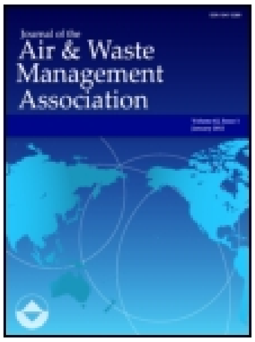

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Determination of Atmospheric Nitrogen Input to Lake Greenwood, South Carolina: Part 2—Gaseous Measurements and Modeling

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ABSTRACT

The Reedy River branch of Lake Greenwood, SC, has repeatedly experienced summertime algal blooms, upsetting the natural system. A series of experiments were carried out to investigate atmospheric nitrogen (N) input into the lake. N 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. Episodic atmospheric measurements during January and March 2001 have shown that the dry N flux onto the lake ranged from 0.9 to 17.4 kg N/ha-yr, and on average is caused by nitric acid (HNO_3; 31%), followed by nitrogen dioxide (NO_2; 23%), fine ammonium (NH_4^+; 20%), coarse nitrate (NO_3^-; 16%), fine NO_3^- (5%), and coarse NH_4^+ (5%). Similar measurements in Greenville, SC (the upper watershed of the Reedy River), showed that the dry N deposition flux there ranged from 1.4 to 9.7 kg N/ha-yr and was mostly caused by gaseous deposition (40% NO_2 and 40% HNO_3). The magnitude of this dry N deposition flux is comparable to wet N flux as well as other point sources in the area. Thermodynamic modeling showed low concentrations of ammonia, relative to the particulate NH_4^+ concentrations.

IMPLICATIONS

Results from sampling as well as thermodynamic modeling clearly show that atmospheric N input into Lake Greenwood could be a significant contributor to algal blooms. More detailed studies are required to fully elucidate the temporal and spatial deposition of atmospheric pollutants into the lake.

INTRODUCTION

Lake Greenwood is a shallow, artificial lake located in the Saluda River watershed in upstate South Carolina. The lake receives the majority of its water from the Saluda River (62.4%). The Reedy River drains the metropolitan Greenville, SC, area and contributes 22.2% of the lake's inflow.[1] Lake Greenwood has had a history of algal blooms, which occur most frequently in the Reedy River branch of the lake, and both the Reedy River and Lake Greenwood have been designated by the South Carolina Department of Health and Environmental Control (SCDHEC) as "impaired waters."[2] There are very few point sources of nitrogen (N) or phosphorous (P) on the Reedy River. Moreover, point-source P has been controlled, but the algal blooms still occur.[3] The remaining possible causes of the blooms are nonpoint loadings of P and N. The algal bloom at Lake Greenwood may be unique because of the high N demand of the predominant species, *Pithophora oedogonia*. This alga has exhibited N-limited growth in previous investigations.[4,5]

This project examined the chemical characteristics of atmospheric aerosols and gases to determine the dry atmospheric contribution of nutrient loading to the lake and to the watershed as a whole. Measurements of gases and particulate matter (PM) 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 measured. Thermodynamic modeling was then used to determine the atmospheric chemical reactions that were most influential during atmospheric transport of N to the lake. Finally, the fluxes obtained in this project were compared with other nonpoint sources to distinguish whether dry atmospheric deposition deserves more attention in setting and implementing nutrient limits for the watershed.

EXPERIMENTAL

The main objective of this project was to determine the dry depositional flux of N-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, 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 sulfur dioxide (SO_2) and nitrogen dioxide (NO_2). Measurements from the sampler at Greenville 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. Both samplers collected atmospheric samples at an approximate height of 1.5 m from the ground.

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

Gas Sampling

Atmospheric gases relevant to this project were measured using a filter pack (FP) technique. Upstream of the FP, a filter was used to remove all PM. The particle-free air then passed through a filter that has been treated to immobilize the gaseous species of interest. A second, identical, filter was placed behind the first filter to capture any gas that penetrated the first filter because of inefficient gaseous capture or filter saturation.

The gas-adsorbing filters for NO_2 and SO_2 were impregnated with varying chemicals to retain the gaseous species. Triethanolamine (reagent grade, J.T. Baker) was used to adsorb the gaseous NO_2 and convert it to nitrite (NO_2^-). The triethanolamine was added to the filter (Whatman 31 ET CHR 47-mm filters, Whatman International) using a mobile phase of methanol and water. Whatman 41 filters were impregnated with potassium carbonate (K_2CO_3) with a mobile phase of water for the conversion of SO_2 to sulfate (SO_4^{2-}). All filters were then stored in individual Petri dishes sealed with Teflon tape and stored in the freezer.

Filter Pack Capture Efficiency

Uncertainty is involved with FP measurements in both the chemical analysis and determining capture efficiency. In this project, two filters in series were placed behind the upstream filter to create the filter pack. The first filter was expected to capture the gaseous species of interest, and the second filter provided a backup if the first filter became saturated. It was expected that nearly all of the gas would be immobilized on the first filter, with very little found on the backup. SO_2 and nitric acid (HNO_3) both behaved as expected. NO_2 measurements exhibited a lower capture efficiency. High penetration using this method of NO_2 measurement has been observed by other researchers.[6] Because there were quantifiable concentrations of NO_2^- on both filters, and none on the unexposed blanks, it is likely that a portion of the total ambient NO_2 passed through the system entirely. Therefore, the capture efficiency was determined for the NO_2 filter packs to calculate ambient concentration.

