Establishing Spatial and Temporal Trends of Atmospheric Nitrogen Deposition in Eastern North Carolina

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Abstract

Atmospheric deposition of nitrogen (AD-N), as wet and dry deposition of dissolved inorganic nitrogen, in the form of $\text{NO}_3^-$ and $\text{NH}_3/\text{NH}_4^+$, and dissolved organic nitrogen (DON), contributes >20% of the total externally supplied or “new” N flux to the waterways of the Neuse River Basin (North Carolina). Excessive nitrogen (N) loading to N-sensitive waters such as the Neuse River Estuary has been linked to changes in phytoplankton and associated microbial community composition and function (harmful algal blooms), hypoxia/anoxia, and fish kills. In a fifty-six month study from July 1996 to April 2001, the weekly wet deposition of inorganic and organic N was calculated at thirteen sites on a northwest-southeast transect in the watershed. The annual mean total (wet only) AD-N flux was calculated to be 1,394 mg/m$^2$/yr. Deposition was fairly evenly divided between nitrate (34%), ammonium (32%) and organics (or dissolved organic N, DON) (34%). Seasonally, the average weekly total N deposition (DIN+DON) was greatest in the summer (June-August) and lowest in the winter (December-February); this is not driven by precipitation amount. There was also spatial variability in AD-N deposition; in general, the middle portion of the basin received the highest total deposition. Estimates of watershed N retention and in-stream riverine processing revealed that this flux contributed from 15-45% of the total externally supplied or “new” N input to the estuary, with direct deposition to the estuary surface accounting for 24% of the total annual AD-N flux to the estuary and 5% of the total “new” N input. Also, ambient atmospheric concentrations of gaseous NH$_3$ and particulate NH$_4^+$ were measured at 12 hour intervals at the Institute of Marine Sciences in Morehead City. There were no significant differences between night and day ammonia/ammonium concentrations. The average twelve hour concentrations of NH$_3$ gas and particulate NH$_4^+$ were 0.47 μg N/m$^3$ (S.D.=0.46) and 0.48 μg/m$^3$ (S.D. = 0.41), respectively. Seasonally, ammonia(ium) concentrations are significantly higher in the summer and fall months. Particulate ammonium concentrations, however, are statistically highest in the spring. Total reduced N concentrations (gas plus particulate) are greatest in the summer. Gaseous ammonia dominates the total reduced N concentrations in the summer and fall, with particulate ammonium being more important in the winter and spring. AD-N is an important source of “new” N to the Neuse River Estuary that should be included in effective nutrient mitigation and management efforts.
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Summary and Conclusions

The Neuse River Estuary (NRE) is an ecologically and economically valuable resource which has been impacted by the symptoms of elevated N inputs from a variety of sources. An important source of “new” nitrogen to this N-sensitive system is atmospherically deposited nitrogen or AD-N.

The objectives of this study were as follows: 1) to quantify the spatial and temporal amounts and variabilities of wet AD-N in the Neuse River Basin (NRB); 2) to use these basin wide AD-N measurements to calculate the relative importance of AD-N to the externally-supplied or “new” N budget for the NRE; 3) to quantify the temporal variability of ambient particulate and gaseous reduced N.

Wet deposition was fairly evenly divided between nitrate (34%), ammonium (32%) and organics (or dissolved organic N, DON) (34%). Wet deposition varied between the seasons with the average weekly total N deposition (DIN+DON) highest in the summer (June-August) and lowest in the winter (December-February); this was not driven by precipitation amount. There was also spatial variability in AD-N deposition; in general, the middle portion of the basin received the highest total deposition on an annual basis.

Estimates of watershed N retention and in-stream riverine processing of AD-N showed that this flux contributed from 15-45% of the total “new” N input to the estuary, with direct deposition to the estuary surface accounting for 24% of the total annual AD-N flux and 5% of the total “new” N input.

Ambient atmospheric concentrations of gaseous NH$_3$ and particulate NH$_4^+$ were measured at 12 hour intervals at the Institute of Marine Sciences, Morehead City, NC. The average twelve hour concentrations of NH$_3$ gas and particulate NH$_4^+$ were 0.47 μg N/m$^3$ (S.D.=0.46) and 0.48 μg/m$^3$ (S.D.= 0.41), respectively. Seasonally, ammonia concentrations are significantly higher in the summer and fall months. Total reduced N concentrations (gas plus particulate) are greatest in the summer. Gaseous ammonia dominates the total reduced N concentrations in the summer and fall, with particulate ammonium being more prevalent in the winter and spring. Modeled dry deposition velocities are needed to use these concentration measurements to calculate dry depositional fluxes.

