conditioner for measuring hygroscopicity or a heated tube for measuring volatility. After passing through the humidifier or heater, particles entered the second DMA (DMA2) and a UCPC which were used to determine the change in size. UCPC concentrations were measured at a discrete set of DMA2 voltages, and the voltage was changed stepwise and always upward in each individual measurement. The particle diameter after conditioning was calculated as the arithmetic mean of the DMA2 diameters weighted by the particle concentration measured by the UCPC. Each measurement took about 5–10 min, depending on the voltage range and particle concentrations. Measurements were repeatedly taken in one of the modes for a certain period of time (e.g., a few days), and then switched to the other mode. In both hygroscopicity and volatility modes, the RH of the aerosol entering DMA1, that of the DMA1 sheath air, and that of the monodisperse aerosol from DMA1 were about 40%, 10–12%, and 13–15%, respectively. The relative sizing accuracy of the two DMAs was checked by selecting particles of a certain size (5 or 8 nm) by DMA1 and measuring their size by DMA2 without conditioning, i.e., at 15% RH at ambient temperature. The agreement between the DMA1-selected and DMA2-measured sizes was within 2%.

[8] In the hygroscopicity mode, experiments were carried out to measure the mobility diameter growth factor (GF) at 90% RH. The growth factor is defined as the ratio of the particle diameter measured in DMA2 at 90% RH to the diameter selected in DMA1 at 15% RH. The Nano TDMA was designed so that the RH throughout the aerosol flow path from the exit of the RH conditioner to the inlet of the UCPC was as close to 90% as possible. We used two Perma Pure MD-110-24S-4 Nafion tubes in series to bring the monodisperse aerosol downstream of DMA1 to 90% RH. Humidification was achieved by passing the aerosol through the inner Nafion tube while air at ~90% RH was fed into the annular gap between the Nafion tube and outer stainless steel shell. This humidified airflow was generated by mixing dry and water-saturated airflows. (The same humidified flow was split and used for the DMA2 sheath air.) Before entering DMA2, the humidified aerosol flowed through a ~100-cm³ chamber which gave an additional residence time of ~4 s to achieve equilibrium before particles were resized in DMA2. The UCPC in the Nano TDMA was modified to ensure that water would not accumulate in its saturator while sampling humid aerosols from DMA2. This was accomplished by drying the UCPC’s sheath air with another Nafion dryer (MD-110-12S-4, Perma Pure LLC).

[9] In the volatility mode, measurements were taken with the temperature of the heated tube fixed. The temperature was typically about 100°C, although it was sometimes set to values in the range between 50 and 150°C. The system was
operated under the driest condition that the system was able to achieve, which gave the RH of ~15% at room temperature throughout the aerosol path in the Nano TDMA. Results of these measurements are reported in terms of the absolute change in particle size rather than the percent change, since theory predicts that when curvature effects can be neglected the absolute change in size is independent of size in the free molecular regime [Hinds, 1999].

In interpreting results from these hygroscopicity and volatility measurements, we considered four chemical compounds and classes as possible components of nucleation mode particles. They were (1) sulfuric acid, (2) sulfates which were completely or partially neutralized by ammonia, (3) organics, and (4) elemental carbon. Elemental carbon can be a significant component of sub-20 nm atmospheric particles and is neither volatile at 100°C nor hygroscopic at 90% RH. Sulfuric acid and ammoniated sulfates take up water at 90% RH [Tang, 1980], while the hygroscopicity of organics depends on the functional groups they possess, and ranges from completely nonhygroscopic to very hygroscopic at 90% RH. For example, many dicarboxylic acids are reported to be hygroscopic [Saxena and Hildemann, 1997; Peng et al., 2001; Prenni et al., 2001]. On the other hand, hydrocarbons such as alkanes are examples of nonhygroscopic organics.

