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# Determination of Atmospheric Nitrogen Input to Lake Greenwood, South Carolina—I. PM Measurements

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## ABSTRACT

The Reedy River branch of Lake Greenwood, SC, has repeatedly experienced summertime algal blooms, upsetting the natural system. This lake's shallow depth makes it susceptible to atmospheric influence. A series of experiments were carried out in order to investigate the effect of atmospheric nitrogen deposition into the lake. Nitrogen was examined because of the insignificant phosphorus dry atmospheric flux and the unique nutrient demands of the dominant algae (*Pithophora oedogonia*) contributing to the blooms.

In this paper, results are presented of the experimental measurement of coarse and fine atmospheric concentrations of atmospheric particulate nitrogen adjacent to and in the watershed of the Reedy River (downtown Greenville) and Lake Greenwood. Experiments were carried out during four 24-hr periods in January 2001 and again during four 24-hr periods in March 2001. Results are presented here for atmospheric particulate nitrogen as well as other constituents of the airborne aerosol. Mass concentrations of  $PM_{2.5}$  averaged 14.0 and 21  $\mu\text{g}/\text{m}^3$  for Lake Greenwood and downtown Greenville, respectively. Mass concentrations of total suspended particulates (TSP) averaged 22.6 and 38.5  $\mu\text{g}/\text{m}^3$  for Lake Greenwood and downtown Greenville, respectively. This ambient aerosol concentration was apportioned to its chemical constituents, and the greatest contributors to  $PM_{2.5}$  mass were organics (45 and 42% for downtown Greenville and the

lake, respectively) and sulfate (14.1 and 19.7% for downtown Greenville and the lake, respectively).

The information gathered here, despite its episodic nature, is important not only in determining atmospheric nitrogen but also in documenting the composition of aerosol in South Carolina, which so far has not been studied. In a companion paper, results for gaseous pollutants as well as thermodynamic modeling of the aerosol and nitrogen flux determinations are presented.

## INTRODUCTION

The atmosphere has been recognized as a significant contributor of pollutants to water bodies, regardless of acidic implication.<sup>1</sup> While most of the nonacidic studies are concerned with toxic organic substances and metals,<sup>2</sup> there are also studies of nutrient loading to natural water bodies that show the importance of atmospheric deposition.<sup>3,4</sup> It has been hypothesized that increased atmospheric deposition increases the frequency of algal blooms to water bodies worldwide.<sup>5</sup>

Depending on the watershed characteristics and use, atmospheric deposition can contribute up to 100% of nitrogen to the water body.<sup>6</sup> Other studies have found that atmospheric dry deposition could contribute as much total nitrogen as agricultural runoff.<sup>3</sup> Dry deposition is of interest because this mechanism provides nutrients continuously, including during critical times of the year associated with low water levels and high temperatures.

Lake Greenwood is a shallow, artificial lake located in the Saluda River watershed in upstate South Carolina. The lake has a surface area of 41.64  $\text{km}^2$  (4164 ha), an average depth of 6.8 m, and a hydraulic retention time of 78 days. The majority of the inflow is from the Saluda River (62.4%) and the Reedy River (22.2%), which drains the metropolitan Greenville area.<sup>7</sup> The Reedy River and Lake Greenwood are designated by the South Carolina Department of Health and Environmental Control (SCDHEC) as

## IMPLICATIONS

Sampling of  $PM_{2.5}$  aerosol in Lake Greenwood has shown that the area is in danger of exceeding the newly promulgated National Ambient Air Quality Standards (NAAQS) for such particles and points to the need for sampling over longer periods of time to better understand the nature of atmospheric fine aerosol and its impact on the lake.

"impaired waters."<sup>8</sup> Lake Greenwood has had a history of algal blooms, occurring most frequently in the Reedy River branch of the lake. Incoming streams to the Reedy River branch of Lake Greenwood are classified as "fully supporting" aquatic life.

Because there are only a few municipal wastewater treatment plants on the Reedy River, non-point sources are strongly believed to be the major contributors to the nutrient overloading. Currently, limits on growth have been set on the Reedy River corridor to reduce the influence of non-point sources such as septic system leaching. Point source phosphorous has been controlled without cessation of the blooms.<sup>9</sup> Remaining possible factors causing the blooms are non-point loadings of phosphorus and nitrogen.

Algal growth is often limited by bio-available phosphorus or nitrogen.<sup>10</sup> The atmosphere can be a significant contributor of nitrogen, mainly in the form of gaseous  $\text{HNO}_3$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ , and particulate  $\text{NH}_4^+$  and  $\text{NO}_3^-$ .  $\text{NO}_3^-$  is of particular concern because it serves as a readily available source of nitrogen to the algae.<sup>11</sup> Ammoniacal forms of nitrogen both induce eutrophication by adding nutrients—spurring algal growth—as well as reducing oxygen concentrations directly through the process of nitrification.<sup>12</sup> Atmospheric contributions of nutrients are often overlooked in freshwater systems because the nutrient limiting algal growth is often phosphorus. The atmosphere is neither a source nor a sink for any significant species of phosphorus.<sup>13</sup> Examination of the nitrogen cycle, however, shows the many potential interactions between the surface and air as well as the multiple chemical reactions that impact fluxes.

The algal bloom at Lake Greenwood may be unique because of the high nitrogen demand of the predominant species, *Pithophora oedogonia*. This alga has exhibited nitrogen-limited growth in previous investigations.<sup>14</sup> While temperature and phosphorus concentration also have been shown to limit the growth of *Pithophora*, the nitrogen-limited growth is rare for a freshwater alga. *Pithophora* is known to form thick, free-floating mats in shallow lakes throughout the midwest and southeast United States.<sup>15</sup> This alga is known as a species that is difficult to manage because of its resistance to algaecides such as copper sulfate. Consequently, the best management technique recommended is lowering the nitrogen and phosphorus concentrations below their respective half-saturation coefficients,<sup>15</sup> which represent the concentration at which the organism is active at one-half its maximum metabolic rate.