In conclusion, wet AD-N is an important source of “new” N to the Neuse River Estuary that needs to be considered in an integrated, basin-wide nutrient management strategy.
Recommendations

Continued long term monitoring of atmospherically deposited nitrogen is required to quantify temporal trends which cannot be evaluated with a study of this short duration. Further research is also needed to quantify appropriate dry deposition velocities which could be used with the measured ambient N concentrations reported here to calculate dry depositional fluxes. The inclusion of dry deposition of N to the estimation of the importance of AD-N to the “new” N budget for the Neuse River Estuary could significantly add to the importance of the atmosphere as a “new” N source. Another area of future research is a quantification of the direct deposition of N to Pamlico Sound, which due to its large surface area is potentially a large receiving body for direct N deposition.

Current legislation regarding the reduction of external or “new” N loading to the Neuse Estuary (NC House Bill 15A NCAC 2B.0232 1997) does not explicitly include AD-N as a source of “new” N to be reduced. As written, the Neuse River Sensitive Waters Management Strategy (i.e., “Neuse Rules”), which was the driving document behind the legislation, only includes indirect AD-N as a part of runoff from agricultural fields and urban stormwater runoff because the reference loading is the riverine loading at the head of the estuary (Streets Ferry Bridge). This will mean that the municipalities row crop farms and intensive animal operations may have to remove this N from their loadings, even though it is not N that originated due to their activities. Since direct deposition accounts for 5% of the total “new” N flux to the estuary, ignoring this flux will make achieving a 30% N reduction more difficult to achieve.

Given the relative importance of AD-N relative to other “new” N inputs, this source should receive serious consideration in the context of an overall long-term N input reduction strategy for the Neuse River Estuary. Management strategies which do not adequately address AD-N are not likely to achieve targeted N input reduction goals based on integrated reduction plans.
Introduction

Nitrogen (N) limited coastal waters, which make up only 15% of the world ocean surface area, account for up to one-half of the "new" global marine primary productivity (Mackenzie et al. 1991). This new productivity has been attributed in part to the increase in anthropogenic N inputs to coastal waters (Ryther and Dunstan 1971, Nixon 1986, Asman et al. 1993, Paerl 1995). Atmospherically deposited nitrogen (AD-N) is a historically overlooked, yet potentially quite important source of N to coastal waters (Valigura et al. 1996, Paerl et al. 2001). Precipitation and the deposition of gases and aerosols (dry deposition) contain a variety of organic and inorganic N compounds. N forms in deposition include inorganics (HNO$_3$, NO$_3^-$, NO$_2^-$, NH$_3$, NH$_4^+$) and organics (amino acids, urea, organonitriles, N-heterocyclics) (Timperely et al. 1985, Mopper and Zika 1987, Duce et al. 1991, Paerl 1995) many of which are available to phytoplankton (Peierls and Paerl 1997).

Previous studies have shown that AD-N is an important source of externally supplied or “new” nitrogen, contributing from 20 to >40% of the “new” N flux to U.S. east coast estuarine and coastal waters (Paerl 1985, Fisher and Oppenheimer 1991, Paerl 1995, Paerl and Whitall 1999, Valigura et al. 2000, Whitall 2000, Whitall and Paerl, 2001). Eutrophication is often associated with altered phytoplankton community structure and function in coastal systems. These perturbations can lead to nuisance algal blooms and/or hypoxia/anoxia, both causative agents in fish kills, and changes in microbial and algal community composition, resulting in ecological and economic losses. Such changes in biodiversity have been observed in the Neuse River Estuary which drains one of North Carolina’s most productive and rapidly developing urban, industrial and agricultural watersheds (Paerl et al. 1998). The Neuse River drains a watershed of over 16,000 km$^2$ which is dominated by forest and agricultural land with increasing urbanization. The surface area of the estuary is approximately 400 km$^2$. Over the past 20 years, symptoms of eutrophication, including nuisance cyanobacterial and dinoflagellate blooms, associated bottom water hypoxia/anoxia, fish kills and altered food web structure have plagued this productive and economically valuable estuary (Tedder et al. 1980, Paerl 1983, Christian et al. 1986, Paerl et al. 1998).

Wet AD-N has been documented to be increasing in at a long term monitoring site in eastern North Carolina (NADP/NTN site NC35, Paerl and Whitall 1999). It is also important to note that both the total N flux is increasing and the partitioning between dissolved inorganic nitrogen (DIN) species is changing. In addition, the relative proportion of NH$_4^+$ to NO$_3^-$ deposition is increasing (Paerl and Whitall 1999). This can have profound impacts on the algal community structure because these DIN species may be differentially utilized by specific algal groups (Collos 1989, Stolte et al 1994).

