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Back-Trajectory Analysis and Source-Receptor Relationships: Particulate Matter and Nitrogen Isotopic Composition in Rainwater

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ABSTRACT

The southeastern portion of North Carolina features a dense crop and animal agricultural region; previous research suggests that this agricultural presence emits a significant portion of the state's nitrogen (i.e., oxides of nitrogen and ammonia) emissions. These findings indicate that transporting air over this region can affect nitrogen concentrations in precipitation at sites as far as 50 mi away. The study combined nitrate nitrogen isotope data with back-trajectory analysis to examine the relationship between regional nitrogen emission estimates independent of pollutant concentration information. In 2004, the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to determine potential sources of nitrogen in rainwater collected at an urban receptor site in Raleigh, NC. The $\delta^{15}\text{N}$ isotope ratio signatures of each sample were used to further differentiate between sources of the rainwater nitrate. This study examined the importance of pollution sources, including animal agricultural activity, and meteorology on rainfall chemistry as well as the implications in fine particulate matter ($\text{PM}_{2.5}$) formation. Samples that transited the dense crop and animal (swine) agricultural region of east-southeastern North Carolina (i.e., the source region) had lower $\delta^{15}\text{N}$ isotope ratios in the nitrate ion (average = $-2.1 \pm 1.7\text{‰}$) than those from a counterpart nonagricultural region (average = $0.1 \pm 3\text{‰}$). An increase in $\text{PM}_{2.5}$ concentrations in the urban receptor site (yearly average = $15.1 \pm 5.8 \mu\text{g}/\text{m}^3$) was also found to correspond to air transport over the dense agricultural region relative to

air that was not subjected to such transport (yearly average = $11.7 \pm 5.8 \mu\text{g}/\text{m}^3$).

INTRODUCTION

Wet and dry acid deposition is a major concern in the eastern United States. The chemical components of these acids, including nitrogen oxides (NO_x = nitric acid $[\text{NO}]$ + nitrogen dioxide $[\text{NO}_2]$), nitrate ions (NO_3^-), ammonia (NH_3), and ammonium ions (NH_4^+), have important effects on rainfall chemistry and fine particulate matter ($\text{PM}_{2.5}$) formation. NH_3 may be scavenged from the air by rain, absorbed by plants, or rapidly converted to NH_4^+ aerosol. NO_x is a precursor to nitric acid and can react with NH_3 to produce ammonium nitrate, $\text{NH}_4\text{NO}_3(\text{s})$.¹ Increases in emissions from anthropogenic sources of NO_x correspond to increases in nitric acid deposition.²

Specifically, North Carolina is home to approximately 10 million hogs, which are almost exclusively confined to the southeastern portion of the state. Walker et al.³ suggest that swine agriculture represents approximately 21% of the state's nitrogen emissions. The study concludes that NH_4^+ concentrations in precipitation at downwind sites were 50% higher on weeks when at least 25% of the precipitation came from the swine agricultural source region. The atmospheric emissions of the source region were substantial enough to influence the nitrogen content of wet deposition at a receptor site over 50 mi away.

A more accurate measurement of animal operations' influence on rainfall chemistry, independent of concentration analysis, was thus pursued because it would prove helpful in further verification of the hypothesis. To this end, we examined the isotopic composition of the nitrogen compounds in rainwater, taking advantage of the severe isotopic depletion associated with agriculturally related biological activities, including nitrification and volatilization. Specific isotopic signatures may allow for differentiation between natural and anthropogenic source contributions.⁴

BACKGROUND

The distribution of light stable isotopes in the environment is controlled by chemical, physical, and biological processes that can be viewed as reversible equilibrium reactions or irreversible unidirectional kinetic reactions. The heavier isotope has a higher disassociation energy,

IMPLICATIONS

Understanding the source (emission)-receptor (deposition) relationships will provide information that is important for regulators and policy-makers. The potential of the stable isotopes of nitrogen and sulfur to investigate the source-receptor relationships for atmospheric sulfur and nitrogen has long been recognized. By combining the isotopic composition of the major acidic components of atmospheric deposition (nitrogen and sulfur) with information on the air mass source region, it is possible to determine the geographic origin of the nitrogen and sulfur compounds. This paper addresses this important issue involving analyses of regional meteorology, origins of air masses, and rainfall isotopic measurements.

and is generally less likely to be involved in kinetic processes than its lighter counterpart. For example, NH_3 volatilized off a waste lagoon preferentially incorporates ^{14}N , concentrating ^{15}N in the liquid of the lagoon.^{5,6} Thus, a compound containing a higher ratio of ^{14}N is more likely to be the product of a physical or organic process, whereas the heavier compound is more likely to be the unused (residual) portion of the reactant.⁴ Because of the computationally identical situations, the redistribution of isotopes can be described by a fractionation factor, which is approximated by Rayleigh exponential equations for open and closed equilibrium systems as well as for kinetic fractionations. In some circumstances, such as intensively managed agriculture, it is hypothesized that enough fractionation occurs because of biological, chemical, and physical processes that products and residuals can behave as naturally generated tracers in larger ecosystem studies. Results presented in Schulz et al.⁷ indicate that highly depleted isotope values were found in manure from swine and cattle, and that this negative nitrogen isotope signal could be transported via atmospheric processes to the bark of trees in the surrounding area.