Regarding volatility, our measurements with laboratory-generated 10-nm ammonium sulfate and bisulfate particles showed that no size change occurred at 100°C for either compound. Previous measurements with 50-nm sulfuric acid show that evaporation occurs at temperatures well below 100°C [Orsini et al., 1999]. However, in our laboratory measurements we found that 12-nm sulfuric acid particles were as nonvolatile as ammonium sulfate and bisulfate at 100°C, which is inconsistent with the observation by Orsini et al. We have not identified the reason for the discrepancy between these results. A possible reason is that our apparatus was contaminated with sufficient ammonia to neutralize 12-nm sulfuric acid particles before they entered the heating tube of the Nano TDMA. On the basis of this observation, we conclude that the Nano TDMA was not able to distinguish ammonium sulfate, ammonium bisulfate, and sulfuric acid from each other by volatility, and that all of them appeared nonvolatile at 100°C. Therefore we categorize these three compounds, all of which are hygroscopic and nonvolatile, as a single class "sulfates", and we rely on TDCIMS measurements to determine whether ammonia was part of the particle composition. It should be mentioned that, for both ammonium sulfate and sulfuric acid, size decreases of ~5 nm were observed at 150°C.

Volatility of organics that may be relevant to atmospheric nucleation and growth have been reported to have vapor pressures greater than 10^-9 Pa at 25°C. For example, the vapor pressures of C6–C8 dicarboxylic acids are about 10^-3–10^-6 Pa [Tao and McMurry, 1989; Chattopadhyay et al., 2001]. Diacyl peroxides, which were recently proposed to be nucleating agents, have vapor pressures of about 10^-7–10^-8 Pa [Ziemann, 2002]. C32 n-alkane, which has the vapor pressure of ~10^-9 Pa at 25°C, evaporates significantly at ~100°C (by 5 nm or more for 30-nm particles) in our Nano TDMA. Therefore, while observations of relevant organic behavior are limited, for this TDMA method we assume that organics in the atmosphere

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**Figure 1.** Schematic of the Nano TDMA. The thick arrows that run from the top to the bottom the flow path of the sampled aerosol in the hygroscopicity mode. LFM, laminar flowmeter; RC, reaction chamber; CO, critical orifice; DP, dew point hygrometer; T, thermocouple; and RH, relative humidity sensor.
are volatile. These are summarized in Table 1. It is expected from Table 1 that combined knowledge of hygroscopicity and volatility would provide us useful information about the chemical composition of measured particles.

In the above consideration, water was not included as a possible major constituent of the particles. This is because the setup of the Nano TDMA did not allow determination of the amount of water in the particles, since particles were always exposed to dry air at ~15% RH when they entered the Nano TDMA and then must have released all or most of water. This drying process, on the other hand, may have affected our measurements.

The PSD and Nano TDMA systems were located next to each other in a mobile research laboratory, and samples of the ambient aerosol were taken from the same sampling line through the laboratory roof, which had a PM10 inlet located about 5 meters above the ground level. The sampling line was equipped with another RH conditioner, similar to the one used in the PSD system of the St. Louis-Midwest Supersite study [Shi, 2003], which maintained the RH of the aerosol sample at 40% at its exit. After the RH conditioner, the sample flow was split to the PSD and Nano TDMA.

In addition to these particle measurements, many gas and meteorological measurements as well as other particle measurements were taken at the site. Among them, concentrations of gaseous sulfuric acid and the hydroxyl radical were measured by a Selected-Ion Chemical Ionization Mass Spectrometer (SICIMS) [Eisele and Tanner, 1991, 1993]. The SO₂ concentration was measured using a high-sensitivity instrument utilizing standard pulsed fluorescence detection techniques (TECO model 43S, Thermo Environmental Instruments, Inc.). Measurements of ammonia by SICIMSs [Fehsenfeld et al., 2002; Nowak et al., 2002] were also carried out at the site. In addition, data from measurements of pollutant gases such as SO₂, CO, NO, and NOₓ, and meteorological parameters (temperature, RH, wind direction and speed, and total solar radiation) were provided from the instruments for the SEARCH project [Hansen et al., 2003] located in a separate measurement facility at the same site.

3. Results and Discussion

3.1. Aerosol Climatology

Table 2 summarizes days during the ANARChE study on which nucleation events were observed as well as local wind directions on each day of the study. Note that we observed nucleation events 16 times in the 30-day period. “Wind Direction” represents that at 12:00 at the measurement site at about 5 m above the ground level.