Dry deposition measurements of NH$_3$ have not previously been made for coastal North Carolina. Dry deposition of N occurs when gaseous N compounds or aerosols (airborne particles) are deposited on a ground (soil, rock, leaves, grass, asphalt etc.) or water surface due to chemical gradients and micrometeorological factors. Particulate organics have been measured, but their atmospheric chemistry is poorly understood (Gorzelska et
The most prevalent N gas species are NH$_3$, NO, NO$_2$ and HNO$_3$. Ammonium sulfate aerosols are usually the most abundant NH$_4^+$ containing particles in the atmosphere because they are relatively unreactive compared to ammonium chloride and ammonium nitrate, which are both easily dissociable in the reverse of their formation reactions (Rendell et al. 1993). The formation of ammonium nitrate particles is dependent on NH$_3$ availability via the reaction:

\[
\text{NH}_3(g) + \text{HNO}_3(g) \rightarrow \text{NH}_4\text{NO}_3(p). \quad \text{(Meng et al. 1997)}
\]

HNO$_3$ not converted to particulate ammonium nitrate may be lost from the atmosphere to deposition. Gaseous HNO$_3$ has a high affinity for dry deposition to almost any surface; therefore, HNO$_3$ has a relatively short half-life of 30 hours (Meng et al. 1997). Particulate NH$_4$NO$_3$, on the other hand, has only one-tenth the affinity for deposition as HNO$_3$ and therefore an atmospheric half-life an order of magnitude larger than that of HNO$_3(g)$. Thus, the atmospheric concentrations of NH$_3$ directly influence the relative amount of HNO$_3$ which remains in the atmosphere (Meng et al. 1997).

Measurements of the dry deposition of N have been done using a variety of methods. Surrogate surface techniques, ranging from collection buckets (Willey and Keifer 1993) to artificial Christmas trees (Garten 1996), have been employed with varying degrees of success. These techniques allow dry deposition to accumulate on the collection surface which is then washed and the deposited N collected. The advantage to this method is that a depositional flux is actually being measured. However, the collection surface is not likely to accurately represent any natural surfaces and surrogate surfaces are therefore considered an inaccurate measurement of dry deposition. Measuring ambient air concentrations of gases and particulates can be done with both filter packs and annular denuder systems with good accuracy and precision. However, the EPA’s Clean Air Status and Trends Network, which has a coastal site in Beaufort, North Carolina, employs a filter pack system which does not measure gaseous NH$_3$. Furthermore, in order to translate these ambient air concentrations to depositional fluxes, a depositional velocity must be employed.

\[
F = V_d \ast C_a \quad \text{where } F = \text{depositional flux in ng cm}^{-1} \text{s}^{-1} \\
V_d = \text{depositional velocity in cm s}^{-1} \\
C_a = \text{ambient air concentration in } \mu \text{g L}^{-1}.
\]

The depositional velocity ($V_d$) is the reciprocal of the resistance of a chemical species to deposition. (Duyzer 1994) This resistance depends on the chemical species in question, the physical and chemical characteristics of the depositional surface, which varies diurnally and seasonally. Estimating dry deposition velocities is extremely difficult and is beyond the scope of this study. Dry deposition is not considered further in this study.

**Sources of AD-N**

While natural sources of AD-N exist (Paerl and Whitall 1999), anthropogenic sources tend to be much larger in magnitude, and more temporally variable. Unlike natural sources, anthropogenic sources can be managed through regulations and are the focus of
this study. Figure 1 shows the contribution of various anthropogenic N sources to the atmospheric N emissions budget for North Carolina. Fossil fuel combustion (automobiles, point sources and non-road mobile sources in Figure 1) is a large source of nitrogen oxides (NO\textsubscript{x}) (Likens et al. 1974, Levy and Maxim 1987, Duce 1991) and a smaller source of NH\textsubscript{3} gas. HNO\textsubscript{3} can be transported over relatively large distances (600-800 km, Dennis 1997) due its relatively long atmospheric lifetime (atmospheric half-life of 30 hours, Meng et al. 1997). The Neuse River Basin may receive HNO\textsubscript{3} from metropolitan areas in the eastern U.S. (Atlanta, Charlotte, Richmond, Norfolk, Washington D.C., Pittsburgh) in addition to within basin urban (Raleigh-Durham) and localized sources.

![Figure 1: Relative contribution of various nitrogen (N) sources to the atmospheric N emissions budget for North Carolina (black) and coastal North Carolina (white). From NC Department of the Environmental and Natural Resources, Division of Air Quality, 1996 data.](image)

While oxidized N species are usually the dominant forms of DIN in rainfall, in areas with intensive agriculture, NH\textsubscript{3} (g) and NH\textsubscript{4}\textsuperscript{+} (aqueous or particulate) can also be major DIN components as well (Bujsiman et al. 1987). Anthropogenic sources of NH\textsubscript{3} include stack emissions, sewage treatment plants, septic systems and agricultural emissions (both from chemical fertilizers and animal waste). The atmospheric lifetime of NH\textsubscript{3} is 1-5 days (Aneja et al. 1998), resulting in transport distances of up to several hundred kilometers. A likely source of new NH\textsubscript{3} to eastern North Carolina is volatilization from animal waste, which has increased in scope with large increases in poultry and swine production since 1990. Furthermore, Neuse River basin is within the range of influence of the majority of these swine operations, both within the basin and in nearby counties (Walker 1998).

