1. Introduction

[2] The chemical components of single particles were measured with the Particle Analysis by Laser Mass Spectrometry (PALMS) instrument in Atlanta in August 1999 during the Environmental Protection Agency (EPA) Southern Oxidants Study (SOS) PM2.5 Supersite Project. The objective and design of the Atlanta Supersite Project were described by Solomon et al. [2002]. This paper presents the results of nitrate and oxidized organics in the Atlanta particles. Other results of the chemical components in single particles measured by PALMS during the Atlanta Supersite Project were shown elsewhere focusing on the organic/sulfate, lead, soot/hydrocarbon, and mineral particles [Lee et al., 2002]. A comparison of particle mass spectrometry data from several instruments is shown by Middlebrook et al. [2003].

[3] Ammonium nitrate is the most important form of aerosol nitrate. It forms from the gas-phase nitric acid and ammonia when the thermodynamic conditions are satisfied and transforms reversibly between the gas and aerosol phases. The thermodynamic behavior of ammonium nitrate under tropospheric temperatures has been extensively studied [Stelson and Seinfeld, 1982; Clegg et al., 1998; Mozurkewich, 1992]. Other types of particulate nitrate may be formed by surface reactions on dust and soot particles [e.g., Zhang et al., 1994; Ammann et al., 1998]. Aerosol nitrate formation also includes aqueous processes [Orel and Seinfeld, 1977]. Mass spectrometry can help us to examine the forms of aerosol nitrate by measuring what other species are associated with nitrate at a single particle level.

[4] Carboxylic acids are among the most important oxidized organic molecules in the atmosphere. Formic and acetic acids are the abundant organic acid species in the gas phase, but are also present in cloud water and in aerosol particles [see Chebbi and Carlier, 1996, and references therein]. Like nitrate, the partitioning of organic monoacids between the gas and aerosol phases is sensitive to the humidity, temperature, aerosol acidity, and other factors [Meng et al., 1995; Khan et al., 1995]. Oxidized organic species with a higher molecular weight, including diacids, ketoacids, and other multifunctional carbonyl and organosulfur compounds, are condensable and also partition into particles [Saxena and Hildemann, 1996; Blando and Turpin, 2000]. Oxidized organics have a variety of sources.
are emitted as primary aerosols from both biogenic and anthropogenic sources. They are also formed as secondary organic aerosols via aqueous-phase reactions or gas-phase oxidation of hydrocarbons [Grosjean and Seinfeld, 1989; Jacobson et al., 2000]. Oxidized organics also alter the hygroscopic behavior of atmospheric particles [Saxena et al., 1995].

2. Experiments

PALMS can measure a wide range of chemical components from individual ambient particles [Murphy and Thomson, 1995; Thomson et al., 1997, 2000]. Very briefly, a YAG laser (532 nm) is used to detect particles and an excimer laser (193 nm) is used for the laser desorption and ionization processes. The ions formed are detected by a time of flight mass spectrometer. Either positive or negative ion mass spectra are obtained by changing the polarity of the mass spectrometer voltages. Particle sizes can be approximately estimated with the YAG laser scattered light intensities: on average larger particles scatter more light than smaller particles [Lee et al., 2002].

The experimental setup of the PALMS instrument in Atlanta was previously described in detail [Middlebrook et al., 2000; Lee et al., 2002]. Single particle mass spectra were taken in Atlanta from 3 to 24 August 1999, mostly between 0600 to 1800 Eastern Standard Time (EST). Nighttime measurements were conducted on 5, 10, and 15 August. For most of the campaign period (from 3 to 20 August), a Nafion dryer was used in the inlet to reduce the effect of water on laser ionization efficiencies. We selected only the spectra that had a signal to noise ratio greater than 100 in positive spectra and greater than 10 in negative spectra (negative spectra usually had less total ion current and lower signal to noise ratios). As a result, about 236,000 positive ion spectra and 144,000 negative spectra were selected from 546,000 spectra taken during the entire period of the campaign. Only the dried particles were used in this work. The wet particles are more difficult to analyze because of the variable water content.