Capture efficiency was calculated using two assumptions: (1) capture efficiency was constant with respect to concentration, and (2) capture efficiency was constant from site to site and event to event. Total atmospheric concentration, therefore, only relates to the concentration measured on the first filter based on the capture efficiency. It was found that the fraction of the total NO_2 captured on the first filter was 40% and the fraction captured on the second filter was 40% of the NO_2 that penetrated the first filter, or 24%. Of the total NO_2 present, 36% bypassed the sampler completely. Total ambient concentration (C_a) was determined by extrapolating this finding to account for the theoretical amount that penetrated the sampler based on the amount captured on the filters.

Thermodynamic Modeling

Thermodynamic modeling was performed using ISORROPIA v1.5. This model predicts the atmospheric concentrations of inorganic atmospheric aerosol constituents simultaneously with their gaseous precursors.[7] The model can be run in two scenarios: "forward" problems, where the total atmospheric concentrations are known; and "reverse" problems, where the aerosol concentrations are the only known variables. In reverse cases, the gas-phase concentrations are predicted based on the aerosol composition and concentration. Aerosol is treated as one of two types, metastable or stable. In the stable state, salts precipitate out of solution if saturation is exceeded, and the aerosol is allowed to be solid, liquid, or a combination of the two phases. Metastable aerosol is when salts remain in solution under supersaturated conditions. This forces the aerosol to be a wholly aqueous solution.

Assumptions in ISORROPIA are made to improve computational performance. The model ignores particle size variation and assumes that SO_4^{2-} and sodium (Na^+) have no significant gas-phase form. This is based on the low vapor pressure of sulfuric acid (H_2SO_4), and the absence of any major gaseous Na^+ chemical. Another assumption is that the thermodynamically preferred form of SO_4^{2-} is ammonium sulfate [$(NH_4)_2SO_4$]. These assumptions cause the model to behave in two regimes based on the SO_4^{2-}-to-cation ratio. Simply put, if there are enough cations (Na^+ and ammonium [NH_4^+]) to neutralize the SO_4^{2-}, then the excess NH_4^+ reacts with the remaining anions (chloride [$Cl-$] and nitrate [NO_3^-]) to form volatile salts. On the other hand, if the aerosol is Na^+-rich and there are not enough cations for neutralization, then the SO_4^{2-} builds up in the aerosol as H_2SO_4, lowering the pH and driving NO_3^- and Cl^- into the gas phase.[8]

ISORROPIA was selected because of the ability to perform reverse problems, robustness, and the advanced handling of mutual deliquescence relative humidity (RH) points.[9] Being an equilibrium model, sampled concentrations may differ from model predictions because equilibrium conditions may not be reached under field conditions. Typical equilibration times in atmospheric aerosol have a strong dependence on particle size, with smallest particles having the shortest reaction times.[10] Large particles have equilibration times that may be orders of magnitude longer. An inherent assumption in the model is that the aerosol is larger than 0.1 μm in diameter, because the Kelvin effect (the change in vapor pressure over a curved surface relative to a flat surface) is neglected.[7] All aerosols are treated as internally mixed, meaning that all particles have the same composition.[9]

Modeling in this way serves to validate the measurements as well as to shed light on the atmospheric chemical reactions involved during sampling. This helps to determine the sensitivity of the atmospheric system to parameter changes. The model was run under the conditions and concentrations found during sampling to predict equilibrium concentrations. Monte Carlo techniques were also performed to consider analytical error and to account for parameter variation that might affect aerosol concentrations not explicitly measured during sampling, such as temperature and RH.

Modeling Dry Depositional Flux

Dry deposition may be generally described as the transport of atmospheric species from the atmosphere onto surfaces in the absence of rain. Many factors affect this deposition. Atmospheric turbulence, especially at the layer nearest the receiving surface, is important in determining the rate at which the depositing substance is delivered at the surface. The nature of the depositing species, whether it is in particulate or gaseous form, together with its physicochemical characteristics (e.g., size, density, solubility) may govern not only the rate at which deposition occurs but also whether capture will occur when the depositing species comes in contact with the surface. The characteristics of the receiving surface also play an important role in the deposition of atmospheric species. For instance, different deposition rates may be observed onto water than a dry surface, or onto a surface with high surface roughness than an aerodynamically smooth surface.[8]

For the purposes of this work, a simplified model was chosen to determine the atmospheric input of N-containing compounds onto the lake. This is based on a universally used formulation of dry deposition.[8] Once atmospheric concentrations of aerosols and gases are known, a deposition velocity must be used as the final step in calculating deposition flux. Deposition velocity is dependent on several parameters. The deposition velocity may change because of a change in form and N species as atmospheric reactions transform it from the gaseous to the solid phase, such as the transformation of particulate NO_3^- to gaseous HNO_3 vapor. Surface characteristics also affect deposition velocity as different physical mechanisms affect the deposition. A particle deposits onto a land surface in a different way than it would to the surface of a water body. Flux to a surface (ϕ, units of μg/m²-sec) is calculated from the following:

$$\phi = v_d \times C \tag{1}$$

where v_d is the deposition velocity (units of m/sec) and C is the atmospheric concentration (units of μg/m³). Deposition to land and water surfaces was determined using deposition velocities found in the literature.[8,11–14] When particle size data were needed, fine aerosol was treated as 1-μm-diameter particles, and coarse aerosol was assumed to be 5 μm. These deposition velocities are presented in Table 1.