**Study Objectives**

The objectives of this study were as follows: 1) to quantify the spatial and temporal variability of wet AD-N in the NRB; 2) to use these basin wide AD-N measurements to calculate the relative importance of AD-N to the “new” N budget for the NRE; 3) to quantify the temporal variability of ambient particulate and gaseous reduced N.

**Experimental**

**Sample Collection and Storage**

Wet deposition sampling sites were located along a longitudinal transect in the Neuse River Basin in eastern North Carolina (Figure 2). Wet deposition was sampled using a series of wet/dry collectors (Aerochem Metrics, model 301) on a weekly basis from July 1996 to April 2001.
Figure 2: Site location map. Numbers show the locations of wet atmospheric deposition of nitrogen (WAD-N) collectors and rain gauges (see also Table 1). WAD-N and rain gauge pairings are shown with like shapes (e.g. circles paired with circles). Zones shown are delineations for in-stream N degradation model (see Table 3). IMS is the UNC-Chapel Hill Institute of Marine Sciences in Morehead City, which is the location of the annular denuder ambient atmospheric nitrogen sampling system.

Previous studies (Vet et al. 1989, Lamb and Comrie 1993, Butler and Likens 1998) have reported significantly lower NO₃⁻ and NH₄⁺ concentrations in co-located sampling stations visited weekly versus those sampled on a daily basis. This has been attributed to biological utilization of N in the wet bucket during the weekly interval (Sisterson et al. 1985, Ramundo and Seastedt 1990, Vesely 1990). To address this problem, thymol (C₁₀H₁₄O) was used as a biocide (Gillet and Ayers 1991) in the wet bucket. Collectors have covered "wet" buckets which, in combination with the inherently low rain water pH (4<pH<5), minimizes the potential for NH₃ loss through volatilization.

Sample buckets were cleaned weekly with 1% HCl and Nanopure deionized water. All samples were filtered through precombusted Whatman GF/F filters and stored frozen (-20°C) in acid washed HDPE bottles, which had been pre-rinsed with the sample, until analysis.

Ambient atmospheric ammonia/ammonium concentrations were measured at the Institute of Marine Sciences in Morehead City from 11/8/99 to 1/14/01. This sampling location is in close proximity to, but not in, the Neuse River basin. This sampling was conducted according to the U.S. EPA standard method for the determination of reactive acidic and basic gases and particulate matter in indoor/outdoor air (US EPA 1989).

Gas and particulate samples were taken with a URG, Inc. annular denuder system with Teflon filter packs utilizing both Teflon and Nylon filters, 150 mm stainless steel annular denuder tubes and a flow rate of 10 L/min. Acid gases were captured by coating the tubes with a sodium carbonate in methanol solution (1% sodium carbonate in 50/50% methanol/Nanopure water) and base gases were captured with a citric acid solution (1% citric acid in methanol).

Samples were taken in two 12 hour segments (morning and evening) on sampling days (at least three days per week). Air was actively pumped through the filter pack/denuder tubes equipment at a constant flow rate of 10 L/min.
Denuder tubes were extracted in 10 ml of Nanopure water and extract solutions stored in scintillation vials at 4° C until analysis. Filters were stored dry in scintillation vials at 4° C until analysis.

**Chemical Analyses**

The collected wet deposition samples were analyzed for NH$_4^+$, NO$_3^-$, and TKN, using a Lachat QC8000 Autoanalyzer (NH$_4^+$ after Diamond and Huberty 1996, NO$_3^-$ from Schetig 1997, TKN from Wendt 1997). Organic N was determined by difference (TKN-NH$_4^+$).

Denuder filters were stored dry under the same conditions. Filters were extracted in perchloric acid and ethanol in an ultrasonic bath. The extracts of both filters and tubes were analyzed at North Carolina State University, Raleigh (Dr. W Robarge) via standard ion chromatography techniques.

**Wet Deposition Calculations**

Annual atmospheric nitrogen deposition was calculated by:

$$\text{deposition (mg/m}^2\text{/yr}) = \Sigma [(\text{rainfall depth (cm)} \times \text{nitrogen concentration (µg/L)})/100]$$

Both N concentration in the rainfall and rainfall depth have exhibited large spatial variabilities on a weekly basis (Peierls and Paerl 1997). Therefore, it was desirable to employ as many collection sites as possible. An array (6) of precipitation gauges, managed by the North Carolina State Climate Office (NCSCO), was used to complement the seven locations in the basin which have atmospheric deposition collectors and co-located rain gauges (See Figure 2 and Table 1). Stand alone (NCSCO) gauges were paired with concentration data from the closest wet/dry collector for deposition calculations. This allowed the estimation of depositional fluxes at 6 additional locations. Two of the sites are parts of national monitoring programs; site 2 is a National Atmospheric Deposition Program/National Trends Network (NADP/NTN) site and site 12 was a Clean Air Status and Trends Network (CASTNet) site is now part of the NADP/NTN network; since these monitoring programs do not measure organic N, data from the closest site measuring organics was used.