We used the ion fraction of each species relative to the total ion current in the spectrum instead of the ion peak area for representing the relative amount of the species in particles, since the former is more reproducible than the latter [Murphy and Thomson, 1997]. Nitrate produces NO$_2^-$ and NO$_3^-$ ions at m/e = 46 and 62, respectively (Figure 1), and NO$^+$ ions at m/e = 30. Only the negative ions are shown in this paper. Interpretation of NO$^+$ is complicated by the possibilities that other species besides nitrate may produce NO$^+$, and that CH$_2$O$^+$ (also m/e = 30) could present an interference. Nevertheless, the diurnal pattern and RH dependence of NO$^+$ were similar to the negative ion results shown here.

Some oxidized organic ions were identified from the negative ion spectra. Fragmentation during the ionization process precludes identification of the parent molecules. For example, the 45 peak (CHO$_2^-$, formate, or CH$_3$CH$_2$O$^-$, ethoxide) may represent the presence of formic acid, a fragment of a larger organic acid, or even a fragment of a molecule that is not an acid. However, a peak at mass 45 is still reasonably specific for oxidized organics. Laboratory experiments showed that the mass spectra from hydrocarbons (without oxygen) do not produce a peak at this mass. Other oxidized organic ions are 59 (CH$_3$CO$_2^-$, acetate, or CH$_3$CH$_2$CH$_2$O$^-$, n-propoxide), 73 (CH$_3$CH$_2$CO$_2^-$, propionate or CHOCO$_2^-$, glyoxalate), and 111 (CH$_3$(OH)SO$_3^-$, hydroxymethanesulfonate or HMS) as shown in this spectrum. There were also other oxidized organics observed in the Atlanta particles (see text and Table 1).
malonate), and 117 (HOOC(CH2)2CO2, succinate). The 73 ion peak can overlap with a soot/hydrocarbon ion, 73 (C6H/C0). However, soot/hydrocarbons particle spectra usually showed much more distinct Cn and CnH (n = 1, 2, 3, etc.) patterns. Potential interferences of aluminosilicate ions (e.g., 59 = AlO2 and 103 = AlSiO3) with organic peaks were also ruled out by examining other aluminosilicate ions such as 76 (SiO3) peaks within the same spectrum.

Hydroxymethanesulfonate (HMS) was identified by a negative peak at m/e = 111 (CH2(OH)SO3) (Figure 1). HMS forms by sulfur dioxide reacting with formaldehyde in aqueous solutions such as clouds or fogs [e.g., Boyce and Hoffmann, 1984]. Besides being HMS [Neubauer et al., 1996], the negative 111 ion peak could also be another organosulfur compound, CH3OSO3 (methylsulfate). However, methylsulfate is unlikely to be present in the Atlanta

Figure 2. The ion fraction of the chemical components as a function of YAG laser scattered light intensities for (a) carbonaceous and sulfate, (b) nitrate, oxidized organics, HMS, aluminosilicates, and lead ion peaks. In general, larger particles scatter more light than smaller particles. The corresponding sizes range from about 0.35 to 2.5 μm in aerodynamic diameter. 10,000 spectra are used at each point for averaging the ion fraction of each chemical species. Carbonaceous components are shown by the sum of 12 (C1) and 36 (C2) ions; sulfate, 97 (H2SO4); nitrate, 46 (NO2) and 62 (NO3); oxidized organics, 45 (CHO2), 73 (CH3CHO2), 87 (CH3COCO2), 89 (HCOOCH2CO2), 103 (HOOCCH2CO2), and 117 (HOOC(CH2)2CO2); HMS, 111 (CH2(OH)SO3); aluminosilicate, 59 (AlO2), 76 (SiO3), and 119 (AlSiO4); and lead 206 (206Pb+), 207 (207Pb+), and 208 (208Pb+). Note, the “carbonaceous” peaks shown here do not include any oxygen atoms. Also, the upper (a) and lower (b) graphs have different scales of the ion fractions. Lead ion peaks did not show any size dependence and aluminosilicate containing particles had much higher scattered light signals than other species [Lee et al., 2002].
particles, since the formation of methylsulfate requires relatively high acid concentrations in particles and low temperatures [Kane and Leu, 2001].