In this type of event, nucleation mode particles (less than 10 nm) start to appear in the morning or early afternoon and grow continuously for several hours to larger sizes (e.g., 30–100 nm). Figure 2a is a contour plot of aerosol size distributions measured during a regional nucleation event on 11 August 2002, where particle size is shown on the ordinate and time of day on the abscissa in the U.S. Eastern Standard Time. The color indicates the values of the size distribution function (dN/dlog₁₀Dₚ). In this example, nucleation mode particles first appeared at about 9:30 and grew to 50 nm by ~13:00.

### Table 1. Hygroscopic and Volatile Properties of Major Chemical Compounds and Classes That Are Relevant to Nucleation Mode Particles

<table>
<thead>
<tr>
<th>Chemical Compounds and Classes</th>
<th>Hygroscopicity (RH = 90%)</th>
<th>Volatility (100°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Sulfates””</td>
<td>hygroscopic</td>
<td>nonvolatile</td>
</tr>
<tr>
<td>Organics</td>
<td>may range from nonhygroscopic to hygroscopic</td>
<td>volatile</td>
</tr>
<tr>
<td>Elemental carbon</td>
<td>nonhygroscopic</td>
<td>nonvolatile</td>
</tr>
</tbody>
</table>

“Sulfates”” indicates sulfates which are completely or partially neutralized by ammonia or pure sulfuric acid. The reason that sulfuric acid is considered nonvolatile is given in the text.

### Table 2. Outstanding Events and Wind Directions During ANARChE

<table>
<thead>
<tr>
<th>Date</th>
<th>Nucleation Event</th>
<th>Wind Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 August</td>
<td>regional</td>
<td>E</td>
</tr>
<tr>
<td>2 August</td>
<td>(no measurement)</td>
<td></td>
</tr>
<tr>
<td>3 August</td>
<td>E</td>
<td></td>
</tr>
<tr>
<td>4 August</td>
<td>E</td>
<td></td>
</tr>
<tr>
<td>5 August</td>
<td>regional</td>
<td>NW</td>
</tr>
<tr>
<td>6 August</td>
<td>plume</td>
<td>NW</td>
</tr>
<tr>
<td>7 August</td>
<td>E</td>
<td></td>
</tr>
<tr>
<td>8 August</td>
<td>regional</td>
<td>S</td>
</tr>
<tr>
<td>9 August</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>10 August</td>
<td>regional</td>
<td>SE</td>
</tr>
<tr>
<td>11 August</td>
<td>regional</td>
<td>S</td>
</tr>
<tr>
<td>12 August</td>
<td>plume and regional</td>
<td>SW</td>
</tr>
<tr>
<td>13 August</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>14 August</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>15 August</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 August</td>
<td>SE</td>
<td></td>
</tr>
<tr>
<td>17 August</td>
<td>plume</td>
<td>SW</td>
</tr>
<tr>
<td>18 August</td>
<td>plume</td>
<td>W</td>
</tr>
<tr>
<td>19 August</td>
<td>plume and regional</td>
<td>NW</td>
</tr>
<tr>
<td>20 August</td>
<td>plume</td>
<td>N</td>
</tr>
<tr>
<td>21 August</td>
<td>SE</td>
<td></td>
</tr>
<tr>
<td>22 August</td>
<td>plume</td>
<td>W</td>
</tr>
<tr>
<td>23 August</td>
<td>plume and regional</td>
<td>NW</td>
</tr>
<tr>
<td>24 August</td>
<td>plume</td>
<td>NW</td>
</tr>
<tr>
<td>25 August</td>
<td>plume and regional</td>
<td>NW</td>
</tr>
<tr>
<td>26 August</td>
<td>plume</td>
<td>NW</td>
</tr>
<tr>
<td>27 August</td>
<td>E</td>
<td></td>
</tr>
<tr>
<td>28 August</td>
<td>E</td>
<td></td>
</tr>
<tr>
<td>29 August</td>
<td>SE</td>
<td></td>
</tr>
<tr>
<td>30 August</td>
<td>E</td>
<td></td>
</tr>
</tbody>
</table>