RESULTS AND DISCUSSION

PM Measurements

The full results of PM measurements are presented elsewhere,[15] with a brief summary given here. Mass concentrations of $PM_{2.5}$ averaged 14 and 21 μg/m³ for Lake Greenwood and downtown Greenville, respectively. Mass concentrations of TSP averaged 22.6 and 38.5 μg/m³ 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

Table 1. Summary of deposition velocities.

	Deposition Velocity (cm/sec)					
	Continental			Water		
	High	Low	Suggested	High	Low	Suggested
NO_2	—	—	0.1 (ref 8)	1.5 (ref 5)	0.02 (ref 8)	0.1
HNO_3	4 (ref 8)	1 (ref 12)	2	—	—	1 (ref 8)
Fine PM	0.15 (ref 12)	0.09 (refs 8,12)	0.1	0.3 (ref 11)	0.03 (ref 8)	0.2 (refs 8,12,13)
Coarse PM	0.3 (ref 8)	0.1 (ref 8)	0.2	1 (ref 8)	0.5 (ref 8)	0.75 (refs 8,12,13)

Greenville and the lake, respectively) and SO_4^{2-} (14.1 and 19.7% for downtown Greenville and the lake, respectively).

Gaseous Measurements

Gaseous measurements were taken using an FP method for SO_2, NO_2, and HNO_3. Ammonia (NH_3) measurements were unsuccessful. Gaseous and aerosols measurements were taken to provide input for the thermodynamic model and to better characterize the N species most important for deposition. FP measurement techniques were used for their ease of sampling, extraction, and analysis. FP measurement techniques are usually considered as the upper bound for gaseous concentrations because they will capture both the true gaseous concentrations as well as the byproducts of aerosol volatilization from PM captured on the upstream filter.[17,18]

Accuracy of the FP method can only be determined from independent data, which only exist for sites near the Greenville site and only for SO_2 and NO_2. Data for SO_2 seem to be well correlated with data from the Taylors site (Figure 1). The Taylors site is at Taylors, SC, which is ~10 km from the Greenville site and 20 km from the Lake Greenwood site, and is operated by SCDHEC. Artifacts arising from PM volatilization may be the cause for this bias, because the method is not able to distinguish between SO_2 and SO_4^{2-} captured on the filter. Data from March 12 are missing because the prefilter became clogged, resulting in an unknown sample air volume. SO_2 concentrations were highly variable through the sampling time, ranging from 1.2 to 30.8 $\mu g/m^3$. Concentrations also varied between the sites, with SO_2 concentrations higher by approximately a factor of 3 at Greenville than at Lake Greenwood.

Data for NO_2 show a good correlation with SCDHEC data from Taylors (Figure 2). A probable reason for the systematic underestimation of NO_2 seen is ozone (O_3) interference. As the NO_2 is immobilized and analyzed in the form of NO_2^- on the filter, any exposure to O_3 will convert the NO_2^- to NO_3^-. This effectively removes NO_2^- and therefore would cause a systematic negative bias of NO_2 measurements. O_3 concentrations during the time of sampling were low, because of the winter and early spring sampling time, and any O_3 interference would increase for the warmer months. NO_2 varied from 3.6 to 24.7 $\mu g/m^3$ and was always more abundant at Greenville than at Lake Greenwood. This is perhaps because of the more rural nature of the Lake Greenwood site. The average NO_2 concentrations were 17 and 6.5 $\mu g/m^3$ at Greenville and Lake Greenwood, respectively.

No comparable external measurements were available for HNO_3, although FP methods for determining HNO_3 concentrations are approved by the U.S. Environmental Protection Agency (EPA).[19] HNO_3 data are shown in Figure 3. HNO_3 concentrations varied from just above the level of quantification, 0.1 $\mu g/m^3$, to 2.6 $\mu g/m^3$. The average HNO_3 concentration was 1.4 ± 0.61 $\mu g/m^3$. Although concentrations were low, HNO_3 is important because of its rapid uptake by plants and its reactivity, which leads to a deposition velocity larger than other gaseous N-containing species such as NO_2.

Ion chromatographic analysis of gaseous NH_3 measurements proved impossible. All NH_3 concentrations were to come as a result of thermodynamic modeling later in the project. Although it would be preferred to have samples analyzed rather than model output, NH_3 was not expected to be a large contributor to atmospheric deposition of N for two factors. The first was that examination of

