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ABSTRACT

To characterize atmospheric nitrogen deposition and its potential impact on the Mullica River-Great Bay Estuary, atmospheric sampling was conducted at Rutgers University Marine Field Station in Tuckerton, New Jersey from March 2004 to March 2005. A total of 52 precipitation samples were collected on an event basis using a MIC wet-only automatic precipitation sampler. A total of 23 aerosol samples were also taken during this period of time with a high-volume aerosol sampler. Chemical analysis was performed using a Dionex Ion Chromatograph to determine the concentrations of nitrate and ammonium in precipitation and associated with aerosols. Nitrate concentrations for precipitation samples ranged from 0.53 to 9.2 mg L⁻¹, with an average value of 2.3 mg L⁻¹. Ammonium concentrations for precipitation samples ranged from 0.013 to 1.6 mg L⁻¹, with an average value of 0.42 mg L⁻¹. The nitrate-to-ammonium ratio is 5.5 in precipitation, similar to the values obtained for the Chesapeake Bay and Barnegat Bay, suggesting a regional signature of atmospheric inorganic nitrogen. The pH of each precipitation sample was measured and the average monthly value was 4.3, indicating an acidic nature. High nitrate and ammonium concentrations were related to low pH values. Nitrate and ammonium concentrations in aerosol samples ranged from 1.5 to 9.7 µg m⁻³ and 0.34 to 3.6 µg m⁻³, respectively, and the average concentrations were 3.7 µg m⁻³ for nitrate and 1.6 µg m⁻³ for ammonium.

Atmospheric deposition fluxes of nitrate and ammonium were then calculated using simple wet and dry atmospheric deposition models with incorporation of the in situ concentration data. The results indicate that wet deposition rates vary with season; the highest rate was seen in the spring with an average value of 0.42 g m⁻² month⁻¹,

accounting for ~ 42% of the total wet deposition. Total dry deposition increased approximately 20-30% per month in the spring suggesting that the formation of nitrate and ammonium in the atmosphere could be promoted by increased air temperature and solar radiation intensity. Back trajectory analysis was used to identify possible sources of nitrogen to this estuary and to determine if the origins of the air masses influence the seasonal variation of nitrogen species. During a high wet deposition event occurring in the spring, air masses had an inland origin while for a low wet deposition event, which occurred during the fall, the air masses had more of a marine origin.

The annual wet deposition flux for nitrate and ammonium are $2.7 \text{ g m}^{-2} \text{ year}^{-1}$ and $0.49 \text{ g m}^{-2} \text{ year}^{-1}$, respectively. The annual dry deposition flux is roughly estimated to be $0.38 \text{ g m}^{-2} \text{ year}^{-1}$ for nitrate and $0.087 \text{ g m}^{-2} \text{ year}^{-1}$ for ammonium. In order to estimate the annual dry deposition, it was assumed that there was no seasonal change for the remainder of the year since dry deposition was only directly measured in the spring so there are uncertainties related to these values. Overall, the total direct atmospheric deposition fluxes into the Mullica River-Great Bay Estuary are $3.1 \text{ g m}^{-2} \text{ yr}^{-1}$ for nitrate and $0.58 \text{ g m}^{-2} \text{ yr}^{-1}$ for ammonium. Nitrate deposition is the dominant fraction, accounting for ~ 84% of the total inorganic nitrogen deposition to this estuary. These annual fluxes were then used to calculate the total nitrogen deposition to the water surface and watershed of this estuary. The total atmospheric inorganic nitrogen directly deposited to the Mullica River-Great Bay Estuary is estimated to be $15 \times 10^7 \text{ g year}^{-1}$ and the total atmospheric nitrogen deposited to the Mullica River watershed is estimated to be $5.5 \times 10^9 \text{ g year}^{-1}$.

Remotely sensed ocean color data was used to investigate the relationship between the atmospheric nitrogen input to this estuary and chlorophyll *a*, an indicator of plant biomass. The satellite images suggest that atmospheric nitrogen deposition could influence chlorophyll *a* concentrations for the Mullica River-Great Bay Estuary. When there was a high atmospheric nitrogen deposition event, chlorophyll *a* concentrations eventually increased in response and vice versa. Other sources of nitrogen, including runoff from the Mullica River, may also influence these chlorophyll *a* concentrations. Combining this atmospheric nitrogen data with the water column nutrient data that is being collected at the Jacques Cousteau National Estuarine Research Reserve will assist in generating nutrient budgets to better manage the coastal resources of the Mullica River-Great Bay Estuary.