Although stable isotope ratios have been examined for over half a century in geology and environmental science, many of the chemical clues these isotope ratios leave in the environment have been largely unexplored and underutilized by atmospheric scientists. More recently, studies including Heaton⁸ found in South Africa that the $\delta^{15}\text{N}$ of NO_x from cars ($13 \pm 2\%$) was different from the $\delta^{15}\text{N}$ of NO_x emitted from coal combustion ($+6 \pm 9\%$). Fryer⁹ observed seasonal $\delta^{15}\text{N}\text{-NO}_3$ variations in rain in Germany and suggested that the higher winter $\delta^{15}\text{N}$ was the result of fossil fuel combustion as opposed to soil NO_x contributions. Freyer et al.¹⁰ suggested that the seasonal $\delta^{15}\text{N}\text{-NO}_3$ variations were influenced by photochemical reactions as well as seasonal source variations. Russell et al.¹¹ utilized $\delta^{15}\text{N}\text{-NO}_3$, NO_3^- concentration in rainwater, and back-trajectory analysis and determined that the NH_4^+ in the precipitation in the Chesapeake Bay region had its dominate sources in local fertilizer, soil, and animal excreta, and NO_3^- had its dominant source in fossil fuel combustion. Hastings et al.¹² observed seasonal

variations in the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ compositions of NO_3^- . Using back-trajectory analysis, they suggest that the seasonal $\delta^{15}\text{N}\text{-NO}_3$ variations are related to the source region, whereas the $\delta^{18}\text{O}\text{-NO}_3$ variations are related to atmospheric chemistry.

The study presented here investigated the isotope composition of nitrogen in rainfall with N species flux rates, $\text{PM}_{2.5}$ concentrations, and back-trajectory air mass analysis in Raleigh, NC. The National Oceanographic and Atmospheric Administration's (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPPLIT) was used with various meteorology datasets to model forward and back trajectories of air masses. Using the 2004 Eta Data Assimilation System (EDAS 40) data, HYSPLIT provided the best spatial resolution (40 km) of any of the possible models.¹³ HYSPLIT incorporates modeled meteorological grid data that give more accuracy in less developed areas than observation-based models. Capable of simulating back trajectories for the entire 2004 dataset, HYSPLIT could estimate the recent path history of an air parcel that arrived at the receptor at a given time.

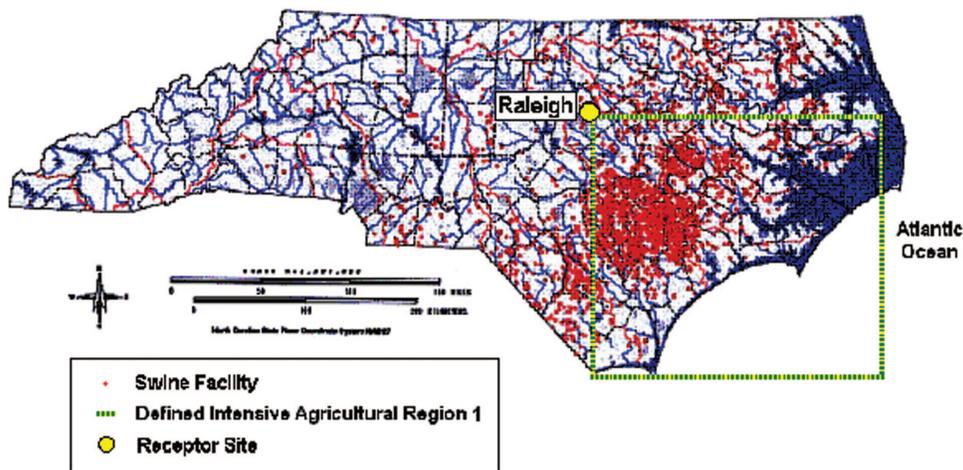
OBJECTIVES

The project objectives were to: (1) verify whether or not Raleigh is a receptor of pollutants from North Carolina's large agricultural corridor (Region 1; Figure 1) and to determine if the seasonal N flux and $\delta^{15}\text{N}$ trend in precipitation nitrogen is related to air mass trajectory, and (2) to determine the amount and effect of farm emissions transport on $\text{PM}_{2.5}$ levels in Raleigh.

METHODS

Sample Collection

This study used $\delta^{15}\text{N}$ values from 31 rainfall samples from 2004 collected on the roof of Jordan Hall at North Carolina State University (35.78 °N, 78.68 °W) at a height of 23 m above ground level. Wet fall samples were collected in a National Atmospheric Deposition Program (NADP) bucket collector at the site according to NADP guidelines.¹⁴ Wet samples were collected on a weekly basis if a precipitation event occurred during the sampling interval. Samples were usually collected within a few days



Map Courtesy of North Carolina Swine Waste Management Systems

Figure 1. Map of North Carolina depicting the animal (hog) agricultural region.

following rainfall events. Samples were immediately filtered after collection through a 0.45- μm filter and kept at 4 °C until processed for nutrient concentrations and isotopic composition. Samples were processed for isotopes and several chemical concentrations within 1 week of collection. Tests indicated that samples archived at 4 °C needed to be processed within 4 weeks for concentrations and isotopes to avoid storage artifacts. Bucket collection has been criticized because nitrogen compounds can be lost or converted while in the bucket, but sample collection within 6 days and then storage at 4 °C for less than 1 week helps to minimize these effects. Spoelstra et al.¹⁵ suggest that the bulk NO_3^- ^{15}N and ^{18}O isotopic compositions remain unchanged for up to 2 weeks in precipitation collectors. Event and weekly samples collected using two different collectors were similar in concentration and isotopic composition for up to 1 week; longer comparisons were not made. Samples of 15- μM nitrogen were processed for concentration and for ^{15}N and ^{18}O isotopes. This limited the number of events that could be processed, and isotope data could not be generated for the smaller storms unless these storm events were combined. Thus, back trajectories had to be classified by the amount of their contribution to total rainfall volume in the specified period, especially with the occurrence of multiple small storm events.