This project examined the chemical characteristics of atmospheric aerosol and gases to ascertain what the dry atmospheric contribution of nutrient loading is to the lake and the watershed as a whole. Measurements of gas

and particulate matter were taken at a site adjacent to Lake Greenwood and upstream in the Reedy River watershed. Atmospheric concentrations were translated to deposition fluxes using simple models for each species examined. Thermodynamic modeling was then used to elucidate the atmospheric chemical reactions that were most influential during atmospheric transport of nitrogen to the lake. Finally, the fluxes obtained in this project were compared with other non-point sources to distinguish whether dry atmospheric deposition deserves more attention in setting and implementing nutrient limits for the watershed. In this paper, the experimental results for the measurement of atmospheric particulate nitrogen are presented. Results from gaseous measurements as well as computational modeling of atmospheric nitrogen will be published later.<sup>16</sup>

## EXPERIMENTAL SECTION

The main objective of this project was to determine the dry depositional flux of nitrogen-containing compounds from the atmosphere to Lake Greenwood and the Reedy River watershed. To accomplish this, particulate and gaseous measurements were taken to resolve temporal and spatial variability. Two sampling sites were selected: one at the shore of Lake Greenwood and the other in downtown Greenville. The Greenville site was selected for its proximity to the Reedy River, for its collocation with a PM sampler operated by SCDHEC, and as a representative of the upper watershed. Other SCDHEC sites in the vicinity (in Greenville county) would also produce comparable measurements of  $\text{SO}_2$  and  $\text{NO}_2$ . Measurements from this site would yield atmospheric concentrations characteristic of the upper watershed of the Reedy River on its approach to Lake Greenwood. The second site was chosen within 10 m of the shoreline of Lake Greenwood. Measurements from this sampler would be characteristic of the atmospheric concentrations directly above the lake's surface.

Simultaneous measurements were obtained to clarify any differences between the two sites. Sampling occurred for a total of eight days in January (11, 12, 14, and 16) and March (6, 8, 10, and 12) 2001. Sampling was for 24-hr periods, measured from midnight to midnight in order to associate each sampling event with a calendar day.

### Aerosol Sampling

Atmospheric aerosol was collected on 47-mm diameter filters. Chemical speciation fell into three categories: water soluble ions; elemental carbon (EC) and organic carbon (OC); and crustal constituents, including metals. Each set of filters contained chemically inert polytetrafluoroethylene (PTFE Teflon) filters (Teflo 47 mm; 1- $\mu\text{m}$  and 2- $\mu\text{m}$  pore sizes, Gelman Sciences) for crustal, trace

element, and ionic analysis. Other filters for particulate matter in each set of filters consisted of quartz fiber filters (47-mm PALLFLEX QAO, Gelman Sciences) for EC and OC contributions to the total aerosol mass.

Total particulate matter was collected by drawing a known flow of ambient air through a filter in an open-face filter holder (Figure 1, top). An aluminum shield was placed above the open-faced filters to prevent excessive solar heating and for protection from falling debris.

The second set of filters was preceded by a cyclone whose aerodynamic cut diameter is 2 μm when operated at 28 L/min and, therefore, collected fine particulate

matter (Figure 1, bottom). This cyclone, based on the well-known AIHL design,<sup>17</sup> is identical to cyclones used in numerous studies in the past 20 years. To eliminate any contamination from the sampler, all tubing used upstream of the filters was Teflon. Additionally, the aluminum cyclone and cyclone head were coated with a Teflon layer.

The open-faced filter holders and filter packs were plastic and were washed with a laboratory detergent prior to sampling. The cyclone inlet was manufactured from glass and was cleaned thoroughly before use with glassware cleaning solution and was then rinsed with dilute

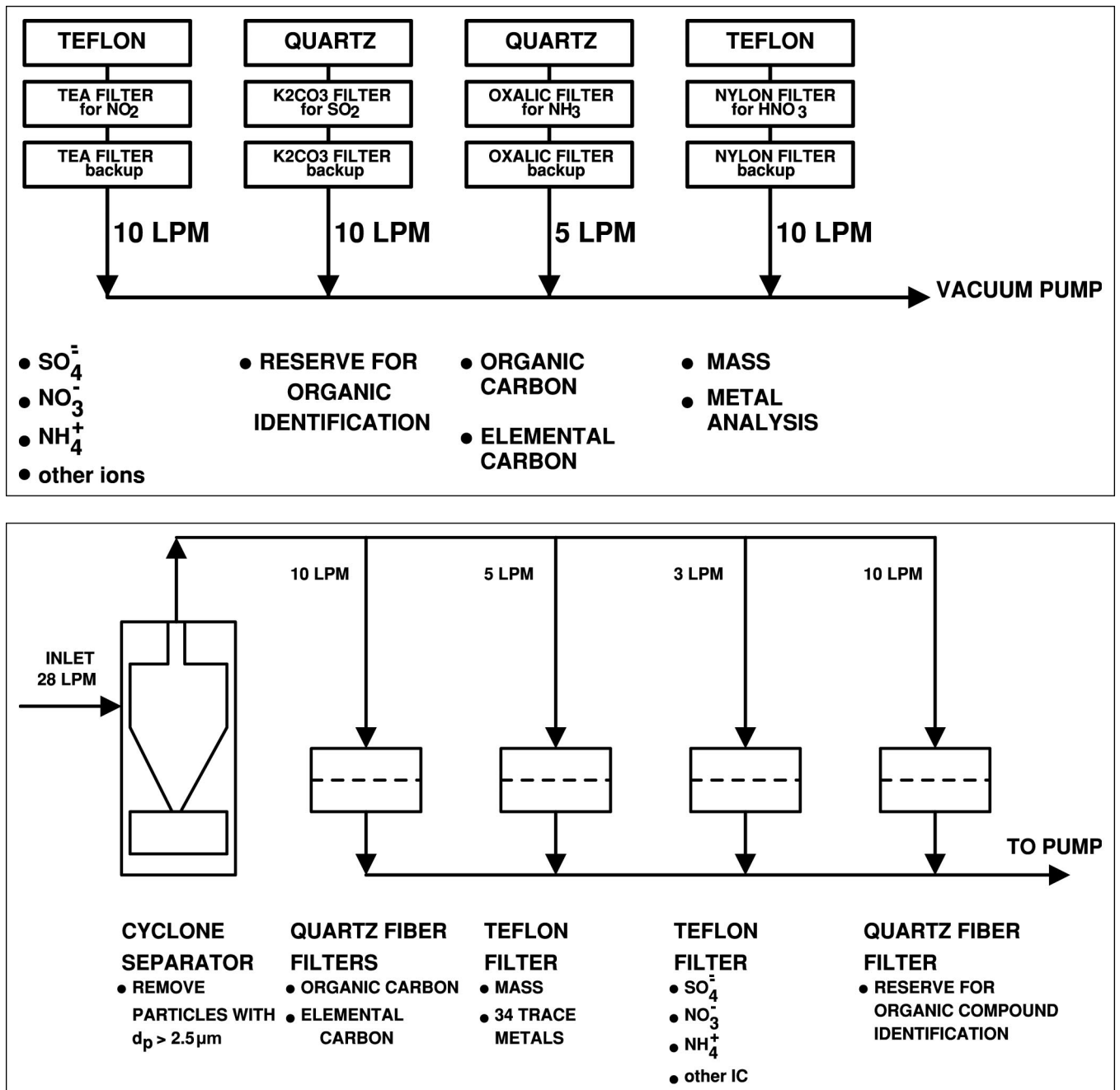


Figure 1. Diagram of the total PM sampler (top) and the fine PM sampler (bottom).