*Descriptions of the events are given in the text.*
“Plume” stands for plume impact events, which we believe occurred when the plume from a point source containing elevated levels of SO$_2$ and other gases impacted the sampling site. Plumes that impacted during daytime typically contained extremely high concentrations of sub-10 nm particles that we believe were formed photochemically as the plume was transported toward our sampling site. Similar events were frequently observed in the St. Louis-Midwest Supersite study [Shi, 2003]. A contour plot of size distributions on a day when the site experienced such plume nucleation events superimposed upon a regional nucleation event is shown in Figure 3a. The white areas in the 4–10 nm size range between 13:00 and 17:00 indicate that the size distribution function values exceeded 10$^6$ particles/cm$^3$.

Figures 3b–3c show very high concentrations of sulfur dioxide and sulfuric acid vapor during these periods, occasionally exceeding 50 ppb and 1 $\times$ 10$^8$ molecules/cm$^3$, respectively. (Sulfuric acid data were not collected between 9:10 and 12:15.) The spikes of the high concentrations of the gas species and sub-10 nm particles coincide. These are similar to observations in the St. Louis study where high SO$_2$ concentrations in excess of 50 ppb that coincided with very high concentrations of sub-20 nm particles (10$^5$ particles/cm$^3$ or more between 3 and 20 nm) were observed during plume impact events [Shi, 2003].

3.2. Hygroscopicity and Volatility During Nucleation Events

3.2.1. Results of Hygroscopicity Measurements During Regional Nucleation Events

The hygroscopic growth factors of 10-nm particles measured by the Nano TDMA during the regional nucleation event on 11 August 2002 are shown in Figure 2c, with the SO$_2$ concentration plotted above this in Figure 2b. Figure 2c shows data only after 4:00. This is because the data before 4:00 were scattered because of very low concentrations of particles and perhaps also external mixing of particles of different hygroscopicities. At the onset of the event, which is marked with a vertical dashed line, the SO$_2$ concentration started to increase from 2 ppb, and reached to

![Figure 2](image_url)
the daily maximum concentration of 20 ppb at about 10:30 and then decreased to return to the initial concentration in the following 2–3 hours. At 9:30, when freshly nucleated particles were being sampled by the Nano TDMA, the growth factor of 10-nm particles increased abruptly from ~1.2 to ~1.4 and remained at this value for 3–4 hours before gradually returning to ~1.2 at 18:00–20:00. This contrasts with the temporal variabilities in the SO$_2$ concentration, which had shorter tails before returning to the initial values. The gradual decrease of the growth factor indicates gradual change of particle composition during this period.

Figure 3. Summary of major observations on 25 August 2002 when both a regional nucleation event and multiple plume impact events were observed. (a) A time series contour plot of the particle size distribution from 4 nm to 2 μm; (b) sulfur dioxide concentrations; (c) sulfuric acid concentration; and (d) diameter change of 10-nm particles at 100°C determined by the TDMA in the volatility mode, with negative values indicating decreases in size. A horizontal gray line is drawn in Figure 3a to indicate the size at which the TDMA measurements were carried out.

[36] It should be noted that no external mixing of particles of different hygroscopicities was observed after the event began. The disappearance of the particles of the GF of 1.2, which were present before the onset of the event, means that the newly formed particles did not simply intermingle with the preexisting particles. Instead, it is likely that as new particle formation occurred, the preexisting particles grew out of the 10 nm size range and were replaced by the freshly nucleated particles. In addition, because particle growth during these periods was so fast (~10 nm/hour), condensational growth upon primary particles would have caused...
them to rapidly approach the composition of the freshly nucleated particles. It is also possible that vertical mixing led to enhanced levels of SO$_2$ during these regional nucleation events, and simultaneously depleted concentrations of less hygroscopic particles at the surface. The fact that, when new particles were first observed, they were significantly larger than the minimum detectable size of 3 nm suggests that new particle formation may have occurred aloft, and the newly formed particles were brought down to the surface because of the mixing. (See, for example, Stratmann et al. [2003, and references therein] for discussion about the effect of vertical mixing on nucleation.)