Atmospheric deposition may reach the estuary via two pathways: direct deposition to the estuary surface waters and deposition to the watershed itself, which can enter the waterways of the basin in runoff and through groundwater (indirect deposition). In order to calculate a watershed level indirect AD-N budget, the watershed was divided into polygons based on rain gauge locations using the Thiessan Method (Schwab et al. 1993), which is a geometric method for subdividing a watershed based on the location of rain gauges. This allows for spatially weighted indirect AD-N fluxes based on area (area of polygon A (km$^2$) $\times$ deposition flux polygon A (mg/m$^2$/yr) = total deposition for polygon A (mg/yr)). For direct deposition calculations, the estuary surface area was similarly divided with the Thiessan method using the 5 AD-N sites which bound the estuary (sites 9, 10, 11, 12 and 13, Figure 2).
Table 1. Sampling locations and site descriptions. See also Figure 2. North Carolina State Climate Office (NCSCO) sites are equipped with a rain gauge. National Atmospheric Deposition Program (NADP) sites are equipped with a rain gauge and an Aerochem Metrics Model 301 collector. UNC-IMS sites are equipped with a rain gauge and an Aerochem Metrics model 301 Collector. The predominant land use type for all stations is forest, followed by agriculture and urban.

<table>
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<th>Name</th>
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Nitrogen Retention and In-Stream Degradation Models

In order to determine the relative importance of AD-N fluxes to the N budget of the estuary, we have attempted to estimate how much of the indirect deposition would be retained by the landscape with the use of a N retention model. A problem with N retention models of this type, which use average retention values for generalized land use types, is that true nutrient retention depends on a variety of land parcel specific parameters such as soil N content, historical acid deposition, soil type, land slope, elevation and vegetative type (Valigura et al. 1996). By using average values for an entire watershed, an estimate of the N retained in the land parcel can be calculated, but these values are not absolute and must be considered estimates.

This N retention model was designed after compiling literature watershed retention values (Valigura et al 1996, Tyler 1988, Hinga et al 1991, Fisher and Oppenheimer 1991) and uses 1996 GIS land use data for the 267 sub-basins in the watershed. For each land use type an N retention value from 0 to 1 is assigned. A value of 0.25 means that 25% of the flux would be retained by the land and 75% would reach the waterways. Table 2 shows the 3 sets of input parameters for the model, representing the highest and median values reported in the literature for studies of the Chesapeake Bay, as well as our “best estimate” values. Initially, the lowest reported retention values were also considered, but these were quickly invalidated, as they predicted that 91% of the total “new” N load was atmospherically derived. Point source discharges alone accounted for more than 8% of the total; this would imply that other non-point sources (agricultural and urban runoff, septic system leaching etc.) could account for only 1% of the total “new” nitrogen budget to the estuary, which is not realistic. Therefore, these “lowest” model input parameters were discarded. The “best estimate” retention model takes into account watershed specific variables such as slope, soil type, tillage, fertilizer application rate, extent of riparian buffers and crop types for the Neuse River Basin. Because of the uncertainty associated with selecting the “best estimate” values, three sets of parameters are shown in order to bound our “best estimate” model with maximum and minimum predicted values. Extensive discussion of this retention model are provided in Whitall, 2000 and Whitall and Paerl, 2001.
Table 2. Three N retention models for estimating % wet atmospheric deposition of nitrogen (WAD-N) retained by various land use types. Median and low models are based on median and lowest reported values for Chesapeake Bay Watershed (Valigura et al. 1996) and serve to bound the Best Estimate model. See discussion in text.

<table>
<thead>
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<th>Model</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Forest</td>
</tr>
<tr>
<td>High retention</td>
<td>100</td>
</tr>
<tr>
<td>Median retention</td>
<td>90</td>
</tr>
<tr>
<td>Best Estimate</td>
<td>99</td>
</tr>
</tbody>
</table>

Table 3: In-stream nitrogen degradation factors for Neuse River Basin. Zones are delineated in Figure 2. Factors are from NC DENR Division of Water Quality.

<table>
<thead>
<tr>
<th>Region</th>
<th>Map Label</th>
<th>N reaching estuary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Above Falls Lake Dam</td>
<td>Zone A</td>
<td>10%</td>
</tr>
<tr>
<td>Falls Lake Dam to Contentnea Cr.</td>
<td>Zone B</td>
<td>50%</td>
</tr>
<tr>
<td>Contentnea Cr. to Streets Ferry Br.</td>
<td>Zone C</td>
<td>70%</td>
</tr>
<tr>
<td>Below Streets Ferry Br.</td>
<td>Zone D</td>
<td>100%</td>
</tr>
</tbody>
</table>

After the amount of AD-N reaching the streams from each sub-basin was determined, these N loadings were applied to a simple in-stream degradation model designed by the North Carolina Division of Water Quality (1993) (see Table 3) to determine how much of this N reaches the head of the estuary. This model accounts for N losses in the streams and rivers due to denitrification and settling as particles; N losses are proportional to distance traveled to estuary.