HCl. The filter holder and the filter support, as well as all the cyclone parts, were cleaned prior to use by sonication first in 100% methanol (anhydrous ACS-grade reagent, VWR Scientific Products) and then 100% hexane (anhydrous, >85% n-hexane, EM Science) to remove all contaminants.

### Extraction and Analysis

Gravimetric analysis was performed on a Mettler-Toledo UMT-2 microbalance. The balance has a display precision of 0.1  $\mu\text{g}$  and a maximum capacity of 2.1 mg. Temperature and humidity in the equilibration/weighing room were controlled, with temperature at  $26 \pm 2$  °C, and a relative humidity of  $44 \pm 4\%$ . Relative humidity and temperature were continuously recorded to ensure consistent results.

Quartz fiber filters were analyzed for OC and EC content by the thermal evolution and combustion technique with optical demarcation (thermal-optical) as described in Birch and Cary.<sup>18</sup> In the thermal-optical method, the sample and filter substrate are placed in an oven under a pure helium atmosphere. The two-stage analysis starts by raising the temperature to approximately 850 °C. This volatilizes the OC-containing compounds, which are then oxidized by catalyst to  $\text{CO}_2$  and subsequently reduced to  $\text{CH}_4$  for quantification using a flame ionization detector (FID). Elemental carbon is analyzed in stage two, where the remaining carbon on the filter is raised to approximately 900 °C under a 4%  $\text{O}_2$ , 96% He atmosphere. Optical transmittance is measured and the amount of carbon evolved after the filter regains its original transmittance is taken as EC.

The component of the aerosol consisting of metals is measured by an X-ray fluorescence (XRF) technique using a Rigaku RIX 3000 instrument (Rigaku/MSC). XRF data were used to complete the chemical mass balance of the collected aerosol and to validate the concentrations of elements found by ion chromatography, namely P, Ca, and S (as  $\text{SO}_4^{2-}$ ). Particulate matter arising from crustal materials is treated in this project as consisting wholly of the oxides of certain metals, namely Si, Al, Fe, Mn, Ti, Ca, and K. Each element was measured separately and then converted to "crustal" mass concentration.<sup>19</sup>

Water-soluble ions were extracted from the Teflon filter principally following the protocol in Solomon et al.<sup>19</sup> The filters were first "wetted" with 200  $\mu\text{L}$  of ethanol (ACS reagent grade, anhydrous, J.T. Baker) to reduce the surface tension of the hydrophobic filter and to allow water to penetrate the matrix of the filter.<sup>20</sup> A volumetric pipette was used to add 9.0 mL of deionized, distilled water (DDI) to the filter in a polypropylene cup. The cup and extract were placed on a shaker table and allowed to equilibrate for 3 hr.

All ions were measured using a Waters 717 ion chromatograph plus autosampler with a Waters 515 HPLC pump and Waters 432 conductivity detector. Anions were analyzed with a Waters IC-Pak Anion HR column with a borate/gluconate eluent. This method allowed measurement of ions that included  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ , and  $\text{PO}_4^{3-}$ . Cations were measured with a Waters IC-Pak Cation M/D column with a 3-mM  $\text{HNO}_3$ /0.1-mM [ethylenedinitrilo]-tetraacetic acid (EDTA) eluent. This method allowed for measurement of cations that included  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ .

### Quality Assurance and Quality Control

Three broad types of controls were used. Field blanks remained in the field while sampling occurred and were transported, stored, and analyzed in the same manner as the samples. Dynamic controls were filters that were transported, stored, and analyzed in the same manner as the actual samples but were put in the filter holders for only a few seconds with no flow. Lab blanks remained in the lab until the time of analysis. Controls were used to determine resolution ability of the chemical analysis and to diagnose contamination.

Flow rates were measured at the start and conclusion of the sampling session using a NIST-traceable flow meter (DriCal DC-Lite 20K Primary Flow Meter, Bios International Corporation). Flow rates were controlled during sampling using a downstream orifice that choked the flow at a constant velocity to ensure steady, measured flow rates. Flow measurements after sampling verified that the flow rate remained the same and did not change because of the filter becoming obstructed by particles. Temperature and relative humidity were measured using a VWR brand Model 380 Humidity/Temperature Thermometer (VWR Scientific Products) during filter loading and removal.

Anticipated concentrations were low because of the nature of atmospheric aerosol, so proper protocol was adopted to reduce error. Filters were always handled with tweezers. Chemically impregnated filters were transported to the site shielded from sunlight and in a cooler. Additionally, samples were transported from the sampling site in a cooler to minimize volatilization, and were kept in a freezer in the lab until analysis.