3.2.2. Results of Volatility Measurements During Regional Nucleation Events

[21] Figure 3a shows that, on 25 August 2002, plume impacts were superimposed upon a regional nucleation event. We first discuss observations made when the plume was not impacting the sampling site. The volatility of 10-nm particles at 100°C was measured throughout this day (Figure 3d). The regional nucleation event began at around 8:00 or 9:00, when elevated particle concentrations in the 10–20 nm range were observed (indicated with a vertical line at 8:30), and the particles apparently grew to ~50 nm by 14:00, or to ~100 nm by 16:00. Before and during this period, the SO$_2$ concentration remained elevated at about 10 ppb (Figure 3b). Measurement of sulfuric acid vapor (Figure 3c) indicated a gradual increase of the concentration at the event onset, from ~5 x 10$^{15}$ molecules/cm$^3$ at 8:00 to ~5 x 10$^{14}$ molecules/cm$^3$ at 9:08. In Figure 3d, diameters of 10-nm particles decreased by up to 2 nm (up to 20% of the initial size or ~50% in mass; diameter changes shown as negative values in Figure 3d) prior to the event, indicating that particles were slightly volatile. As the event began, however, particles were no longer volatile. This continued until late afternoon (16:00–17:00) while the particle growth continued, and also during the plume impact events, which will be discussed further later. Toward evening, particles were again slightly volatile with diameter decreases of about 1 nm.

[22] It should be pointed out that the diameter change was often positive in Figure 3d, meaning that the DMA2 mobility diameter was greater than the DMA1 mobility diameter in those measurements. The increase was not large, only as much as ~0.5 nm or ~5%, but we think this was not due to sizing errors by the Nano TDMA, since the sizing error was determined to be less than 2% by calibrations as discussed in the Experiment section. Particle volume should not increase when particles are heated. We have not identified the reason for this observation. It is possible that when particles were heated they underwent a phase change (e.g., crystallization from amorphous) that transformed them from spheres to a somewhat less spherical shape. Such a transformation would manifest itself as an increase in mobility size. For example, a ~10-nm cube (dynamic shape factor = 1.08) has a mobility diameter that is ~4% greater than a sphere of the same volume [Hinds, 1999].

3.2.3. Results of Hygroscopicity and Volatility Measurements During Plume Impact Events

[23] The data in Figure 3d show that the volatility of 10 nm particles did not change when the plume impacted the site between 13:30 and 16:30 on 25 August 2002, which is clearly indicated by data points on the two vertical dashed lines at 14:00 and 15:00. Those dashed lines were drawn to highlight the two impact events when the concentration of 10-nm particles increased significantly. Therefore freshly nucleated particles in plumes were nonvolatile at 100°C. It should be noted that several data points between 14:00 and 16:00 show diameter decrease of more than 1 nm. They were from measurements when the concentration of 10-nm particles were extremely low, and the data at those low-concentration periods are not representative for the particles in plumes. About hygroscopicity, the growth factors of 10-nm particles during a plume impact event on 12 August 2002 were about 1.3–1.4 (not shown), and hence those particles were hygroscopic. In summary, 10-nm particles during plume impact events were as nonvolatile and hygroscopic as were particles of this size during regional nucleation events.

[24] Measurements on particles smaller than 10 nm were attempted during several plume impact events. While Nano TDMA measurements of those small particles were usually very difficult because diffusional losses led to too low particle concentrations at the UCPC downstream of the two DMAs in series, we were able to measure hygroscopicity and volatility of sub-10 nm particles by taking advantage of extremely high particle concentrations during plume impact events. The purpose of making measurements at smaller sizes was to study less aged particles immediately after nucleation which presumably reflected more of the properties of the nuclei.