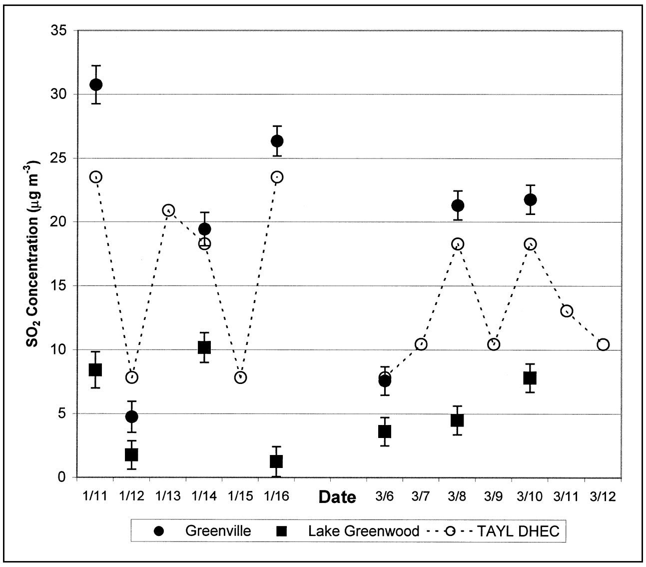

Figure 1. SO_2 measurements at the Greenville and Lake Greenwood sites using the filter pack method. The measurements at the Taylors site were taken by SCDHEC using an automatic SO_2 analyzer.

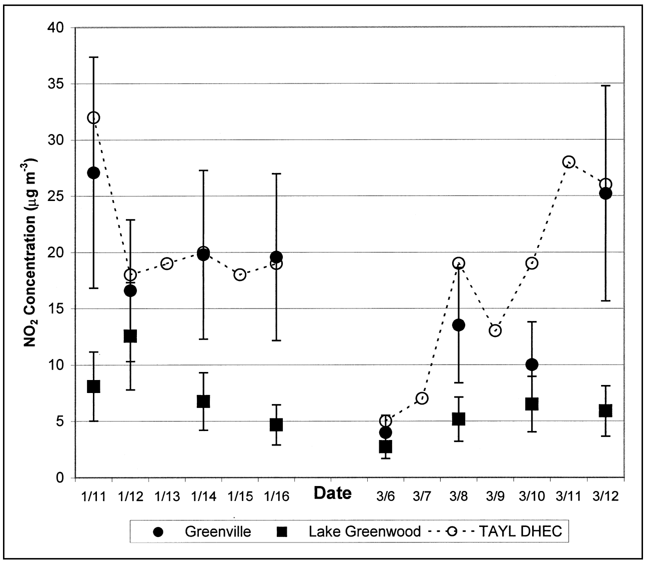

Figure 2. NO_2 measurements at the Greenville and Lake Greenwood sites using the filter pack method. The measurements at the Taylors site were taken by SCDHEC using an automatic NO_2 analyzer.

aerosol proved that the aerosol was SO_4^{2-}-rich and therefore would scavenge NH_3 from the gas to the solid phase. The second is that NH_3 deposition to a water body is highly dependent on the pH and other characteristics of the water body. The gradient driving the gaseous NH_3 deposition was unknown without more information about the surface water characteristics, and under certain conditions the lake itself could be a source of atmospheric NH_3.

Thermodynamic Modeling

Thermodynamic modeling with ISORROPIA required concentrations of inorganic species, temperature, and RH input. All ionic data except Cl^- came from ion chromatographic analysis. Cl^- was taken from wave dispersive X-ray fluorescence analysis. Point temperature data were taken while loading and unloading the filters. Because these data matched well with the temperatures measured at the local airport (Greenville-Spartanburg, GSP), the temperatures recorded at GSP during sampling were used in modeling. RH was measured during loading and unloading, but no reliable data were available during the sampling periods. All calculations and constants used by the model are presented in the original work describing ISORROPIA.[7] The user can change numerical method parameters such as solution accuracy, but the same parameters were used for each run for consistency.

Monte Carlo Method. A simple Monte Carlo method was chosen for modeling to account for the uncertainty in analytical measurements and in the temperature and RH changes through the 24-hr sampling period. This approach was taken to accurately account for the propagation of errors in measurement through the complicated atmospheric thermodynamic model. The Monte Carlo simulation involved computing the output concentrations for many sets of combinations of inputs.[20] Individual inputs were taken at random from distributions that represented analytical error and variation of conditions throughout the 24-hr sampling period. The resulting distribution of outputs, therefore, is a realistic approximation of the aerosol that exists at equilibrium, with a holistic representation of the error, otherwise very difficult to attain by conventional propagation of error techniques because of the complex interaction of the equations.

Analytical error was assumed to have a Gaussian distribution for which average and standard deviation data were developed from replicate measurements. Temperature and RH data also were assumed to have a Gaussian distribution because of the diurnal nature of the 24-hr sampling period. Temperature and RH distributions were expanded in range from the GSP data to represent the probable conditions at the sites.

Each day and site was modeled with 1000 trials, whose input values were taken at random from distributions based on analytical measurements and conditions measured at GSP. The number of trials was chosen to represent the expected distributions and to reduce the effect of outliers, which are inevitable in this type of simulation. If the random distribution produced a negative number, that was replaced with a null value. RH was read on a fractional scale by the model, and therefore all values greater than 1 generated by the random distribution were replaced with a value of unity.