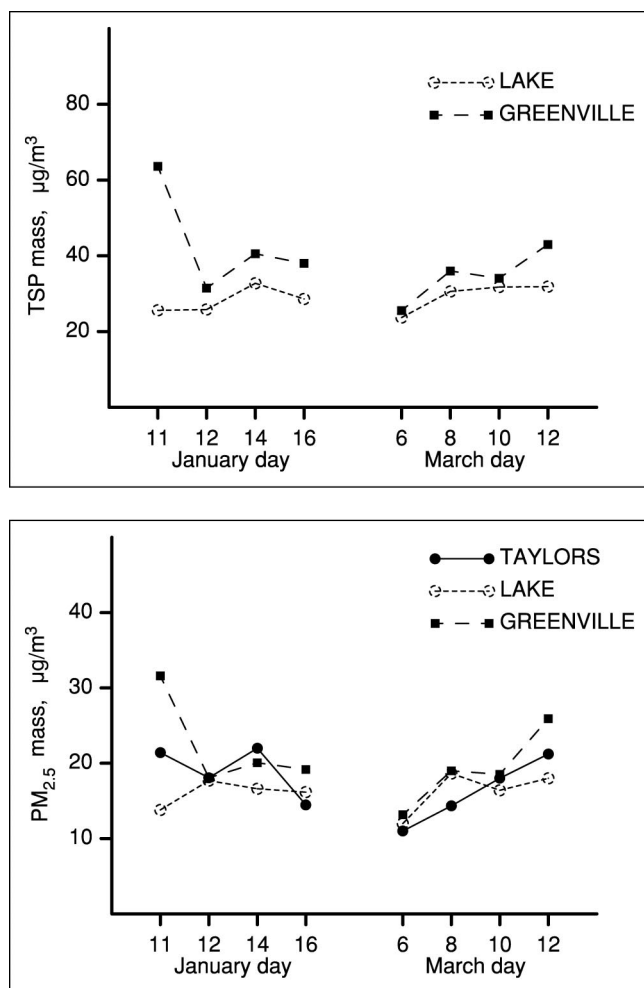
## RESULTS AND DISCUSSION

### Gravimetric Analysis

Results from gravimetric analysis were used as the basis for comparison with chemical measurements. Mass concentration was also measured by SCDHEC samplers, which served as an independent measure of accuracy of the methods used in this project. Total particulate concentrations at Greenville (GV) averaged  $38.5 \mu\text{g}/\text{m}^3$ , while

the value at the Lake (LK) site averaged 22.6  $\mu\text{g}/\text{m}^3$ . Similarly, for the fine mode, the GV average was 21.1  $\mu\text{g}/\text{m}^3$  and the LK average was 14.0  $\mu\text{g}/\text{m}^3$ . Overall, the fine mode contributed about 55% to the total mass. Comparison with the data from the SCDHEC measurements at Taylors can be seen in Figure 2. The Taylors site is located about 5 mi from the Greenville site, and both are urban locations. Many of these samples show an indication of potentially violating the annual  $\text{PM}_{2.5}$  National Ambient Air Quality Standard (NAAQS) of 15  $\mu\text{g}/\text{m}^3$  at the time of this project. Gravimetric measurements of  $\text{PM}_{2.5}$  and TSP can be seen in Figure 2.

Precision in replicate measurements was excellent, with an average standard deviation of 2.1  $\mu\text{g}/\text{filter}$ , which was on the order of 0.0001% of the total mass of the filter and sample, and on the order of 1% of the sample mass. Gravimetric results were obtained for every site and size fraction for at least two duplicate filters. Comparing adjacent filters served as another measure of precision and showed a high degree of correlation for both size fractions ( $r^2 = 0.99$ ).

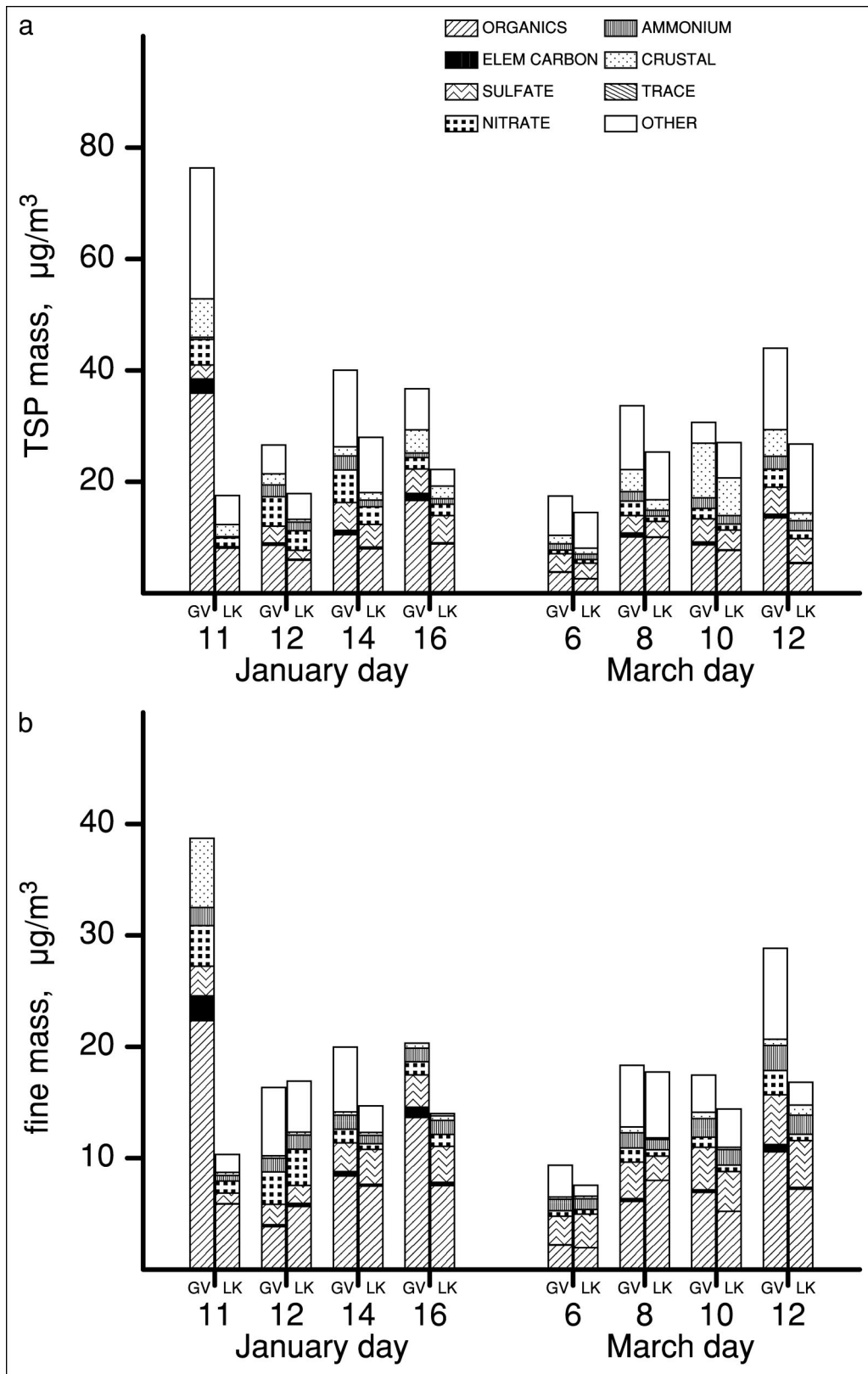


**Figure 2.** TSP mass concentration (top) and fine mass concentration (bottom).

Mass concentrations showed a large variation over the sampling events, despite the samples being taken only two days apart. Also, a large percentage of total mass is attributed to the fine mode. Fine mode particles are primarily the result of atmospheric gaseous reactions that result in a solid or liquid aerosol.<sup>21</sup> Removal of these particles from the atmosphere is slow compared with that of the larger particles, so the fine mode is more evenly distributed and subject to extensive atmospheric transport. There are very few industrial facilities in the vicinity of Lake Greenwood, and the lake is relatively far removed from heavy traffic areas associated with interstate or urban routes. Therefore, fine atmospheric particle concentrations—approaching and exceeding the NAAQS limits—at this site may be the result of atmospheric transport, and the origin of the secondary particles lay upwind.