[25] On 23 August 2002, multiple intense plume impact events were superimposed on a regional nucleation event. On that day we measured the hygroscopicity of 4 nm particles during those short plume impacts (not shown). While the uncertainty of each measurement was large because the particle concentration in the Nano TDMA was still low, the growth factor of 4 nm particles was consistently about 1.2 throughout multiple impacts that intermittently occurred in a ~3-hour period. As is discussed in the next section, a growth factor of ~1.2 for 4-nm particles is equivalent in hygroscopicity to that of ~1.4 for 10-nm particles after accounting for the Kelvin effect, and indicates that those 4-nm particles were hygroscopic. The volatility of 6-nm particles was measured during a few intense plume impact events on 19 August 2002 (not shown). These measurements showed clearly that the particles were nonvolatile.

[26] In addition to the measurement at ~100°C, volatility measurements were carried out at a higher temperature during a plume impact event on 17 August 2002 (not shown). When 8-nm particles were heated at 150°C, the diameter decreased by about 4 nm. This indicates that the compounds that composed the particles started to evaporate as the heating temperature increased to above 100°C.

3.2.4. Discussion on the Observations During Nucleation Events

[27] Including the observations discussed above, particles of 4–10 nm diameter were repeatedly observed to be hygroscopic and nonvolatile when regional nucleation and/or plume impact events occurred. Those observations suggest that particles of 4–10 nm during the nucleation events were hygroscopic and also nonvolatile in both types of events. On the basis of Table 1, these observations are
consistent with the hypothesis that those particles consisted primarily of "sulfates".

[25] The observed growth factor of ~1.4 for 10-nm particles during the event periods is also consistent with this conclusion. Our laboratory experiments showed that the growth factor of 12-nm ammonium sulfate particles generated with an electrospray was 1.3–1.4 at 90% RH. Similar results of the GF of ~1.4 have been reported for ammonium sulfate particles of about 10 nm [Hämeri et al., 2000; Han et al., 2002]. In these laboratory experiments, the reduced growth factors, compared to 1.7–1.8 for much larger particles, were attributed to the Kelvin effect as follows: At the equilibrium between a droplet of an aqueous solution and the surrounding humid air, the relative humidity RH is related to the water activity \( a_w \) and the Kelvin correction term \( C_K \) as

\[
\frac{RH}{100} = a_w C_K
\]

where \( C_K = \frac{p}{p^*} \), where \( p \) and \( p^* \) are the pressure above the droplet surface and the equilibrium vapor pressure above a flat surface, respectively [Hämeri et al., 2000]. For very small particles, \( C_K \) is greater than unity and an equilibrium is reached at a lower water activity for a given RH. This means the particles take up less water, and hence the growth factor is smaller than that for large particles that are not affected by the Kelvin effect.

[29] The growth factor of ~1.2 for 4-nm particles, which was observed during plume impact events, is also expected for particles composed of "sulfates". This interpretation is based on the finding by Han et al. that the growth factor of 4.8-nm ammonium sulfate particles at 90% RH was about 1.2 [Han et al., 2002]. The reduced growth factor is again attributed to the Kelvin effect. Therefore the hygroscopicity of freshly nucleated 4-nm particles was equal to that of ammonium sulfate particles.

[30] The observation that the diameter of 8-nm particles decreased by about 4 nm at 150°C provided further support for the hypothesis that the particles were composed of "sulfates". This is because the observed diameter change is consistent with our aforementioned laboratory experiment with 10-nm particles of ammonium sulfate, ammonium bisulfate, and sulfuric acid that the diameter decreased by ~5 nm when heated to 150°C in our apparatus.

[31] It should be noted that the observed nonvolatility suggests that particles did not contain water by a detectable amount after DMA1. This means that the water issue discussed in the Experiment section did not affect our measurements during the nucleation events, and that our measurements of the growth factor were accurate.

[32] Direct TDCIMS measurements of the particle composition during nucleation events support our conclusion that these particles were composed primarily of "sulfates", and, more importantly, rule out the possibility that the particles were of pure sulfuric acid [Smith et al., 2005]. Briefly, both ammonium and sulfate ions were observed to be present in sub-20 nm particles that were collected during intense particle nucleation events, and ions associated with other species (e.g., organics) were not detected. More details are given in the companion paper.