Results

Total Annual Wet Deposition

The results presented here are for wet deposition only. Total wet N deposited from the atmosphere to the land area of the Neuse River Basin was estimated to be 1.6 Gg N/yr (standard deviation between study years ± 6.2 Gg N/yr). Using a nitrogen retention model and in-stream riverine degradation model (see discussion above and Tables 2 and 3), we estimated the WAD-N retained in a land parcel based on land use type and how much of the N reaching the waterways was transported to the estuary. This flux ranged from 0.7 Gg N/yr to 2.9 Gg N/yr, depending on the nutrient retention values used (Table 4). Using our “best fit” values, this flux via indirect deposition was estimated to be 1.3 Gg N/yr.

Table 4: Predicted relative importance of wet atmospheric deposition of nitrogen WAD-N to the total “new” nitrogen (N) flux to the Neuse River Estuary. See Table 2 for N retention values for the 3 models.†

<table>
<thead>
<tr>
<th>Total wet N deposition (Gg/yr)</th>
<th>Model used</th>
<th>AD-N Exported (Gg/yr)</th>
<th>AD-N reaching estuary (Gg/yr)</th>
<th>Direct Deposition to estuary (Gg/yr)</th>
<th>Total “new”N flux to estuary (Gg/yr)</th>
<th>AD-N as % of total flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.4</td>
<td>High</td>
<td>0.81</td>
<td>0.7</td>
<td>0.4</td>
<td>7.4</td>
<td>15</td>
</tr>
<tr>
<td>16.4</td>
<td>Median</td>
<td>4.2</td>
<td>2.9</td>
<td>0.4</td>
<td>7.4</td>
<td>45</td>
</tr>
<tr>
<td>16.4</td>
<td>Best Estimate</td>
<td>1.8</td>
<td>1.3</td>
<td>0.4</td>
<td>7.4</td>
<td>23</td>
</tr>
</tbody>
</table>

† Total “new” N flux to the estuary calculated by summing riverine loading at the head of the estuary (at Streets Ferry Bridge (SFB) above New Bern), direct WAD-N deposition and point and non-point sources below SFB, see discussion in text. Total wet indirect N deposition and direct deposition to estuary are measured values. All other values are estimates based at least in part on model output.

Direct deposition to the estuary surface (based on sites 9,10,11,12 and 13 which bound the estuary) was 0.4 Gg N/yr (standard deviation ± 0.1 Gg), resulting in a total AD-N flux to the estuary of between 1.1 Gg N/yr and 3.2 Gg N/yr (“best” estimate = 1.7 Gg N/yr). When compared to the total flux of nitrogen to the estuary of 7.3 Gg N/yr (riverine
Figure 3: Seasonal variability in weekly total wet nitrogen deposition for 13 sites pooled for 1996 to 2001. Letters show significant differences between groups (One way ANOVA with post-hoc Bonferroni analysis, \( \alpha = 0.05 \)). Groups with common letters are not significantly different from each other.

![Graph showing seasonal variability in weekly total wet nitrogen deposition](image)

Figure 4: Seasonal variability in weekly wet \( \text{NH}_4^+ \) deposition for 13 sites pooled. Letters show significant differences between groups (One way ANOVA with post-hoc Bonferroni analysis, \( \alpha = 0.05 \)). Groups with common letters are not significantly different from each other.

![Graph showing seasonal variability in weekly wet \( \text{NH}_4^+ \) deposition](image)

Over the four year study period, deposition of nitrogen was fairly evenly divided between nitrate, ammonia and organics (spatially weighted annual averages of 34\%(s.d.=8\%), 32\%(s.d.=2\%) and 34\%(s.d.=9\%) respectively). The deposition of organic N has recently been shown to be a potentially important component of AD-N in coastal North Carolina (Peierls and Paerl 1997) and data from our current study support this assessment. The organic N fluxes reported here are to those reported for coastal North Carolina in Peierls and Paerl (26\%, 1997) and they fall within published reports from other areas (Timperley et al 1985, Knapp et al. 1986).

Variations in Weekly AD-N Flux

Seasonally, the total weekly wet N deposition is highest in the summer (June-August) and lowest in the winter (December – February) (significant at \( \alpha = 0.01 \) one-way ANOVA with post-hoc Bonferroni means comparison; see Figure 3). This same pattern is seen for average weekly \( \text{NH}_4^+ \) deposition (Figure 4) and similar patterns are seen for average weekly \( \text{NO}_3^- \) deposition (Figure 5) and average weekly DIN deposition (Figure 6). There are no seasonal patterns in DON deposition. These seasonal patterns in deposition do not mirror seasonal precipitation patterns; seasonally, spring has the lowest average weekly precipitation (Figure 7). This suggests that other factors,
including the direction from which a storm system originates and seasonal changes in sources, including natural sources, may be involved in causing these differences.