### Chemical Analysis

Chemical analysis was performed on the collected particulate matter to determine the concentrations of the relevant nitrogen-containing species as well as to characterize the overall chemical composition of the aerosol to elucidate the atmospheric reactions that created it. Daily results are presented in Figure 3, and average results are shown in Figure 4. The main constituent of sampled aerosol is organic compounds. Components most relevant to atmospheric deposition of nutrients—nitrate and ammonium—respectively contribute 11 and 4% to TSP mass and 10 and 6% to  $\text{PM}_{2.5}$  mass. Chemical composition of collected aerosol for this project seemed to differ from results obtained by other studies (Table 1). EC and  $\text{SO}_4^{2-}$  were lower than expected. On the other hand,  $\text{NO}_3^-$  quantities were higher than what was found by the nearest comprehensive study.<sup>22</sup> Comparison with aerosol compositions found in other studies show that the aerosol sampled in this project does not fit into any ideal category. The main reason for the differences between these categories is probably a combination of the averaging time of the values and the sampling conditions for this project. Concentrations from this project are a representation of only a few samples taken in winter and early spring, with a small variation in temperature. Comparison with data from the same site from a different season<sup>23</sup> shows a much larger  $\text{SO}_4^{2-}$  contribution, and it is not unreasonable to assume that aerosol composition has a strong annual variation. The other sources are the result of studies lasting at least one year, and their data reflect samples from all seasons and take into account the annual variation in chemical composition of atmospheric aerosol.



**Figure 3.** (a) Chemical TSP mass concentration, (b) chemical fine mass concentration. Crust is the sum of the oxides of Al, Ca, Fe, K, Mn, Si, and Ti; other includes measured quantities such as Cl, Mg, Na, Pb, and the balance between chemical and gravimetric measurements.

*Nitrate.*  $\text{NO}_3^-$  is an ion that is directly available to contribute to the eutrophication of a water body and is therefore the most germane anion to this project.  $\text{NO}_3^-$  can be

found in many compounds in both the fine and coarse modes of particulate matter in ambient air.  $\text{NO}_3^-$  data collected in this project are presented in Table 2.

One of the potential forms of particulate  $\text{NO}_3^-$  is ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). Because  $\text{NH}_4\text{NO}_3$  volatilizes readily over the range of typical atmospheric temperatures, there exists the possibility of temperature-dependent  $\text{NO}_3^-$  concentrations.<sup>24,25</sup>  $\text{NO}_3^-$  is found in the fine mode as a secondary aerosol, arising from gas-phase oxidation of  $\text{NO}_2$  to form  $\text{HNO}_3$ .<sup>26</sup> Temperature also affects the size distribution of  $\text{NO}_3^-$ . As the temperature increases, the fine-mode  $\text{NO}_3^-$  volatilizes and is scavenged by the coarse soil and salt particles, shifting the  $\text{NO}_3^-$  from the fine mode to the coarse.<sup>27</sup> In the present study, lower  $\text{NO}_3^-$  content in PM was observed during March than during January. This corresponds to the higher temperatures observed during March.

Precision of  $\text{NO}_3^-$  measurements was found to be independent of concentration, with an average standard deviation of replicate measurements of 0.15 ppm. This translates into an average atmospheric nitrate concentration uncertainty of  $0.125 \mu\text{g}/\text{m}^3$  and  $0.096 \mu\text{g}/\text{m}^3$  for the total and fine fractions, respectively. There was no detectable  $\text{NO}_3^-$  on blank filters. There was a significant

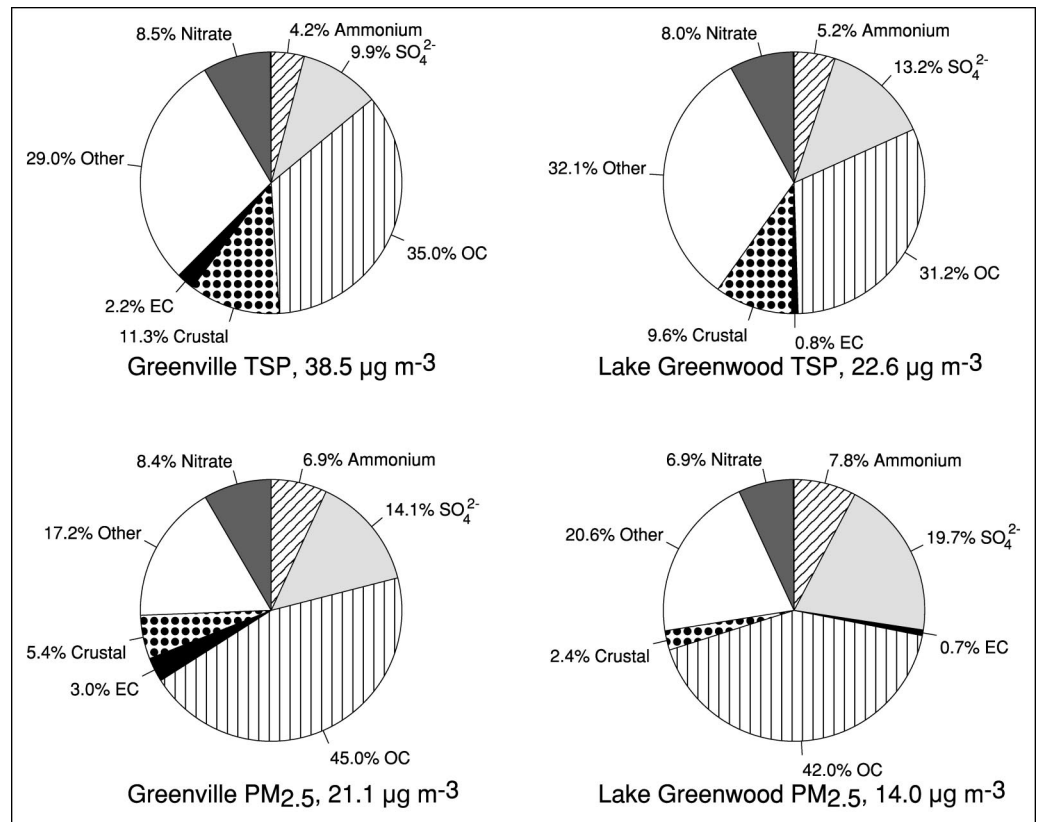


Figure 4. Average aerosol composition.