3. Results and Discussion

3.1. Nitrate

More than 20% of the negative spectra contained NO$_2^-$ and NO$_3^-$ ions. And an even much larger fraction of the positive ion spectra contained an NO$^+$ peak [Lee et al., 2002], so small amounts of nitrate might have been present in most particles. Nitrate ion peaks comprised a higher ion fraction in larger particles with higher scattered light intensities (Figure 2).

Figure 3. Time of day variation (a, c, e, g) and wind direction dependence (b, d, f, h) of the ambient RH and ion fractions for nitrate, oxidized organics, and HMS. About 74,000 negative ion mass spectra measured from 3 to 20 August 1999 and sorted by ambient RH, wind speed and wind direction measurements are shown. Note that each species has different scales for ion fractions.

[iii] Figure 3 shows the ion fraction of nitrate, oxidized organic, and HMS peaks as a function of time of day and wind direction. The ambient relative humidity (RH) was higher at night than during the daytime and peaked at wind directions from east and southwest. Nitrate peaks showed a diurnal variation similar to the ambient RH variation, with a significant peak during the morning. Nitrate peaks showed a clear correlation with RH (Figure 4a), indicating that the diurnal variation was mainly driven by the ambient RH variation. This result is consistent with the temperature and relative humidity dependence of solubility and dissociation constants of ammonium nitrate derived from the fundamental thermodynamic principles [Stelson and Seinfeld, 1982; Mozurkewich, 1992]. Nitrate peaks also had a small local
maximum in the afternoon (at about 16 EST) when the HNO₃ concentrations were high (P. C. A. Jongejan, private communication, 1999) while the RH had a minimum value. Nitrate peaks did not show clear wind direction dependence. In general, our nitrate’s diurnal variation showed a trend similar to that of the semicontinuous measurements by other methods such as ion chromatography or integrated collection/vaporization cell methods [Middlebook et al., 2003; Weber et al., 2001; E. Edgerton et al., unpublished manuscript, 2002; S. Hering, private communication, 1999; P. C. A. Jongejan, private communication, 1999]. However, quantitative comparisons between the single particle mass spectral data and the semicontinuous measurements are difficult.

One type of information that we can add to the semicontinuous measurements is how the nitrate ion peaks vary on different types of particles. Figure 4a shows the nitrate ion fraction as a function of the ambient RH on different types of particles: the total particles, soot/hydrocarbon, aluminosilicate (mineral), and organic/sulfate particles. Soot/hydrocarbon particles are identified by the distinctive pattern of the C₅, C₆H+, and C₇H₂ (n = 1, 2, 3 etc.) ion peaks. The aluminosilicate particles are indicated by the coexistence of 59 (AlO₂⁻), 76 (SiO₃⁻), and 119 (AlSiO₄⁻) ions. Nitrate was well correlated with the ambient RH, showing that nitrate’s diurnal variation was driven mainly by the RH variation. (b) Diurnal variation of nitrate ion fraction on different types of particles such as the total particles, soot/hydrocarbon, aluminosilicate, and typical organic/sulfate particles. The afternoon peak of nitrate was more apparent for the soot/hydrocarbon and mineral particles than for the typical organic/sulfate particles. 95,000 negative ion spectra taken from 3 to 20 August 1999 and sorted by RH measurement are used.