Spatial Variability in Annual AD-N Flux
On an annual basis, the highest AD-N flux occurs in the middle segment of the watershed (Figure 8) with the lowest fluxes occurring in the upper and lower watershed. This pattern was similar for NH₄⁺, NO₃⁻ and DIN deposition (Figures 9-11). Deposition of NH₄⁺ does not vary spatially, but NO₃⁻ deposition is significantly higher at site 6 (Goldsboro) than sites 1,2,3,4,12 and 13. DON deposition is lower at site 4 than at sites 8,11 and 12 (Figure 12). Rainfall amount does not significantly vary across the watershed, although coastal sites receive slightly more annual rain than inland sites (Figure 13).

Ambient Atmospheric Nitrogen Concentrations
There were no statistically (One way ANOVA, α=0.05) significant differences between night and day samples for NH₃ (day, mean=0.48 µg N/m³, s.d.=0.45; night, mean=0.49, s.d.=0.47) or NH₄⁺(day, mean=0.50 µg N/m³, s.d.=0.37; night, mean=0.45, s.d.=0.44). Figure 14 shows the average 12 hr concentrations for gaseous NH₃, particulate NH₄⁺ and for total reduced N (NH₃ + NH₄⁺). Total reduced nitrogen is fairly evenly divided into gaseous and particulate fractions with the particulate form accounting for 51% of the total over the study period.

Seasonally, there were many differences in the ambient atmospheric concentrations of reduced nitrogen. NH₃ concentrations were significantly (ANOVA analysis with Bonferroni means comparison) higher in the summer (mean=0.65 µg N/m³, S.D.=0.60) and fall (mean=0.49 µg N/m³, S.D.=0.40) than in the winter (mean=0.30 µg N/m³, S.D.=0.31) and spring (mean=0.31 µg N/m³, S.D.=0.28) (Figure 15). Particulate NH₄⁺
concentrations were highest during the spring \((\text{mean}=0.74 \mu\text{g N/m}^3, \text{S.D.}=0.40)\) and lower in the summer \((\text{mean}=0.41 \mu\text{g N/m}^3, \text{S.D.}=0.36)\), fall \((\text{mean}=0.40 \mu\text{g N/m}^3, \text{S.D.}=0.42)\) and winter \((\text{mean}=0.50 \mu\text{g N/m}^3, \text{S.D.}=0.41)\) (Figure 16). Total reduced nitrogen \((\text{NH}_3 + \text{NH}_4^+)\) concentrations were highest in the summer \((\text{mean}=1.06 \mu\text{g N/m}^3, \text{S.D.}=0.60)\) and lowest in the winter \((\text{mean}=0.80 \mu\text{g N/m}^3, \text{S.D.}=0.54)\) (Figure 17). The relative importance of gaseous versus particulate fractions of reduced nitrogen varied seasonally as well. Gaseous \text{NH}_3 dominated the total reduced nitrogen budget for the summer and fall (statistically different from winter and spring, ANOVA with post-hoc Bonferroni means comparison) (Figure 18).

**Discussion**

The data presented here indicate that AD-N is fairly evenly distributed between the chemical species in wet deposition. From an ecological response perspective, however, the inorganic species may be more important than the organic species due to their high degree of availability to phytoplankton. Although some organic nitrogen species (urea, amino acids, primary amines) can be utilized directly by phytoplankton (Antia et al. 1991), nutrient addition bioassays conducted with rain water have shown that only 20-30% of the organics in AD-N can be utilized by phytoplankton on time scale of hours to days (Peierls and Paerl 1997). Previous studies (Paerl and Whitall 1999) using National Atmospheric Deposition Program/National Trends Network (NADP/NTN) data from a site in eastern North Carolina (NC35) have indicated that \text{NH}_4^+ has contributed to an increasingly larger percentage of the AD-N budget over the past two decades. The short duration of our current study precludes us from making similar conclusions. Chemical speciation of AD-N may be
important from an estuarine phytoplankton response perspective because different phytoplankton groups are able to utilize different N compounds differentially (Collos 1989, Stolte et al 1994). This apparent historical shift in the forms of bioavailable N may cause a shift in algal community composition, which is important both from biogeochemical (i.e., C flux) and trophic perspectives, including a potential shift towards nuisance/toxic species.

The seasonal variability in weekly AD-N flux cannot be explained by variability in precipitation amount alone (Figure 4). Therefore, this seasonal pattern must be explained by some other driving force such as: seasonal fluctuations in source emissions of atmospheric N and other meteorological factors. During the summer, elevated air temperatures lead to relatively high NH3 volatilization rates from animal waste stored in lagoons or applied to land (Aneja et al. 1998). The seasonal influx of tourists to coastal North Carolina translates into periods of elevated fossil fuel emissions (containing both NOx and NH3) from mobile sources. Seasonal variations in emissions of NH3 from natural sources, including elevated NH3 emissions from vegetation during the summer and fall, may influence these patterns as well.