difference in  $\text{NO}_3^-$  concentration between the samples taken in March and January, a situation for which there was no difference with respect to mass (Table 2). The temporal variation of  $\text{NO}_3^-$  was not corroborated by the mass concentration measurements most probably because any  $\text{NO}_3^-$  changes were masked by changes in more prevalent chemical components.

Although both  $\text{NO}_3^-$  and mass concentrations fluctuated during sampling, the percentage of  $\text{NO}_3^-$  that was in the fine mode compared to the coarse mode was consistently around 55%. This value is strikingly similar to the percentage of TSP attributable to  $\text{PM}_{2.5}$ , hinting that the  $\text{NO}_3^-$  is moved efficiently between particle size

Table 1. Comparison of  $\text{PM}_{2.5}$  composition between regions.

| Region                       | Mass ( $\mu\text{g}/\text{m}^3$ ) | EC (%) | OC (%) | $\text{NH}_4^+$ (%) | $\text{NO}_3^-$ (%) | $\text{SO}_4^{2-}$ (%) |
|------------------------------|-----------------------------------|--------|--------|---------------------|---------------------|------------------------|
| Remote <sup>a</sup>          | 4.8                               | 0.3    | 11.0   | 7.0                 | 3.0                 | 22.0                   |
| Lake Greenwood <sup>b</sup>  | 14.0                              | 0.8    | 25.7   | 5.2                 | 8.0                 | 13.2                   |
| Rural <sup>a</sup>           | 15.0                              | 5.0    | 24.0   | 11.0                | 4.0                 | 37.0                   |
| Greenville <sup>c</sup>      | 16.2                              | 1.0    | 29.0   | NA                  | NA                  | 37.0                   |
| Greenville <sup>b</sup>      | 21.1                              | 2.2    | 28.8   | 4.2                 | 8.5                 | 9.9                    |
| Smoky Mountains <sup>d</sup> | 25.8                              | 1.0    | 11.0   | 7.9                 | 0.8                 | 35.7                   |
| Urban <sup>a</sup>           | 32.0                              | 9.0    | 31.0   | 8.0                 | 6.0                 | 28.0                   |

<sup>a</sup>Seinfeld and Pandis<sup>31</sup>

<sup>b</sup>This study

<sup>c</sup>Swartout et al.<sup>23</sup>

<sup>d</sup>Andrews et al.<sup>22</sup>

Table 2. Summary of nitrate measurements.

|  | Greenville    |       | Lake Greenwood |       |
|--|---------------|-------|----------------|-------|
|  | January       | March | January        | March |
| TSP $\text{NO}_3^-$ ( $\mu\text{g}/\text{m}^3$ )               | avg. 4.44     | 2.09  | 2.59           | 1.02  |
|  | $\sigma$ 1.45 | 0.97  | 0.78           | 0.27  |
| $\text{PM}_{2.5}$ $\text{NO}_3^-$ ( $\mu\text{g}/\text{m}^3$ ) | avg. 2.33     | 1.22  | 1.39           | 0.54  |
|  | $\sigma$ 1.13 | 0.63  | 0.90           | 0.07  |
| % of $\text{NO}_3^-$ in $\text{PM}_{2.5}$                      | avg. 55       | 61    | 55             | 55    |
| % of $\text{NO}_3^-$ in TSP                                    | avg. 11       | 6     | 12             | 4     |
| % of $\text{PM}_{2.5}$ that is $\text{NO}_3^-$                 | avg. 10       | 6     | 10             | 4     |



fractions. This would imply that gas-phase  $\text{HNO}_3$  was very active in particle-to-particle  $\text{NO}_3^-$  transport.

**Sulfate.**  $\text{SO}_4^{2-}$  was the largest ionic contributor to aerosol mass. Particulate  $\text{SO}_4^{2-}$  is most often a secondary aerosol arising from gas-phase reactions of  $\text{SO}_2$  with other chemicals.<sup>28</sup>  $\text{SO}_4^{2-}$  modeling is simpler than  $\text{NO}_3^-$  modeling because the major  $\text{SO}_4^{2-}$ -containing compounds do not have the same volatility complications as many  $\text{NO}_3^-$  compounds do. For example,  $\text{HNO}_3$  has a much higher vapor pressure than  $\text{H}_2\text{SO}_4$ . Predominant  $\text{SO}_4^{2-}$  salts also have low vapor pressures.<sup>29</sup> Thus, once  $\text{SO}_4^{2-}$  reaches a solid state, it is stable and will be removed relatively slowly from the atmosphere by chemical reactions.<sup>30</sup> Deposition is a major removal mechanism that acts slowly because of the small size of  $\text{SO}_4^{2-}$ -containing particles, resulting in a well-mixed atmosphere with respect to  $\text{SO}_4^{2-}$ .

Measurements showed no significant difference in  $\text{SO}_4^{2-}$  concentrations between the two sites for any circumstances. However, there was a significant difference in  $\text{SO}_4^{2-}$  between the January and March samples. March  $\text{SO}_4^{2-}$  measurements were higher than those from January. Samples from the GV site taken the previous summer showed higher  $\text{SO}_4^{2-}$  concentrations than any taken during this project.<sup>23</sup> It is therefore reasonable to assume an annual  $\text{SO}_4^{2-}$  cycle, with lower concentrations in the winter and higher concentrations in the summer. This may explain why this project has  $\text{SO}_4^{2-}$  concentrations much lower than those found in other projects (Table 1). Unlike  $\text{NO}_3^-$ , which had comparable mass in both size fractions, the majority of  $\text{SO}_4^{2-}$  (85%) was found in the fine mode. The average  $\text{SO}_4^{2-}$  concentration was  $3.4 \mu\text{g}/\text{m}^3$ , with a standard deviation of  $1.3 \mu\text{g}/\text{m}^3$ . This formed 10 and 13% of the TSP mass to the GV and LK sites, respectively.  $\text{SO}_4^{2-}$  contributed 14% of the  $\text{PM}_{2.5}$  mass to Greenville and 20% of the  $\text{PM}_{2.5}$  mass to Lake Greenwood. The percentages varied between the sites and size fractions because of the fluctuations of the other chemical components, while  $\text{SO}_4^{2-}$  concentrations remained steady.