Aerosol sampled in this project mainly exhibited SO_4^{2-}-rich conditions where neutralization was achieved. Modeling data showed correlation within a factor of 2

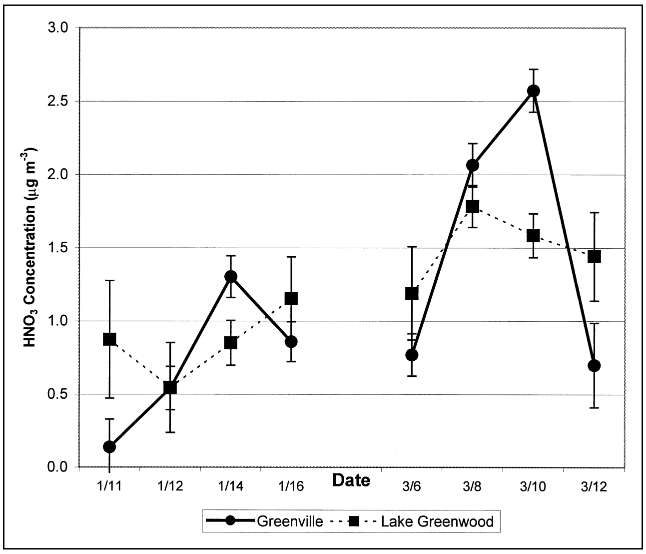

Figure 3. HNO_3 measurements at the Greenville and Lake Greenwood sites using a nylon filter.

with analytical measurements for the individual chemical species. Discrepancies between model predictions and measurements can be attributed to departures from equilibrium.[21] Analysis of much larger data sets has shown occurrences of inconsistencies between modeled and measured concentrations of inorganic species.[10,22] Hypotheses for model departure have been suggested, such as the Kelvin effect, transport limitations, osmotic regime shifts, and surface interactions with organic compounds.[10] These processes are all equilibrium conditions not accounted for by the available modeling software.

Ammonia

NH_3 from modeling was the only major species not measured by analytical means and, therefore, could not be checked for accuracy. From theory, it was expected that concentrations would be low, because there was still NH_3 scavenging capacity in the form of excess SO_4^{2-} in the aerosol. Modeling showed that, on average, there was ~6 times more particulate NH_4^+ than gaseous NH_3. Daily results of NH_3 concentrations as predicted by ISORROPIA are shown in Figure 4.

Average NH_3 concentrations were higher at Greenville than at the Lake Greenwood site, 0.28 and 0.21 $\mu g/m^3$, respectively. Standard deviations were large with respect to the averages because of the analytical errors in measuring the chemicals and also the variation in temperature that would cause higher NH_3 concentrations at high temperatures from ammonium nitrate (NH_4NO_3) volatilization. It is therefore concluded that NH_3 is not a major N-containing species for the conditions and sites sampled in this project. The dominance of aerosol NH_4^+ over gaseous NH_3 is a thermodynamic argument that deposition of reduced N mainly arises from particulates.

Nitric Acid

HNO_3 was the other major gaseous species modeled that was present at significant concentrations. Model-predicted concentrations were higher than measured concentrations in the majority of cases. This was unexpected, because the filter pack methods are regarded as measuring both the true HNO_3 as well as artifact HNO_3 resulting from volatilized NH_4NO_3. Therefore, the measurements would have concentrations higher than those predicted from thermodynamic modeling. Model predictions of HNO_3 were approximately twice the sampled concentrations at the Greenville site and matched well on average to the samples taken at Lake Greenwood (Figures 5a and b).

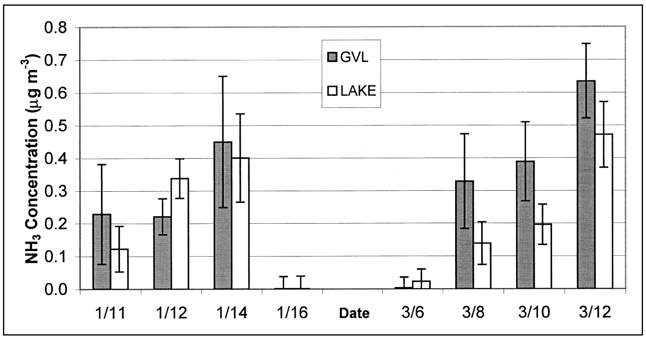

Figure 4. NH_3 concentrations at the Greenville and Lake Greenwood sites as predicted by ISORROPIA modeling.

Discrepancies in HNO_3 concentrations between model and measurements are likely caused by the compounds in the aerosol not considered by ISORROPIA that HNO_3 could react with, such as the organic material. A disconnect between prediction and measurements may also be attributed to the assumption in the model that the aerosol is internally well mixed.[7] Analysis showed that the aerosol was not well mixed for every ion. For example, most of the SO_4^{2-} was found in the fine fraction and most of the Na^+ was found in the coarse fraction.[15] Because of the low gas-phase concentrations of possible SO_4^{2-} species, a reasonable conclusion is that the SO_4^{2-} and Na^+ ions had little interaction in the atmosphere. However, ISORROPIA treats all of the aerosol's components as interacting equally with each other, because it is a thermodynamic equilibrium model. Further explanation of the differences between model output and sample analysis is reached by examining the solid-phase species modeled, with a focus on the SO_4^{2-} species.

Solid Species

SO_4^{2-} species are closely linked with the NO_3^-—HNO_3 tandem as the anions compete for NH_4^+ and Na^+. Modeled particulate species were dominated by $(NH_4)_2SO_4$. The major NO_3^--containing salt was NH_4NO_3. All of the Na^+ was found by the model to be in the form of sodium sulfate (Na_2SO_4). Event-specific data are presented for Greenville and for Lake Greenwood in Figures 6a and b, respectively.