Isotopic Analysis

Approximately 50 mL of the filtered water was analyzed in an automated flow injection La Chat Quick-Chem 8000 ion chromatograph (IC) for NO_3^- + nitrite (U.S. Environmental Protection Agency [EPA] Method 353.2), phosphate (EPA Method 365.1), total Kjeldahl nitrogen (EPA Method 351.1), and NH_4^+ (EPA Method 350.1).¹⁶ During each La Chat IC run, an external standard (EPA) and several internal quality control (QC) standards were run with 10 dilution standards and one spiked rainwater sample to quantify matrix effects. An additional internal QC standard was run for every 10 samples analyzed.

The $\delta^{15}\text{N}$ of dissolved NO_3^- and NH_3 was analyzed using a modification of the technique developed by Chang et al.^{17,18} Enough samples to yield 15- μM nitrogen were passed through a double ion exchange resin column (first—cation—5 mL Biorad AG 50-WX8; second—anion—2 mL Biorad AG 2-X8). The cation column was prewashed with deionized water. The anion column was prewashed with 3-N HCl and then repeatedly washed with deionized water to remove all acid residues. Prewashing the anion column with the same strength acid as the eluant allowed 15- μM dissolved samples to be analyzed without an isotopic correction.¹⁷ NO_3^- was eluted from the anion column with 30 mL of 3-N HCl. The HCl was neutralized with 15 gm of silver oxide, and the sample was filtered with a Whatman GFF filter. The filtrate was then passed through a cleaning column composed of 10 mL polyvinylpropylene, 2 mL silica gel, 2 mL cat ion resin, and 2 mL of SPE C18 modified from Haberhauer and Blochberger.¹⁹ This process removed organic contaminants and other oxygen-containing compounds. The filtrate was then freeze-dried to yield a fine white powder of silver nitrate. If the powder was brown or discolored, it

was redissolved and passed through the cleaning column again. Half of the sample was placed in a tin boat, combusted in a Carlo Erba NC2500 elemental analyzer, and isotopically analyzed with a Finnigan Mat Delta+ XLS CF-IRMS to determine $\delta^{15}\text{N-NO}_3$. The other half of the sample was placed in a silver boat, pyrolyzed with a Thermoquest thermal conversion elemental analyzer (TCEA), and isotopically analyzed with a Finnigan Mat Delta+ XL CF-IRMS to determine $\delta^{18}\text{O-NO}_3$. The $\delta^{15}\text{N}$ results were calibrated against National Institute for Standards and Technology (NIST) 8550, NIST 8548, NIST 8547, and four internal ^{15}N standards. The $\delta^{18}\text{O}$ results were calibrated against NIST 8542, NIST 8549, National Bureau of Standards (NBS) 120c, NBS 127, and two internal ^{18}O standards. For NH_3 analysis, the order of the resin columns was reversed, the cation resin was air dried at 65 °C, and 100–400 μg of resin was placed in a tin boat and combusted in a Carlo Erba NCS 2500 elemental analyzer. A carbon trap was placed behind the water trap in the elemental analyzer to remove the carbon dioxide (CO_2) peak, which would record an interference at mass 28/29, and the $\delta^{15}\text{N-NH}_4$ was determined by CF-IRMS. Nitrogen and oxygen isotope ratios were reported as parts per thousand (‰) deviations from the international reference standard.⁴

Back-Trajectory Analysis

Atmospheric transport patterns were evaluated by examining 48-hr back trajectories originating from the building on each day rainfall was recorded at the North Carolina State Climate Office site on Lake Wheeler Road (~4 mi south of campus). The entire path of each trajectory was evaluated to determine a path of transit for the air parcels. The HYSPLIT model provided information as to the origin of the air at the rooftop level. We initiated each trajectory at a 23-m altitude to simulate air at the rooftop of Jordan Hall. Originally several different heights (21, 23, and 25 m) were investigated, but the difference in path features was minimal in all tested scenarios, so for simplicity, only the 23-m altitude was included. We were able to use EDAS 40¹³ to allow a 40-km resolution for the trajectories.

Daily trajectories were examined for each date when rainfall would have contributed to the total collected in the sample buckets using daily rainfall data from the North Carolina State Climate Office site, approximately 5 mi south of the collection site. Using the daily rainfall data, we were able to classify multiday samples according to whether or not the majority of a sample was collected from a given region during periods of transport. The transport regions of primary interest in this study were the intensively managed crop and animal agricultural region of southeastern North Carolina, defined in Figure 1 as Region 1, and the Atlantic Ocean (Figure 1). The agricultural region lies to the southeast of the receptor site, encompassing an area of 20,800 mi^2 (160- by 130-mi rectangle). The definition of a “source” region was the region (agricultural, ocean, neither, or both) from which the majority (by volume) of the rain sample originated. We designated samples in which a minimum of 50% of the rainfall would have transited across the given source

region as “agricultural” (for Region 1) or “marine” (for oceanic) air. Samples where less than 50% of the rainwater collected was from systems that transported it across Region 1 were labeled “nonagricultural,” and we described samples that had no transit across the ocean as “nonmarine.” Thus descriptive combinations of characteristics included “agricultural marine,” “nonagricultural marine,” “agricultural nonmarine,” and “nonagricultural nonmarine” samples.

To further investigate the effects of NH_3 and NO_x emissions on $\text{PM}_{2.5}$ formation, the North Carolina Department of Air Quality (DAQ) $\text{PM}_{2.5}$ records for the same time period were also examined. Trends in the particulate matter (PM) formation during the 55 dates corresponding to each contributing trajectory were examined. The data were based on daily averaged hourly PM concentrations at the Millbrook Road DAQ site in downtown Raleigh, which were obtained at the website DAQ.²⁰ Precipitation amounts were obtained for the North Carolina State University weather station from the North Carolina State Climate Office,²¹ which maintains a continuously recording weather station at the collection site. Notably, wind direction averages from the North Carolina State Climate Office web site have indicated that winds in Raleigh come from the general direction of the agricultural region (east, southeast, south) 30.6% of the year, but more prevalently from the southwest, west, and northwest directions 32.4% of the year.