The direction from which a storm system originates and the amount of time the system is over land will both relate to the potential for the air parcel to gain N. Air parcels which pass over relatively unpolluted areas (storms of marine origin, for example) should contain a small amount of N and the flux from such weather systems should be low. Conversely, air parcels passing over areas having high atmospheric N emissions (cities and areas of intensive agriculture) should contain relatively more N and the flux from such systems should be higher. Previous studies (Walker 1998) have shown NADP/NTN depositional data to be well correlated with storm back trajectories from the NOAA-ARL's HYSPLIT 4 model (NOAA ARL 2000).
Spatial variability in weekly DIN wet deposition for 4 seasons pooled. Letters show significant differences between groups (One way ANOVA with post-hoc Bonferroni analysis, α=0.05). Groups with common letters are not significantly different from each other.

Spatial differences in total N deposition are driven by differences in wet NO$_3^-$ deposition. In theory, enhanced NO$_3^-$ deposition in the middle to lower portion of the watershed may be due to interaction of HNO$_3$ with sea salt aerosols (Harrison et al. 1983, Brimblecombe and Clegg 1988), but this is unlikely to be the case because the site nearest to the ocean (site 11) had significantly less NO$_3^-$ deposition than the inland Goldsboro site. This pattern suggests that prevailing meteorology and spatial distribution of source emissions may play a greater role in driving these observed differences than sea salt interactions.

The magnitude of ambient atmospheric reduced nitrogen is significantly less than measurements made inland, in closer proximity to animal operations (W. Robarge, North Carolina State University, in prep). This is not surprising, since there are far fewer large sources of ammonia in the coastal zone.

Seasonally, ambient NH$_3$ concentrations are highest in the summer, which can be explained by higher air temperatures leading to increased ammonia volatilization from agricultural sources. The seasonality of NH$_3$ concentrations in coastal North Carolina suggests that there must be transport to the coast from inland agricultural sources.

This study is one of the first efforts to quantify the importance and patterns in AD-N on a watershed-level scale for an N-sensitive coastal watershed. Wet AD-N clearly is an important component of the N flux to the Neuse River Watershed, accounting for between 15% and 45% of the total "new" nitrogen flux to the estuary. The direct depositional component, which makes up 4-7% of the total "new" N loading, may be particularly important because the resultant N...
Figure 13: Spatial variability in weekly precipitation for 4 seasons pooled. There were no statistically significant differences between groups (One way ANOVA with post-hoc Bonferroni analysis, α=0.05).

Figure 14: Average 12 hour ambient concentrations of NH$_3$ gas, particulate NH$_4^+$ and total reduced nitrogen (NH$_3$ + NH$_4^+$) at UNC-IMS in Morehead City from 11/18/99 to 1/14/01. Sampling is not continuous and represents at least 3 sample days (a day consists of 2 continuous 12 hour sampling periods) per week.

Flux is delivered directly to the estuary and is not altered or utilized by in stream processes. Further work examining the direct depositional component to the nitrogen budget of N-limited Pamlico Sound is an important research direction. Due to the large surface area of the sound, direct deposition of AD-N to the Sound may play a very large role in the “new” nitrogen budget for this system.

This was the first study to measure ambient atmospheric reduced nitrogen concentrations in coastal North Carolina. While the coastal concentrations of atmospherically deposited ammonia(ium) are less than recorded in inland, more agricultural areas, there is evidence of transport of this “new” N source from inland to the coast. An important next step is to develop appropriate dry deposition velocities to use in conjunction with the measured concentrations to calculate dry deposition flux rates. The inclusion of dry deposition of oxidized and reduced N to the watershed N budget will add to the significance of AD-N to the “new” N budget of the NRE. It is also important to develop source apportionment values to determine the relative importance of the various sources of atmospheric N emissions to N deposition.
Figure 15: Seasonal variability in 12 hour ambient concentrations of NH₃ gas at UNC-IMS in Morehead City, NC. Letters show significant differences between groups (One way ANOVA with post-hoc Bonferroni analysis, α=0.05). Groups with common letters are not significantly different from each other.

Figure 16: Seasonal variability in 12 hour ambient concentrations of particulate NH₄⁺ at UNC-IMS in Morehead City, NC. Letters show significant differences between groups (One way ANOVA with post-hoc Bonferroni analysis, α=0.05). Groups with common letters are not significantly different from each other.
Figure 17: Seasonal variability in 12 hour ambient concentrations of total reduced nitrogen (NH₃+NH₄⁺) at UNC-IMS in Morehead City, NC. Letters show significant differences between groups (One way ANOVA with post-hoc Bonferroni analysis, α=0.05). Groups with common letters are not significantly different from each other.

Figure 18: Seasonal variability in NH₃ gas as percent of total reduced nitrogen at UNC-IMS in Morehead City, NC. Letters show significant differences between groups (One way ANOVA with post-hoc Bonferroni analysis, α=0.05). Groups with common letters are not significantly different from each other.
List of References


Tyler, M. 1988. Contributions of atmospheric nitrate deposition to nitrate loading in the Chesapeake Bay. VERSAR Inc. Maryland Department of Natural Resources Report RP1052.