**Ammonium.**  $\text{NH}_4^+$  was the major cation present in the aerosol samples. As a reduced form of nitrogen,  $\text{NH}_4^+$  is germane to this project as a nutrient source. Furthermore,  $\text{NH}_4^+$  contributes to lake eutrophication because of the consumption of oxygen as it is oxidized by biological processes.<sup>12</sup>  $\text{NH}_4^+$  can exist in many stable and unstable chemical compounds in atmospheric aerosol. A stable form of  $\text{NH}_4^+$  is  $(\text{NH}_4)_2\text{SO}_4$ , which is the thermodynamically favored form of  $\text{SO}_4^{2-}$  under most atmospheric conditions.<sup>31</sup> Unstable forms of  $\text{NH}_4^+$  include the previously discussed  $\text{NH}_4\text{NO}_3$ .

**Table 3.** Summary of ammonium measurements.

|  |          | Greenville | Lake Greenwood |
|--|----------|------------|----------------|
| TSP $\text{NH}_4^+$ ( $\mu\text{g}/\text{m}^3$ )               | avg.     | 1.61       | 1.17           |
|  | $\sigma$ | 0.71       | 0.46           |
| $\text{PM}_{2.5}$ $\text{NH}_4^+$ ( $\mu\text{g}/\text{m}^3$ ) | avg.     | 1.46       | 1.09           |
|  | $\sigma$ | 0.36       | 0.36           |
| % of $\text{NH}_4^+$ in $\text{PM}_{2.5}$                      | avg.     | 91         | 93             |
| % of $\text{PM}_{2.5}$ that is $\text{NH}_4^+$                 | avg.     | 7          | 8              |
| % of TSP that is $\text{NH}_4^+$                               | avg.     | 4          | 6              |

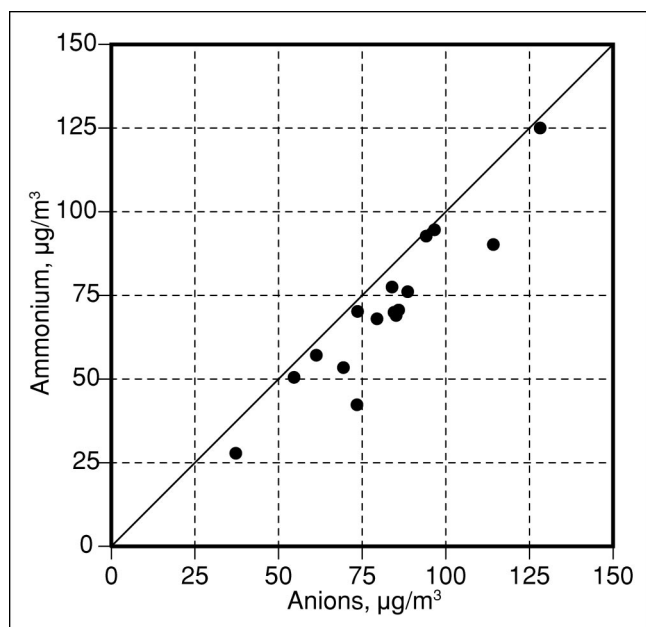
Total concentrations of  $\text{NH}_4^+$  averaged  $1.39 \mu\text{g}/\text{m}^3$  with a standard deviation of  $0.64 \mu\text{g}/\text{m}^3$  (Table 3). Almost all (92%) of the  $\text{NH}_4^+$  was found in the fine fraction. There was no significant difference between the  $\text{NH}_4^+$  concentrations during January and March sampling. While  $\text{NH}_4^+$  concentrations were relatively constant, the overall mass concentrations fluctuated, resulting in the percentage contribution varying between sites and size fractions.

### Neutralization of the Aerosol

Comparison between the molar concentrations of major anions ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) and the major cation ( $\text{NH}_4^+$ ) showed evidence of  $\text{NH}_4^+$  neutralization by  $\text{SO}_4^{2-}$  for most of the sampling events. Charge balances based on the fine mode rather than those based on the TSP-associated ions are presented for two reasons. The first is that chemical reactions are orders of magnitude faster for fine than for coarse aerosol.<sup>31</sup> The second is that total aerosol includes cations associated with primary particles such as soil that may obscure the charge balance relationship, namely the inclusion of  $\text{NO}_3^-$  that is not participating in the neutralization of rather than those based on the TSP-associated ions. Every sample exhibits an  $\text{NH}_4^+$  deficiency in the fine mode when  $\text{NO}_3^-$  is included in the charge balance, and about half of the samples show neutralization attributable to  $\text{SO}_4^{2-}$  alone. Aerosol neutralization is presented graphically in Figure 5, where it can be seen that excess anions were consistently present. All points fall below the diagonal, which signifies excess  $\text{NH}_4^+$ -neutralization capacity.

### Other Cations

Water-extractable cations other than  $\text{NH}_4^+$  were present in atmospheric aerosol in low concentrations. These cations exist in aerosol as soil and sea salt particles.<sup>32</sup> Non- $\text{NH}_4^+$  cations were not expected to play a significant role in atmospheric reactions because of their low concentrations. A possible exception is a reaction of  $\text{Na}^+$  with  $\text{HNO}_3$  to form particulate  $\text{NaNO}_3$ . Other cations