DATA AND RESULTS

Although precipitation was moderate for 2004, total wet nitrogen flux was high compared with previous years (Figure 2a). Therefore 2004 was chosen for back-trajectory analysis for this study. Rain nitrogen species concentrations were high during the first part of the year when precipitation was low, and NO_3^- was generally higher than the other species except for a peak in NH_4^+ concentration in early May and a peak in organic nitrogen concentration in late August (Figure 2b). Nitrogen species concentrations in rainfall dropped after mid-July when rainfall amounts increased. Generally, the chemical analysis of the rainfall showed NO_3^- was the highest concentration of the different nitrogen species, followed by NH_3 , and then organic nitrogen (Table 1 and Figure 2b). During the spring and summer of 2004, high NH_3 concentrations and flux occurred in early May, whereas high dissolved organic nitrogen (DON) concentrations and flux occurred in mid-August associated with the remnants of Hurricane Charlie, which passed over North Carolina on August 14, 2004 (Figure 2c). In early spring, associated with high NH_4^+ fluxes, $\delta^{15}\text{N-NH}_4$ compositions were lowest. In contrast, in the late summer the $\delta^{15}\text{N-NO}_3$ compositions were lowest and in the winter were more positive. In the late summer, $\delta^{18}\text{O-NO}_3$ compositions were lowest and in the winter and early spring were highest (Figure 2d).

No statistical difference exists between NO_3^- concentrations for samples that showed trajectories over the agricultural region (0.8 ± 0.10 mg/L) and those that

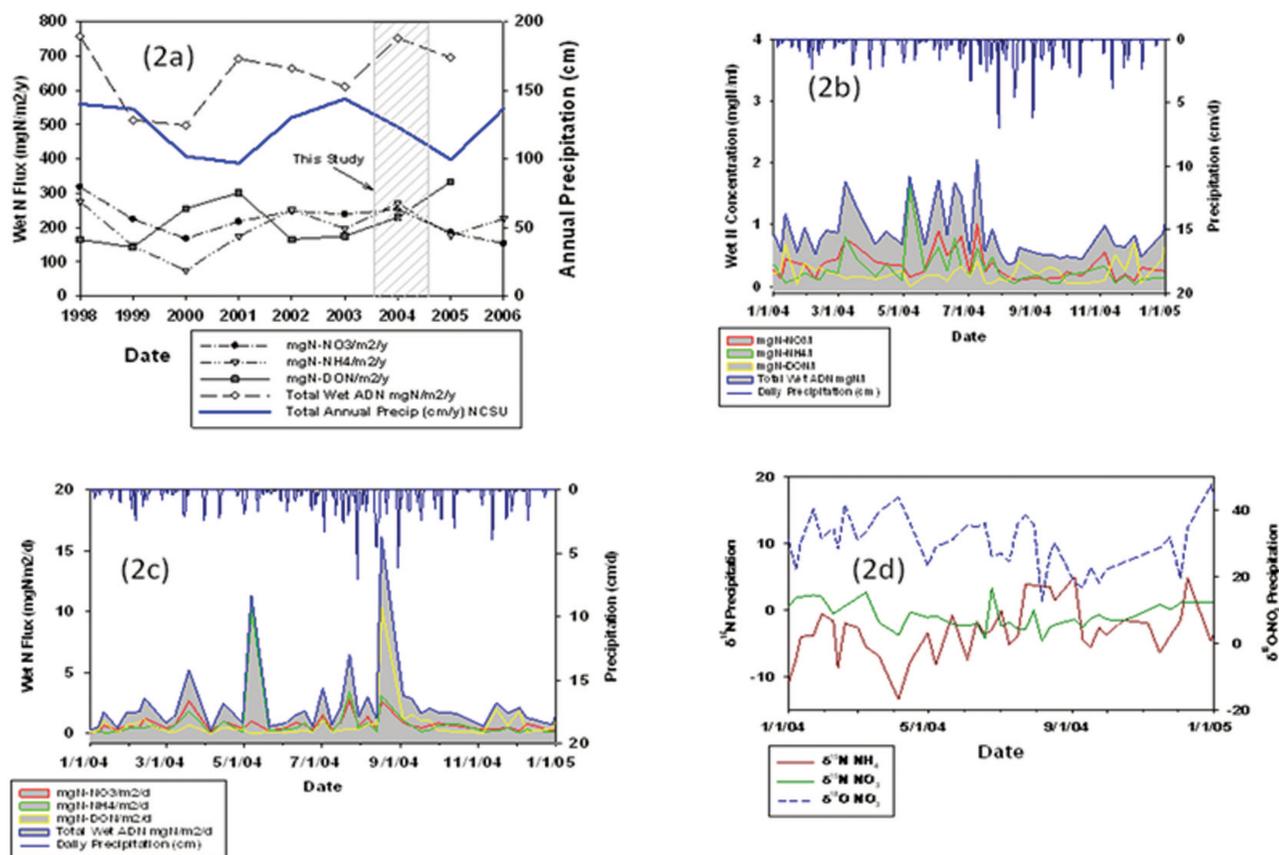


Figure 2. (a) Total wet nitrogen flux and precipitation in Raleigh, NC, for 1998–2006; (b) rain nitrogen concentrations in Raleigh, NC, for 2004; (c) wet nitrogen flux in Raleigh, NC, for 2004; and (d) isotopic composition of the wet nitrogen flux in Raleigh, NC, for 2004.