Some of the species showed greater variation in their Monte Carlo output than others. This is because sulfur (S) and Na^+-containing species had no gas-phase component. Other solids like NH_4NO_3 were dependent on temperature and RH. There were also variation changes from one day to another, when a certain set of conditions spanned two regimes, such as when the SO_4^{2-} neutralization of NH_4^+ was marginal. It was expected that the major NH_4^+ salt was $(NH_4)_2SO_4$ and the major NO_3^- salt was NH_4NO_3. However, the unexpectedly large concentrations of disodium sulfate are probably a misrepresentation of the actual species present in the aerosol, because SO_4^{2-} and Na^+ were not predominantly found in the same size fraction.

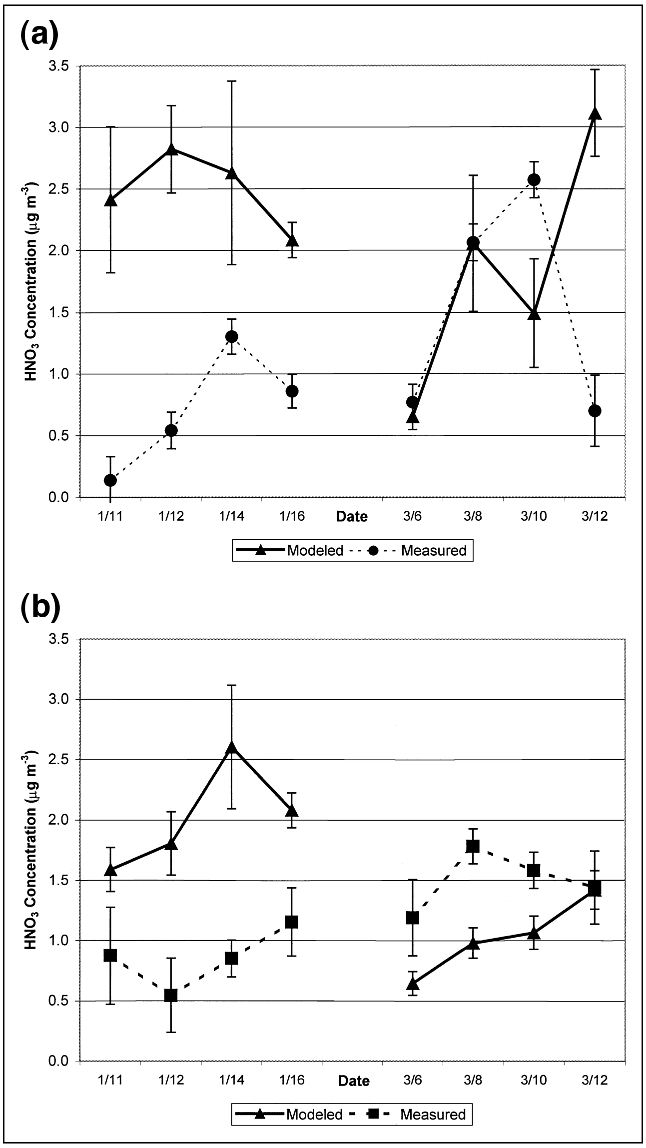

Figure 5. (a) HNO_3 model predictions by ISORROPIA compared with measured concentrations at Greenville. (b) HNO_3 model predictions by ISORROPIA compared with measured concentrations at Lake Greenwood.

Summary

Variation in PM size fractions has an effect on sampled inorganic aerosol species that is unresolved by thermodynamic modeling. It can be suggested that the different size fractions were not in equilibrium with each other during this project. HNO_3 evolved from H_2SO_4 accumulation is left as HNO_3 vapor by ISORROPIA. However, based on the observation of significant coarse NO_3^- in the aerosol, it is likely that the HNO_3 vapor condensed on the larger, more neutral particles. It is also unlikely that there should be the formation of appreciable solid salt combinations of Na^+ and SO_4^{2-}. Analysis of the data shows SO_4^{2-} mainly in the fine PM and Na^+ mainly in the larger particles.

Typical times for reaching equilibrium are orders of magnitude longer for particle-particle interactions compared with interactions that involve a gas-phase conduit.[10] Overprediction of HNO_3 by the model can be justified by the departures from equilibrium attributable to the very slow interactions between Na^+ and SO_4^{2-}. The atmospheric aerosol was therefore unlikely to contain much Na^+-SO_4^{2-} salts. More SO_4^{2-} was available to form NH_3 salts than predicted, resulting in a less acidic aerosol, which would retain solid NO_3^-.

DEPOSITION CALCULATIONS

Deposition flux calculations were made from the measured and modeled atmospheric calculations. The method of using deposition velocity was used, with deposition velocities found in the literature. More sophisticated methods required data that were not collected in this project, and estimates would introduce uncertainties that would not improve the accuracy from using a simple deposition model.