[33] It is instructive to compare our observations with similar TDMA measurements of nanoparticle hygroscopicity during atmospheric nucleation events. Väkevä et al. used a TDMA system to measure the hygroscopicity of freshly nucleated particles on the western coast of Ireland when air was transported across exposed tidal zones [Väkevä et al., 2002a]. Particles of 8–10 nm were found to be only slightly hygroscopic, exhibiting growth factors of ca. 1.05 as relative humidity increased from 4% to 90%. This finding excluded the possibility that these particles consisted of sulfates or other hygroscopic compounds. Instead, the result was consistent with the hypothesis that nucleation and growth at this site was caused by photo-oxidation of organic iodine [O’Dowd et al., 2002; Jimenez et al., 2003]. The significant difference in the observed hygroscopicity indicates that the particle composition and hence the chemical species that were involved in nucleation and subsequent growth were very different between the two sites. Another hygroscopicity measurement was carried out in the boreal forest at Hyytiälä, Finland during regional nucleation events [Hämeri et al., 2001]. Hygroscopicity of 8–10 nm particles was very low (GF ~ 1.1) at the beginning of nucleation events and then increased to 1.2–1.3, which is somewhat lower than our observations for Atlanta. Increases of the growth factor were observed as particle events started, which is similar to the observation in our study, but the increase began a few hours before the onset of a regional nucleation event was detected in their size distribution measurement. In our study, the change in hygroscopicity at the onset of regional nucleation occurred sharply. The reason for this difference is unknown. In the same study in Finland, the dependence of the growth factors on relative humidity in the TDMA was measured. Particles were found to deliquesce at RH lower than 70%. This led the authors to conclude that those particles were not composed of pure ammonium sulfate which deliquesces at 79% RH. We did not carry out similar RH-dependent hygroscopicity measurements during ANARChE, so the degree of neutralization of sulfate by ammonia could not be deduced in this way.

3.3. Observations During Periods of No Nucleation Events

[34] During ANARChE, while no external mixing in nucleation mode particles was observed during nucleation event periods, it was occasionally observed in both hygroscopicity and volatility measurements in other periods. Most of external mixing was observed in periods from early evening (~18:00–20:00) till morning (~4:00–8:00). The mixing was sometimes separable into distinct groups of hygroscopicity or volatility: GFs of more and less hygroscopic particles were ~1.3–1.4 and ~1.0–1.1, respectively, while the decrease in diameter of more and less volatile particles were ~2–4 and ~0–1 nm, respectively. Broad distributions of hygroscopicity and volatility, which suggested that the particles had a continuous range of compositions rather than several distinct types, were also often observed. When external mixing was observed, the concentrations of both nitric oxide and carbon monoxide were typically somewhat elevated (greater than ca. 50 and 500 ppb, respectively), which implies that air masses at the surface was stable and was influenced by emissions from the surface (e.g., traffic). We do not know what sources contributed to the emission of particles of different volatilities and hygroscopicities.
were mean growth factors of more and less hygroscopic particles hours, and occurred even in summer. That external mixing continued for only as long as a few days in winter, while almost no external mixing was observed in spring/summer. This is in contrast with our observations that external mixing occurred for only as long as a few hours, and occurred even in summer.

Volatility and hygroscopicity were somewhere intermediate for the rest of the measurements, i.e., periods without nucleation or external mixing. That is, nucleation mode particles were somewhat hygroscopic and slightly volatile. In hygroscopicity measurements, the growth factor at 90% RH was about 1.2, and in volatility measurements, the particle diameter decreased by about 1–2 nm at 100°C. Although we do not have complete TDCIMS measurements for the chemical composition of these particles and are unable to explain their observed volatility and hygroscopicity with certainty, TDCIMS measurements consistently found the presence of some amount of ammonium and sulfate ions in sub-20 nm particles even during nonevent periods. This may indicate that the particles of intermediate volatility and hygroscopicity were internally mixed, and contained compounds that were slightly volatile and nonhygroscopic or slightly hygroscopic in addition to ammoniated sulfates. It is also possible that water remained in the particles even after they were exposed to 15% RH in DMA1 and contributed to the slight volatility. Summary of the hygroscopicity and volatility measurements during this study for both nucleation and nonnucleation periods is given in Table 3.