Table 1. 2004 Raleigh rainfall concentrations and flux rates.

Raleigh Rain 2004	NO ₃ -N (mg/L)	mg N-NO ₃ /m ² /day	NH ₄ -N (mg/L)	mg N-NH ₄ /m ² /day	DON (mg/L)	mg N-DON/m ² /day	Total N (mg N/L)	Total ADN (mg N/m ² /day)
Average	0.340	0.788	0.274	0.849	0.239	0.813	0.847	2.450
Median	0.257	0.636	0.186	0.450	0.220	0.385	0.686	1.754
Maximum	1.010	2.751	1.620	10.332	0.710	10.437	2.050	16.192
Minimum	0.082	0.096	0.029	0.060	0.040	0.000	0.364	0.257

did not (0.9 ± 0.16 mg/L; Figure 3 and Table 2). Data for NH₄⁺ concentration at Raleigh agreed with the results of Walker et al.,³ which demonstrated a significant increase in mean NH₄⁺ concentration with transport from the agricultural region. A significant ($p = 0.08$) difference existed in concentrations between agricultural (2.3 ± 1.6 mg/L) and nonagricultural transport (0.7 ± 0.19 mg/L) (Figure 3). Much of the difference was due to the higher NH₄⁺ concentrations in marine air (1.4 ± 0.67 mg/L) than in nonmarine air (0.7 ± 0.22 mg/L). The NH₄⁺ concentrations resulting from the agricultural transport (which were strictly a subset of the days when marine transport occurred) were higher than the marine air that did not cross the agricultural area (0.6 ± 0.31 mg/L); however, not enough data were available to classify the difference as statistically significant.

The δ¹⁵N isotope ratios of NO₃⁻ ranged from 6.41 to -4.61‰. The range was well within the limits for rainfall (-16 to +10‰).¹² The values were similar to those cited for the Walker Branch watershed in Tennessee (-2 to 6‰).²² The only values below that set range occurred during periods of air transit across the agricultural region of North Carolina, suggesting that the region may have acted as a source for depleted NO₃⁻. The average value was -0.5 ± 0.51 ‰, with a decreased value (-2.1 ± 0.58 ‰) with transport across Region 1, and an increased value (0.1 ± 0.62 ‰) when no transport from the agricultural region occurred (Figure 4). The large difference in values provided a clear indication that even with the

small number of samples, the difference ($p = 0.05$) between Region 1 and Non-Region 1 source regions was significant.

During periods of transport from the ocean, the δ¹⁵N isotope ratios of NO₃⁻ had an average value of -1.8 ± 0.38 ‰, compared with values of 1 ± 0.90 ‰ for transport from the continent. All air masses that came to Raleigh over the agricultural region resulted from transport from the ocean, making the influence of the farms difficult to separate from the influence of the ocean. NO₃⁻ δ¹⁵N ratios for air that originated over the ocean but did not cross the agricultural region averaged -1.3 ± 0.49 ‰. This measurement was higher than the measurement for total agricultural transport, but was not statistically significant because it occurred only a few times in this dataset.

δ¹⁸O values for NO₃⁻ were also examined but were not found to exhibit any trends in terms of transport patterns. This finding agrees with previous studies that suggest atmospheric chemistry controls the δ¹⁸O-NO₃⁻ composition and not emission sources.¹² Oxygen exchange between ozone (O₃) and NO_x (NO + O₃ → NO₂ + O₂, and NO₂ + hν → NO + O) during NO₃⁻ formation occurs only in the atmosphere and suggests that the δ¹⁸O values of NO₃⁻ have no relationship to the δ¹⁵N values that result from reactions in the soil.

On average, when comparing agricultural (-3.6 ± 1.93 ‰) and nonagricultural (-3.8 ± 0.88 ‰) transport patterns (Figure 4), little difference is shown between the NH₄⁺ isotope ratios. The comparison of the agricultural

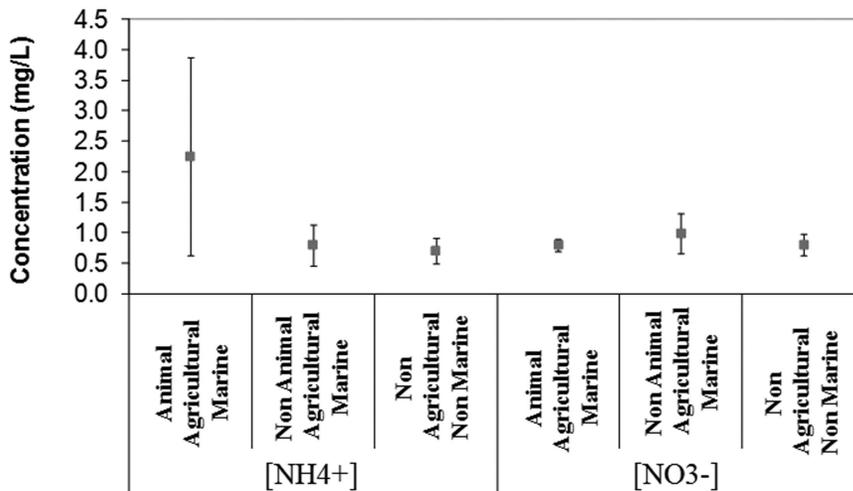


Figure 3. Average pollutant concentrations in rainfall in Raleigh, NC, for the easterly wind sector.

Table 2. Two-way ANOVAs for statistically significant datasets.