**Figure 5.** Charge summary for all aerosol samples collected.

measured with ion chromatography were present in aerosol samples at a much lower concentration than  $\text{NH}_4^+$ . The combined abundance of cations other than  $\text{NH}_4^+$  was only about 1% of total mass.  $\text{Ca}^{2+}$  and  $\text{K}^+$  were detected in all samples at concentrations above the limit of quantification (LOQ), and  $\text{Mg}^{2+}$  and  $\text{Na}^+$  were present in some of the samples at measurable concentrations.  $\text{Na}^+$  measurements were complicated because the extraction method introduced  $\text{Na}^+$  interferences as sodium silicate leached from the glassware. Glassware was nonetheless used because of the higher accuracy provided that was not available with plastic counterparts. Analysis of blank filters had high  $\text{Na}^+$  concentrations, leading to zero or negative values for  $\text{Na}^+$  in many of the samples. Non- $\text{NH}_4^+$  cations can influence nitrogen deposition by the formation of heterogeneous particles.<sup>33</sup>  $\text{NO}_3^-$  associated with the coarse mode particles, and therefore heterogeneous, was fairly well correlated with  $\text{Na}^+$  concentrations as well as with total non- $\text{NH}_4^+$  cations in general. A possible explanation for this is that there were surface reactions of  $\text{HNO}_3$  with  $\text{Na}^+$ , which was present most probably in the form of  $\text{NaCl}$ . The result of the chemical reaction was the removal of  $\text{HNO}_3$  vapor from the gas phase and the formation of heterogeneous  $\text{NO}_3^-$  particles.

#### Elemental and Organic Carbon

EC and OC analysis for this project was performed by the Environmental Quality Laboratory located at the California Institute of Technology at Pasadena, CA. Atmospheric concentrations for OC were estimated from the concentration of carbon atoms associated with organic materials.

The factor used in this project to infer organic material mass from organic-associated carbon mass was 1.7.<sup>34</sup>

EC was measured directly. Blank filter analysis showed that the pre-treatment process reduced blanks to zero, within the measurement error. Error, determined by replicate measurements, varied on the order of 20% for the average EC mass and 5% for the average OC mass. The high percentage for EC is caused by the very low concentrations found.

The mass of organic material collected was statistically different from site to site; however, the percentage contribution of organic material was similar in all cases. Other aerosol constituents such as  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  had stable contributions by mass, but organic material more or less had consistent contributions by percentage across sites and events. The resulting OC percentage contributions to mass are 33% of TSP and 44% of  $\text{PM}_{2.5}$ . EC made up only about 2% of mass. Daily results may be seen in Figure 3.

#### Crustal Elements

Crustal elemental analysis was obtained by WDXRF methods. The crustal contribution to mass was determined by assuming all elements associated with the crustal component are found in the aerosol in their oxide form (e.g., all the Mn is found as  $\text{MnO}$ ). Blanks were analyzed to determine the background variation and concentration of these elements. All values within 3 standard deviations of the blank values were considered below the limits of quantification.

The high blank concentration of aluminum and the high variability of that element in replicate measurements resulted in no detectable atmospheric concentrations, even though it is expected to make up about 10% of the crustal mass.<sup>35</sup> Metal analysis of soils measured in the Piedmont region of South Carolina show the aluminum contribution to soil mass is roughly as large as the iron fraction.<sup>36</sup> If that relationship holds for atmospheric TSP, the aluminum concentrations should be on the order of  $1.3 \mu\text{g}/\text{m}^3$  in its oxide form. The inclusion of aluminum in this way would increase the crustal component 25% on average and increase the crustal contribution to the TSP mass by 4%. Aluminum estimations were not included in any of the aerosol component calculations because of the considerable uncertainties involved in this extrapolation.

#### Mass Balance of Chemical and Gravimetric Methods

Chemical analysis accounted for about 75% of the gravimetric mass on average. This discrepancy, referred to as the "other" fraction, cannot be attributable to analysis uncertainty alone. Extraction efficiency is an unknown source of error, such as if the extraction method only

transferred 70% of the ion to the aqueous phase, potentially leading to a discrepancy between the chemical and gravimetric masses. If extraction procedures were the major cause of the missing mass, then there would be a linear relationship between the unknown mass and the ionic mass. This possibility was ruled out because no relationship could be ascertained between the ions present and the unknown mass fraction.

A more plausible explanation for the mass discrepancy is a combination of the missing aluminum contribution to the crustal fraction and the use of the factor relating OC mass to organic material mass (OC:C factor). Because of the high concentrations of OC in particulate matter relative to the other chemical components, a slight change in the OC:C factor has a large effect on its percentage contribution. The OC:C factor used in this project, 1.7, is based on work performed in a more northern region.<sup>34</sup> Others have suggested significant uncertainties in translating OC:C factors across regions, which they estimate as the most probable cause for the discrepancy between gravimetric and chemical mass determination.<sup>22</sup> A larger data set is necessary to prove this rigorously, because the data from this project does not indicate a well-behaved relationship for this hypothesis, although the Pearson correlation coefficient is positive. Possible explanations for a higher OC:C factor in this study relative to other regions' data lie in the sources of OC for the two locations and the oxidative potential of the different atmospheres. It is left for further investigation exactly what the correct OC:C mass conversion factor should be in this region, but the indication from this data set is that the OC:C factor should be larger.

## CONCLUSIONS

Algal blooms in the Reedy River branch of Lake Greenwood have repeatedly caused an upset of the natural ecosystem despite reductions in upstream nutrient point sources. *Pithophora*, the nuisance species of alga predominant in the affected area, has demonstrated unusually high nitrogen demand relative to phosphorus in other studies. Therefore, atmospheric deposition was investigated by measuring the dry deposition of nitrogen-containing gases and aerosol at the lake and in the upstream watershed. The following are the major findings of the measurements of atmospheric particulate nitrogen:

- (1) Aerosol  $\text{NO}_3^-$  concentrations were higher than expected, consisting of about 8% of the TSP mass.  $\text{NO}_3^-$  concentrations showed significant spatial and temporal variation during sampling.  $\text{NO}_3^-$  was approximately divided evenly between fine and coarse size fractions.
- (2)  $\text{NH}_4^+$  was found to be the dominant cation in collected aerosol, contributing about 5% to TSP

mass. The majority (90%) of  $\text{NH}_4^+$  was found in the fine mode. Concentrations of  $\text{NH}_4^+$  were less variable spatially than  $\text{NO}_3^-$ .

- (3) Gravimetric analysis showed variation between sites as well as concentrations that approached and exceeded NAAQS limits at both the urban Greenville and rural Lake Greenwood locations.
- (4) The collected  $\text{PM}_{2.5}$  aerosol was found to be cation-deficient (Figure 5).
- (5) Sampling over longer periods of time needs to be carried out together with direct deposition measurements to better assess particulate nitrogen levels at the lake. This is necessary to gain a full understanding of the role of atmospheric particulate nitrogen in algal growth in the lake.

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