To use ISORROPIA to calculate depositional fluxes, ambient concentration values of the N-containing pollutants need to be used. The deposition velocity as defined in eq 1 is the inverse of the resistance to deposition. This resistance, as mentioned previously, depends on atmospheric turbulence, the nature of the depositing species, as well as the nature of the receiving surface. Concentration values used in modeling depositional flux were calculated based on the average concentration for the entire set of measurements at each site. Bounds of concentrations used were defined as the average value at a site over all events ±1 standard deviation of that set. Deposition velocities found in the literature are presented in Table 1 and the depositional flux of the N species was calculated from eq 1.

NH_3 was not included in the calculations because the only information available was from thermodynamic modeling. NH_3 concentrations were predicted to be very small and the deposition velocity for NH_3 is likely to be small for expected pH ranges of Lake Greenwood. Results of dry depositional flux calculations are presented in Table 2.

Upper and lower fluxes arrived at in Table 2 are a combination of the respective extreme values for both deposition velocity and concentration simultaneously for each individual compound. This provides boundaries for the actual flux because it is more likely that low concentrations in the solid NO_3^- will be offset somewhat by increased concentrations in HNO_3. Despite lower concentrations at the Lake Greenwood site, fluxes were approximately the same because of the higher deposition velocity to water surfaces than to land. Aerosols are deposited more efficiently to water surfaces because RH increases near the surface, all else being equal. As that occurs, particle size increases with the condensation of water, and

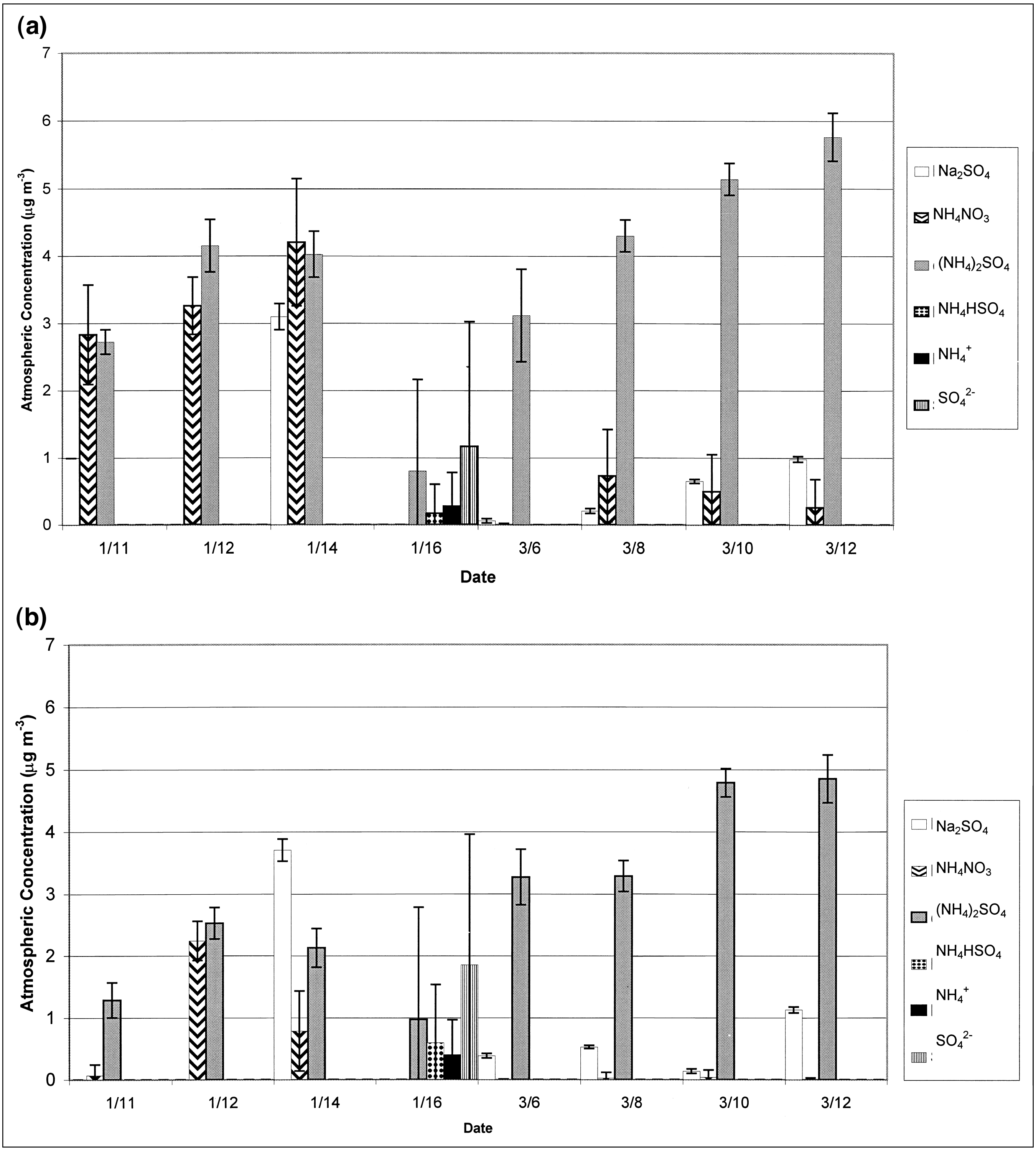

Figure 6. (a) Model predictions by ISORROPIA for solid species at Greenville. (b) Model predictions for solid species at Lake Greenwood.

the deposition velocity is, therefore, higher than if the RH remains low.