NH₄⁺ Concentration						
ANOVA: single factor summary						
Groups	Count	Sum	Average	Variance		
Agricultural	6	13.50601	2.251001	15.77211		
Nonagricultural	23	15.95052	0.693501	0.824376		
ANOVA						
Source of variation	SS	df	MS	F	P value	F _{crit}
Between groups	11.5435	1	11.5435	3.213242	0.084257	4.210008
Within groups	96.99685	27	3.592476			
Total	108.5403	28				
NO₃⁻ δ¹⁵N						
ANOVA: single factor summary						
Groups	Count	Sum	Average	Variance		
Nonagricultural	23	2.188676	0.09516	8.865363		
Agricultural	8	-16.7768	-2.0971	2.728824		
ANOVA						
Source of variation	SS	df	MS	F	P value	F _{crit}
Between groups	28.52604	1	28.52604	3.863156	0.058999	4.182965
Within groups	214.1398	29	7.384129			
Total	242.6658	30				
PM_{2.5} mass						
ANOVA: single factor summary						
Groups	Count	Sum	Average	Variance		
Agricultural	19	282.7	14.87895	52.12287		
Nonagricultural marine	36	350.6	9.738889	31.13902		
ANOVA						
Source of variation	SS	df	MS	F	P value	F _{crit}
Between groups	328.5712	1	328.5712	8.586594	0.004987	4.023008
Within groups	2028.077	53	38.26561			
Total	2356.648	54				

Notes: SS = sum of squares, df = degrees of freedom, MS = mean squares, F = variance ratio, Fcrit = critical frequency.

(thus inherently also marine) transport with nonagricultural marine transport (-1.4 ± 0.67‰) again suggests some interesting interactions; however, the small sample size did not allow sufficient power to determine a statistical difference between these datasets.

On average, transport of the marine air mass provided much lower values for PM_{2.5} (12.5 ± 1.05 µg/m³) than did the nonmarine air (18 ± 1.92 µg/m³) (Figure 5). Initial daily PM_{2.5} mass measurements gave average values of 14.9 ± 1.65 µg/m³ for agricultural air and 14.4 ±

1.04 µg/m³ for nonagricultural air. Most importantly, however, the values were significantly higher for air that traveled over the agricultural region and the ocean (14.9 ± 1.65 µg/m³) compared with air that came over the ocean and did not cross the agricultural region (9.7 ± 0.93 µg/m³) (Figure 5). This indicates that air that traveled over Region 1 did see an increase in PM_{2.5} compared with similar marine air that did not pass over the agricultural area. No matter where the transport of marine air occurred, it still tended to have less PM_{2.5} than the samples

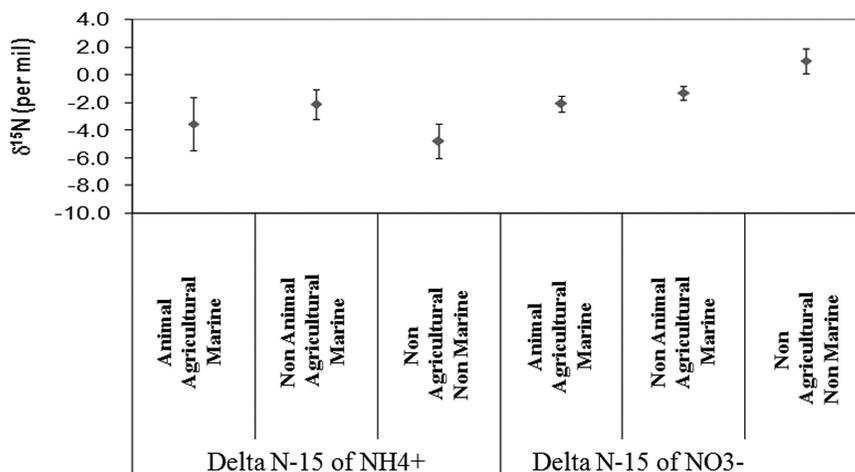


Figure 4. Average δ¹⁵N values in rainfall for the easterly wind sector.

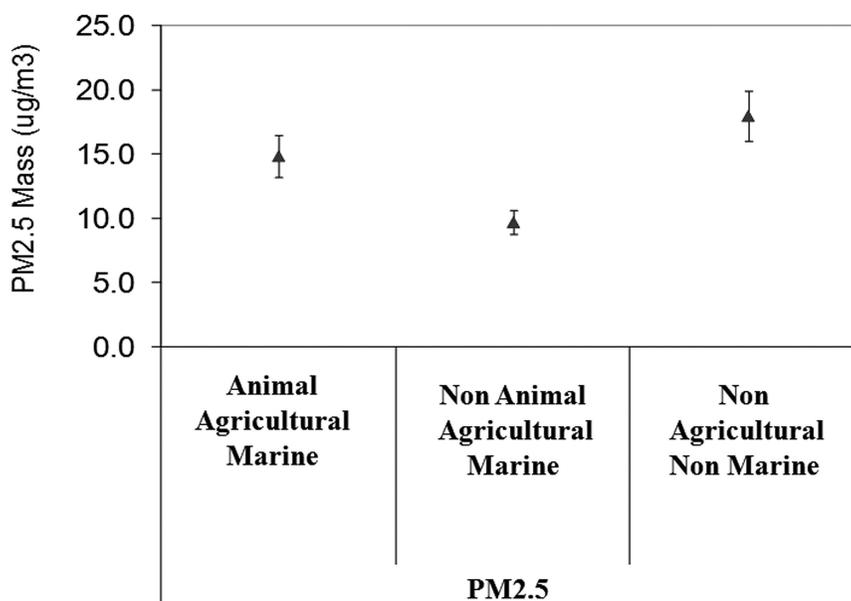


Figure 5. Average PM_{2.5} mass for the easterly wind sector.

from continental transport patterns. Elevated PM_{2.5} levels in nonmarine air were likely related to long-distance transport from sources outside of the state.