Figure 4. (a) Relationship of the nitrate ion fraction to the ambient RH on different types of particles such as the total, soot/hydrocarbon, aluminosilicate (mineral), and organic/sulfate particles. Soot/hydrocarbon particles are identified by the distinctive pattern of the C₅, C₆H+, and C₇H₂ (n = 1, 2, 3 etc.) ion peaks. The aluminosilicate particles are indicated by the coexistence of 59 (AlO₂⁻), 76 (SiO₃⁻), and 119 (AlSiO₄⁻) ions. Nitrate was well correlated with the ambient RH, showing that nitrate’s diurnal variation was driven mainly by the RH variation. (b) Diurnal variation of nitrate ion fraction on different types of particles such as the total particles, soot/hydrocarbon, aluminosilicate, and typical organic/sulfate particles. The afternoon peak of nitrate was more apparent for the soot/hydrocarbon and mineral particles than for the typical organic/sulfate particles. 95,000 negative ion spectra taken from 3 to 20 August 1999 and sorted by RH measurement are used.
Middlebrook et al., 2003; Phares et al., 2001; Rhoads et al., 2003], we consider particles that did not contain soot/hydrocarbon or aluminosilicate components as the typical organic/sulfate particles. The RH dependence was strongest on the organic/sulfate particles. Although the aluminosilicate and soot/hydrocarbon particles also showed some RH dependence for nitrate peaks, relatively high nitrate was still retained on the mineral particles at low RHs. These mineral nitrates may be formed by the neutralization reaction of some cations (e.g., K⁺, Na⁺, and Ca²⁺) with the NO₃⁻ ions as shown by Goodman et al. [2000]. About 85–95% of the Atlanta soot/hydrocarbon and mineral particles contained sulfate and oxidized organic components [Lee et al., 2002]. The RH dependence of nitrate on soot/hydrocarbon and mineral particles may be related to the water uptake by the sulfate component of these particles.

The dip in nitrate peaks near 90% of RH is not well understood at this time. These lower nitrate peaks occurred during certain nighttime periods without clear wind direction dependence. Semicontinuous measurements during the same periods showed relatively low values of nitrate with high values of sulfate [Weber et al., 2001; P. C. A. Jongejan, private communication, 1999], indicating that our nitrate dip was not an artifact of the PALMS single particle data. Trace gas measurements showed relatively clean air masses for the same periods (E. Edgerton et al., unpublished manuscript, 2002; P. C. A. Jongejan, private communication, 1999).

The particle type analysis showed that the afternoon local maximum of the nitrate peaks was more significant on

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**Figure 5.** (a) Ambient RH dependence of the oxidized organics on the total particles. Oxidized organics are identified by the negative ions listed in Table 1. (b) Diurnal variation of oxidized organics on total particles and the typical organic/sulfate particles. We did not attempt to identify oxidized organics on the soot/hydrocarbon and aluminosilicate particles, since some oxidized organics ions can overlap with the soot/hydrocarbon or aluminosilicate ions. The afternoon peak of the oxidized organics was present on the organic/sulfate particles, which was different from the nitrate’s afternoon peak (see Figure 4b). The same data set as in Figure 4 is used here.
3.2. Oxidized Organics and HMS

Besides ammonium nitrate and mineral nitrates, nitrate ions could also be formed from organic nitrates. We did not observe any ions characteristic of organic nitrogen components in our single particle mass spectra, although many spectra showed nitrate and organic ions together (see Figure 1). However, this does not exclude the possibility that some organic nitrogen compounds might be present in the Atlanta particles, since they may have been fragmented by the 193 nm ionization laser [e.g., Lemire et al., 1993].

Table 1. Approximate Frequencies of Oxidized Organic Ion Peaks Appearing in the Total Negative Spectra

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Frequency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total oxidized organics</td>
<td>45</td>
</tr>
<tr>
<td>45 (formate or ethoxide)</td>
<td>40</td>
</tr>
<tr>
<td>59 (acetate or n-propoxide)</td>
<td>15</td>
</tr>
<tr>
<td>73 (propionate or glyoxalate)</td>
<td>15</td>
</tr>
<tr>
<td>87 (pyruvate)</td>
<td>5</td>
</tr>
<tr>
<td>89 (oxalate)</td>
<td>5</td>
</tr>
<tr>
<td>103 (malonate)</td>
<td>4</td>
</tr>
<tr>
<td>117 (succinate)</td>
<td>1</td>
</tr>
<tr>
<td>111 (HMS)</td>
<td>15</td>
</tr>
<tr>
<td>HMS with total oxidized organics</td>
<td>12</td>
</tr>
</tbody>
</table>

Because each species can have different ionization efficiencies, these frequencies shown here are approximate. Although the transmission efficiency varies as a function of particle size [Middlebrook et al., 2000], we did not correct the number of particles since the size characterization by scattered light intensity is not sufficiently accurate [Lee et al., 2002].