### Table 3. Summary of Observed Hygroscopicity and Volatility on Nucleation Mode Particles During This Study

<table>
<thead>
<tr>
<th>Condition</th>
<th>Growth Factor (–) (Hygroscopicity)</th>
<th>Decrease in Diameter (nm) (Volatility)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation event</td>
<td>1.4</td>
<td>0 to –0.5</td>
</tr>
<tr>
<td>10 nm (regional and plume)</td>
<td>1.4</td>
<td>0 to –0.5</td>
</tr>
<tr>
<td>4 nm (plume)</td>
<td>1.2</td>
<td>n/a</td>
</tr>
<tr>
<td>6 nm (plume)</td>
<td>n/a</td>
<td>0</td>
</tr>
<tr>
<td>8 nm (plume)</td>
<td>n/a</td>
<td>4 (at 150°C)</td>
</tr>
<tr>
<td>Nonevent (10 nm)</td>
<td>1.3–1.4/1.0–1.1</td>
<td>2–4/0–1</td>
</tr>
<tr>
<td>No external mixing</td>
<td>1.2</td>
<td>1–2</td>
</tr>
</tbody>
</table>

*aThe growth factors (and diameter decreases) of more and less hygroscopic (volatile) modes are indicated before and after a slash, respectively.

In their hygroscopicity measurements in Helsinki, Väkevä et al. frequently observed external mixing of 10–20 nm particles in winter time [Väkevä et al., 2002b]. The mean growth factors of more and less hygroscopic particles were ~1.26 and ~1.04, respectively, which are similar to the GFs in our measurements during external mixing periods. External mixing was found to continuously occur for many days in winter, while almost no external mixing was observed in spring/summer. This is in contrast with our observations that external mixing continued for only as long as a few hours, and occurred even in summer.

Volatility and hygroscopicity were somewhere intermediate for the rest of the measurements, i.e., periods without nucleation or external mixing. That is, nucleation mode particles were somewhat hygroscopic and slightly volatile. In hygroscopicity measurements, the growth factor at 90% RH was about 1.2, and, in volatility measurements, the particle diameter decreased by about 1–2 nm at 100°C. Although we do not have complete TDCIMS measurements for the chemical composition of these particles and are unable to explain their observed volatility and hygroscopicity with certainty, TDCIMS measurements consistently found the presence of some amount of ammonium and sulfate ions in sub-20 nm particles even during nonevent periods. This may indicate that the particles of intermediate volatility and hygroscopicity were internally mixed, and contained compounds that were slightly volatile and nonhygroscopic or slightly hygroscopic in addition to ammoniated sulfates. It is also possible that water remained in the particles even after they were exposed to 15% RH in DMA1 and contributed to the slight volatility. Summary of the hygroscopicity and volatility measurements during this study for both nucleation and nonnucleation periods is given in Table 3.

### 4. Conclusions

Continuous measurements of hygroscopicity and volatility of atmospheric aerosol particles of 4–10 nm diameter by a Nano TDMA in the ANARChE study revealed that those particles were very hygroscopic and nonvolatile during nucleation events. In our Nano TDMA system, ammonium sulfate, ammonium bisulfate and sulfuriac acid nanoparticles all exhibited similar hygroscopicity and volatility, possibly because of ammonia uptake within the instrument. Atmospheric nanoparticles that had recently been formed by nucleation had hygroscopicity and volatility equal to laboratory-generated particles of these compounds. Parallel TDCIMS measurements detected both ammonium and sulfate ions in sub-20 nm particles in event periods, which indicate that the main composition of the particles was not sulfuric acid but ammoniated sulfates. This finding strongly supports the hypothesis that the nucleation and subsequent growth of particles in Atlanta were driven by reactions that involved sulfuric acid and ammonia. The differences in measured hygroscopicities during nucleation events from previous studies in Ireland and Finland implies that nucleation and subsequent growth mechanisms at these sites were different.

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