DISCUSSION

The two largest atmospheric deposited nitrogen (ADN) events in 2004 at this site in the central Piedmont of North Carolina occurred in early May and in mid-August. The spring flux events were associated with high NH₄⁺ concentrations and relatively low rainfall when marine air was transported across the study region. The second largest ADN event occurred in mid-August when Hurricane Charlie passed over the area. NO₃⁻ and NH₄⁺ concentrations were low, but DON concentrations were high with large amounts of rainfall during this hurricane/tropical storm event. The year 2004 saw intermediate precipitation (113 cm) versus 89 cm in 2001 or 137 cm in 2006 at this site. However, total wet ADN was higher in 2004 (751 mg/m²) as opposed to other years because the NO₃⁻, NH₄⁺, and organic nitrogen fluxes were all high during this period. NO₃⁻ generally had higher concentrations than NH₄⁺ or organic nitrogen, as well as higher flux rates, except for the spring-summer period when NH₄⁺ had higher concentrations and during Hurricane Charlie when DON concentrations were higher. Nitrogen species concentrations were higher during the winter-spring period with moderate amounts of rainfall and lower during the summer-fall period with higher amounts of rainfall.

The NH₄⁺ concentration data provided the most solid evidence of the relationship between the source and receptor. The large difference in NH₃ concentrations in rain between agricultural and nonagricultural air mass transit for marine air provided a statistically significant distinction of source types. This finding agrees with Walker,³ who showed that NH₄⁺ markedly increased in air masses transported over the agricultural regions of North Carolina.

Another statistically significant finding, notable isotopic depletion of NO₃⁻, occurred in samples that had been

transported over Region 1. The low isotope values ($-2.1 \pm 0.58\text{‰}$) in the region were likely the product of both initially isotopically depleted marine air masses and higher biological activity. The low average value characteristic of the marine air mass ($-1.3 \pm 0.49\text{‰}$) that did not cross Region 1 explains only a small portion of the discrepancy between $-2.1 \pm 0.58\text{‰}$ and $0.1 \pm 0.62\text{‰}$. The remaining difference could be attributed to the highly depleted values expected in areas of agriculture concentration where depleted NH₃ is volatilized from waste lagoons, animal houses, applications fields, and fertilized soils. Karr et al.^{5,6} suggest that the isotopic composition of swine waste lagoons is related to air temperature. This implies that the lowest NH₃ volatilization rates and maximum isotopic fractionation would occur during the winter months when the lagoons have the lowest nitrogen isotopic composition. The highest NH₃ volatilization rates and minimum isotopic fractionation would occur during the warm summer months when the lagoons have the highest nitrogen isotopic composition. The trend would reduce the seasonal isotopic variation of NH₃ volatilized over confined animal feeding operation (CAFO) areas. The NH₃ volatilization epsilon described by Thode and Urey²³ and Urey²⁴ varies from -42 to -37‰ from 0 to 40 °C, respectively. If waste lagoons vary from +10 (winter) to +30 (summer) δ¹⁵N-NH₄, then the isotopic composition of NH₃ volatilized off the lagoons would vary from approximately -32‰ in the winter to -7‰ in the summer. Also, δ¹⁵N-NH₄ values in rain vary from -14‰ in the spring to approximately 0‰ in the winter and are slightly positive during the hurricane event. These data suggest that animal waste NH₃ has the greatest influence in Raleigh in the spring season. However, much about the seasonal variation of the isotopic composition of NH₃ volatilized in agricultural areas, such as Region 1 and its transformation into oxidized species, remains unknown.

The increase in the PM_{2.5} mass when marine air transited the high-density agricultural area versus the nonagricultural area also indicated that Raleigh may be a significant receptor of pollutants from the agricultural areas.

Precursor species that are emitted by various agricultural activities may contribute to the increases seen in the amount of PM_{2.5} at the receptor site (i.e., Raleigh). The PM_{2.5} data actually provided the most striking evidence of such a correlation. Although the PM_{2.5} mass was increased during Region 1 transport, it actually decreased for marine transport in general. This decrease allowed the most PM_{2.5} depleted (marine) air masses to either increase in PM_{2.5} by transiting across the agricultural region or to remain without much PM_{2.5} and come across the continent elsewhere. Yeatman et al.²⁵ found that during on-shore flow the dissociation of NH₄NO₃ and the uptake of NH₃ were important, and that dissociation/gas scavenging processes exhibit a positive isotopic enrichment effect. This would tend to increase the PM_{2.5} mass of marine air that transited Region 1, but would offset the uptake of isotopically depleted NH₃ emitted from animal operations. NH₃ emitted from fertilized soils and from car exhaust would also have a similar effect on the isotopic composition of NH₄ deposited by precipitation in Raleigh. The relative importance of these processes can only be determined by investigating the spatial variation of PM_{2.5} and across Region 1.

CONCLUSIONS

Results indicated that concentration, isotope composition, and PM_{2.5} mass data were to some degree dependent on the trajectory that the air at the receptor had traversed. NH₄⁺ concentrations, NO₃⁻ isotope ratios, and PM_{2.5} mass concentrations support previous claims that a strong source/receptor relationship exists between pollutants emitted from the agricultural corridor and the air received in Raleigh. Hurricanes deposited increased amounts of DON and low amounts of dissolved inorganic nitrogen (DIN) in wet precipitation. Low numbers of samples stymied the attempts to study several additional methods of verifying the results; however, these may be remedied by the continued collection of samples in the region.