Gaseous deposition of HNO_3 and NO_2 were the largest contributors to dry N flux at Greenville. Deposition directly to the surface of Lake Greenwood received a majority contribution from those species, but particulate deposition increased in importance relative to the other site. The calculation yielding the highest deposition was influenced most strongly by HNO_3 in Greenville and by NO_2 at Lake Greenwood. These effects arise from the large range in reported deposition values and not as much from concentration variation.

The best estimate for atmospheric dry deposition of N to upstate South Carolina is on the order of 3 kg N/ha-yr.

Table 2. Dry deposition flux calculation.

	Lake Greenwood Flux (kg-N/ha-yr)		Greenville Flux (kg-N/ha-yr)	
	Upper	**Lower**	**Upper**	**Lower**
NO_2	13.6	0.07	2.37	0.89
HNO_3	1.12	0.54	5.44	0.21
Fine NO_3^-	0.38	0	0.31	0.04
Fine NH_4^+	1.08	0.05	0.68	0.24
Coarse NO_3^-	0.76	0.21	0.47	0.06
Coarse NH_4^+	0.47	<LOD[a]	0.39	<LOD[a]
	17.4	0.88	9.66	1.44

[a] Value is below the limit of detection, which for NH_4^+ is 0.015 ppm.

Wet deposition is monitored by the National Atmospheric Deposition Program and is estimated for the area as ~4 kg N/ha-yr.[23] Within probable uncertainty, both wet and dry deposition contribute equally to the total atmospheric loading to Lake Greenwood. The total yearly atmospheric deposition is therefore ~7 kg N/ha. In conclusion, Lake Greenwood annually receives 30,000 kg of atmospheric N directly to its surface.

Atmospheric deposition as a nonpoint source also can be judged in relation to other sources typically investigated as contributors to eutrophication. Table 3 is a list of N loadings from various land-use types, adapted from the EPA protocol for developing nutrient total maximum daily loads.[25] Comparison of the atmospheric flux to the discharge from a large point source and various nonpoint sources leave the possibility that atmospheric deposition contributes a nonnegligible loading of N to Lake Greenwood. The impact of atmospheric deposition to the watershed as a whole was not assessed because of the complexities involved with the transport calculations from the various land uses in the watershed. Even with this omission, atmospheric deposition is likely to contribute significantly to the total N loading to Lake Greenwood.

CONCLUSIONS

The absolute significance of calculated atmospheric fluxes can only be determined from detailed watershed modeling, including more complete knowledge of the other sources and sinks of nutrients and their transport and transformations through the system. An objective of this project was to examine the hypothesis that atmospheric input was a significant source of N to Lake Greenwood, and based on the magnitude of loadings from the various point and nonpoint sources, this possibility has not been ruled out. This remains contingent on the assumption that the algal blooms hampering the lake are at least partially limited by N. Because P concentrations in sampled aerosol were all below the limits of detection, a P-limited system would not likely be affected by atmospheric dry deposition.

Algal blooms in the Reedy River branch of Lake Greenwood have repeatedly caused an upset of the natural system, despite reductions in upstream nutrient point sources. *Pithophora*, the nuisance species of alga predominant in the affected area, has demonstrated unusually high N demand relative to P in other studies. Therefore, atmospheric deposition was investigated by measuring the dry deposition of N-containing gases and aerosol at the lake and in the upstream watershed. Atmospheric concentrations were converted to depositional flux, and thermodynamic modeling was performed to single out the most important processes affecting deposition. Major findings are summarized here.

1. Thermodynamic modeling of sampling events for this project showed low concentrations of NH_3 relative to the particulate NH_4^+ concentrations. This was because of the stability of NH_4^+-containing salts caused by low temperatures and the relative abundance of SO_4^{2-} in PM.
2. Equilibrium concentration predictions were slightly disjointed from atmospheric measurements as a result of kinetically limited solid-phase reactions. This slowed the Na^+-SO_4^{2-} interactions, eventually causing poor model treatment of the NO_3^--HNO_3 system.
3. Deposition modeling showed dry atmospheric flux that was dominated by NO_2 and HNO_3. Particulate contributions to the N deposition were more significant at Lake Greenwood than at Greenville. Total inorganic N annual fluxes ranged between 0.9 and 17.4 kg/ha and 1.4 and 9.7 kg/ha for the Greenville and Lake Greenwood sites, respectively.

Table 3. Nitrogen loading from selected nonpoint sources.

	Loading (kg-N/ha-yr)	
Source	**High**	**Low**
Greenville dry deposition	9.7	1.4
Lake Greenwood dry deposition	17.4	0.9
Wet deposition	5	4
Roadway	3.5	1.3
Commercial	8.8	1.6
Single-family low density	4.7	3.3
Single-family high density	5.6	4
Multifamily residential	6.6	4.7
Forest	2.8	1.1
Grass	7.1	1.2
Pasture	7.1	1.2

(4) The magnitude of N dry deposition measured in this project was of the same magnitude as the wet N flux, and was comparable in magnitude to other nonpoint sources of N.

It must be stated that the results found by this study are based on experiments carried out during the winter season. More atmospheric sampling is needed to fully evaluate the spatial and temporal importance of atmospheric N input into Lake Greenwood. The results from this study show that further investigation is warranted.

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