The mass spectra can be examined for suggestions of formation processes of oxidized organics. Most of the mass spectra with an HMS peak also contained oxidized organic peaks (Figure 1 and Table 1). The coexistence of HMS with oxidized organic peaks in the same particles suggests that some of the oxidized organics were formed by aqueous-phase reactions. The abundance of oxidized organics in larger particles is also consistent with aqueous reactions [Blando and Turpin, 2000]. On the other hand, the RH dependence of oxidized organics suggests that gas-particle partitioning also controls the abundance of the oxidized organics in aerosols. The Henry’s law constants for \((C_1 – C_6)\) carboxylic acids favor partitioning to aerosols during times of high RH [Khan et al., 1995]. Finally, there was a small afternoon maximum of oxidized organics (Figure 3), probably due to photochemical production of the precursors. It is likely that these three processes (aqueous reactions, gas-particle partitioning, and photochemistry) all contributed to the oxidized organics formation in Atlanta particles.

4. Conclusions

The chemical components of single particles (0.35–2.5 µm aerodynamic diameter) were measured by PALMS in Atlanta during August 1999. More than 20% of the negative spectra contained the nitrate peaks, and about 45% contained oxidized organic peaks. Nitrate and oxidized organic peaks were both higher in larger particles.

Single particle mass spectra provided indications about which processes control aerosol nitrate and oxidized organics:

1. The ambient relative humidity drove much of the diurnal variation of aerosol nitrate and oxidized organics. This is consistent with their thermodynamic properties. At higher water content, both ammonium nitrate and organic acids have higher solubility and the gas-particle partitioning process tends toward the aerosol phase.
2. The small afternoon maxima of nitrate and oxidized organic peaks probably occurred due to the photochemical production of the precursors.
3. The afternoon maximum in oxidized organics occurred on the common organic/sulfate particles whereas the nitrate’s afternoon maximum was apparent only on the soot/hydrocarbon and aluminosilicate particles. These results...
suggest a heterogeneous reaction of HNO₃ or NO₂ on the soot and mineral dust particles.

4. Oxidized organics seem to have an alternative formation process via aqueous chemistry as indicated by the coexistence of HMS and oxidized organic peaks in the same spectra. We found no corresponding evidence for aqueous formation of nitrate.

[24] Finally, our Atlanta results may further be compared with the previous single particle data obtained in Idaho Hill [Murphy and Thomson, 1997], a fairly dry and relatively remote environment. Nitrate peaks were often correlated with mineral particles at Idaho Hill, but in Atlanta the nitrate peaks were more often internally mixed with sulfate, at least at high relative humidity. The frequencies of both oxidized organic and HMS peaks appearing in the total spectra were comparable in these two locations.

[25] Acknowledgments. The authors thank Rebecca Washenfelder for helping take data at the Atlanta supersite, and Matt Warshawsky and Donna Sin. We also thank Karsten Baumann and Eric Edgerton for providing meteorological and trace gas data, and Rodney Weber, Piet Jongejan, Sandy Dasgupta, Paul Solomon, and Susanne Hering for sharing their semicontinuous aerosol measurement data. S.-H. Lee would also like to thank Ned Lovejoy, Fred Fehsenfeld, James Roberts, and James Meagher for the helpful comments, and Vicki Grassian for sending us the preprints and reprints.

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Finally, our Atlanta results may further be compared with the previous single particle data obtained in Idaho Hill [Murphy and Thomson, 1997], a fairly dry and relatively remote environment. Nitrate peaks were often correlated with mineral particles at Idaho Hill, but in Atlanta the nitrate peaks were more often internally mixed with sulfate, at least at high relative humidity. The frequencies of both oxidized organic and HMS peaks appearing in the total spectra were comparable in these two locations.

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