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REFERENCES

- Seinfeld J.H.; Pandis, S.P. *Atmospheric Chemistry and Physics*; John Wiley and Sons: New York, 1998; p 531.
- Penner, J.E.; Atherton, C.S.; Dignon, J.; Ghan, S.J.; Walton, J.J.; Hameed, S. Tropospheric Nitrogen: a Three-Dimensional Study of Sources, Distributions, and Deposition; *J. Geophys. Res.* **1991**, *96*, 959-990.
- Walker, J.T.; Aneja, V.P.; Dickey, D.A. Atmospheric Transport and Wet Deposition of Ammonium in North Carolina; *Atmos. Environ.* **2000**, *34*, 3407-3418.
- Kendall, C.; Caldwell, E.A. Fundamentals of Isotope Geochemistry. In *Isotope Tracers in Catchment Hydrology*; Kendall, C., McDonnell, J.J., Eds.; Elsevier: Amsterdam, the Netherlands, 1998; pp 51-86, 203-246.
- Karr, J.D.; Showers, W.; Gilliam, J.W.; Andres, A.S. Tracing Nitrate Transport and Environmental Impact from Intensive Swine Farming Using Delta Nitrogen-15; *J. Environ. Qual.* **2001**, *30*, 1163-1175.
- Karr, J.D.; Showers W.J.; Jennings, G.D. Low-Level Nitrate Export from Confined Dairy Farming Detected in North Carolina Streams Using $\delta^{15}\text{N}$; *Agric. Ecosyst. Environ.* **2003**, *95*, 103-110.
- Schulz, H.; Gehre, M.; Hofmann, D.; Jung, K. Nitrogen Isotope Ratios in Pine Bark as an Indicator of N Emissions from Anthropogenic Sources; *Environ. Monitor. Assess.* **2001**, *69*, 283-297.
- Heaton, T.H.E. $^{15}\text{N}/^{14}\text{N}$ Ratios of NO_x from Vehicle Engines and Coal-Fired Power Stations; *Tellus* **1991**, *42*, 304-307.
- Freyer, H.D. Seasonal Variation of $^{15}\text{N}/^{14}\text{N}$ Ratios in Atmospheric Nitrate Species; *Tellus* **43B**: pp 30-44, 1991.
- Freyer, H.D.; Kley, D.; Volz-Thomas, A.; Kobel, K. on the Interaction of Isotopic Exchange Processes with Photochemical Reactions in Atmospheric Oxides of Nitrogen; *J. Geophys. Res.* **1993**, *98*, 14791-14796.
- Russell, K.M.; Galloway, J.N.; Macko, S.A.; Moody, J.L.; Scudlark, J.R. Sources of Nitrogen in Wet Deposition to the Chesapeake Bay Region; *Atmos. Environ.* **1998**, *32*, 2453-2465.
- Hastings, M.G.; Sigman, D.M.; Lipschultz, F. Isotopic Evidence for Source Changes of Nitrate in Rain at Bermuda; *J. Geophys. Res. Atmos.* **2003**, *108*, 4790.
- Air Resources Laboratory Frequently Asked Questions*; National Oceanic and Atmospheric Administration; available at <http://www.arl.noaa.gov/faq/md3.html> (accessed October 4, 2005).
- Quality Assurance Support for the NADP*; National Atmospheric Deposition Program; available at <http://nadp.sws.uiuc.edu/QA/> (accessed January 8, 2008).
- Spoelstra, J.; Schiff, S.L.; Jeffries, D.S.; Semkin, R.G. Effect of Storage on the Isotopic Composition of Nitrate in Bulk Precipitation; *Environ. Sci. Technol.* **2004**, *38*, 4723-4727.
- Methods for the Determination of Inorganic Substances in Environmental Samples*; 600 R-93 100; U.S. Environmental Protection Agency, Washington, DC, 1993.
- Chang, C.C.Y.; Langston, J.; Riggs, M.; Campbell, D.H.; Silva, S.R.; Kendall C. A. Method for Nitrate Collection for Delta N-15 and Delta O-18 Analysis from Waters with Low Nitrate Concentrations; *Can. J. Fish. Aquat. Sci.* **1999**, *56*, 1856-1864.
- Showers, W.J.; Usry, B.; Fountain, M.; Fountain, J.; McDade, T.; DeMaster, D. *Nitrate Flux from Ground to Surface Waters Adjacent to the Neuse River Waste Water Treatment Plant*; Report No. 316; University of North Carolina; Water Resources Research Institute: Raleigh, NC, 2005; p 38.
- Haberhauer, G.; Bolchberger, K. A Simple Cleanup Method for the Isolation of Nitrate from Natural Water Samples for O Isotope Analysis; *Anal. Chem.* **1999**, *71*, 3587-3590.
- North Carolina Department of Air Quality Web Site; available at <http://daq.state.nc.us/monitor/data/> (accessed October 15, 2005).
- North Carolina State Climate Office Web Site; available at <http://www.nc-climate.ncsu.edu/> (accessed November 10, 2005).
- Garten, C.T. Variation in Foliar ^{15}N Abundance and the Availability of Soil Nitrogen on Walker Branch Watershed; *Ecology* **1992**, *74*, 2098-2113.
- Thode, H.G.; Urey, H.C. Further Concentration of ^{15}N ; *J. Am. Chem. Soc.* **1939**, *7*, 34-39.
- Urey, H.C. The Thermodynamic Properties of Isotopic Substances; *J. Am. Chem. Soc.* **1947**, *5*, 562-581.
- Yeatman, S.G.; Spokes, L.J.; Dennis, P.F.; Jickells, T.D. Comparisons of Aerosol Nitrogen Isotopic Composition at Two Polluted Coastal Sites; *Atmos. Environ.* **2001**, *35*, 1307-1320.

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