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Quantifying Atmospheric Nitrogen Deposition as a Nonpoint Source Pollution and its
Potential Effects on the
Mullica River-Great Bay Ecosystem

by

Jennifer Haag

A Master's Thesis Submitted to the Faculty of

Montclair State University

In Partial Fulfillment of the Requirements

For the Degree of

Environmental Studies, concentration in Environmental Science

Master of Arts

School: CSAM

Thesis Committee:

Department: Earth and Environmental Studies

[Redacted Signature]

(Thesis sponsor signs on line; type name under signature)

Thesis Sponsor Yuan Gao

[Redacted Signature]

(Dean signs above; type name under signature)
Dean

[Redacted Signature]

(Committee member signs on line; type name under signature)

Committee Member Michael J Kennish

5/2/05
(date)

[Redacted Signature]

(Committee member signs on line; type name under signature)

Committee Member HARBANS SINGH/DUKE OPTORI

[Redacted Signature]

(Department chair signs on line; type name under signature)

Department Chair Gregory A. Pope

**Quantifying Atmospheric Nitrogen Deposition as a Nonpoint
Source Pollution and its Potential Effects on the
Mullica River-Great Bay Ecosystem**

By:
Jennifer Haag

A THESIS
Submitted in partial fulfillment of the requirements
For the degree of Environmental Studies,
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The Department of Earth and Environmental Studies in
The Graduate Program of
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1. INTRODUCTION

1.1. Importance of Atmospheric Nitrogen

A portion of nitrogen (N) entering coastal waters is nitrogen of atmospheric origin. Atmospheric nitrogen can reach coastal waters by processes such as precipitation scavenging, either directly or indirectly, and it can cover a large regional area far extending the watershed. Studies conducted along the east coast of the United States indicate that atmospheric nitrogen represents a significant amount of the total nitrogen input to the coastal waters (Castro and Driscoll, 2002; Paerl and Fogel, 1994; Whitall et al., 2003).

Nitrogen is a major nutrient that controls biological productivity in many coastal waters (Ryther and Dunstan, 1971; Vitousek and Howarth, 1991; Nixon, 1995; Paerl, 1995; Paerl and Whitall, 1999; Rabalais, 2002; Driscoll et al., 2003; Galloway et al., 2003). The excessive discharge of nitrogen from non-point sources of pollution is a major contributor to the eutrophication of coastal waters, which is now considered the most widespread water quality problem in the United States (Nixon, 1995; Carpenter et al., 1998).

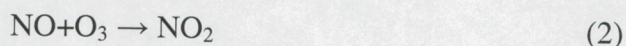
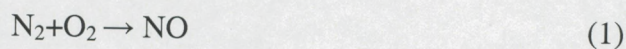
1.2. Source of Atmospheric Nitrogen

Nutrients, such as nitrogen, enter coastal waters from a number of sources. Agricultural products (e.g., fertilizers, nitrogen-fixing crops, animal wastes, and animal feed) can release nutrients into the environment. Other sources that deliver nutrients to coastal waters are wastewater treatment plants, urban runoff, and atmospheric deposition from industrial emissions and the burning of fossil fuels (National Research Council,

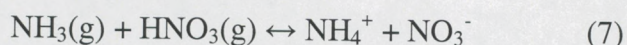
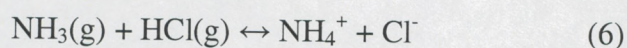
2000). Nutrient inputs to coastal waters occur via direct loading to the water surface or indirect loading from adjoining watersheds via surface runoff and groundwater flow (Figure 1) (Aneja et al., 2001; Bowen and Valiela, 2001; Valigura et al., 2000).

However, only a fraction of the nutrients from a watershed actually enters coastal waters due to processes during transport such as denitrification, retention, and utilization, while all the nutrients deposited directly to the sea surface is available for use (Alexander et al., 2000; Clark and Kremer, 2004). Atmospheric deposition is an important pathway of direct and indirect loading of nutrients to coastal waters.

Most of the nitrogen in the biosphere cannot be utilized by most organisms but must be converted into reactive, biologically usable forms by natural processes or human activities such as industrial emissions, fossil fuel combustion, and agricultural practices. The biologically usable forms of atmospheric nitrogen include inorganic reduced (NH_3 , NH_4), oxidized (NO_x , NO_3^-), and organic compounds (National Research Council, 2000; Galloway et al., 2003). Nitrogen oxides (NO_x) can be derived from the partial oxidation of N_2 or from the release of nitrogen by fossil fuel combustion (Driscoll et al., 2003; Galloway et al., 2003). Atmospheric reactions then convert NO_x to nitrate (see reactions 1 through 4 below). Nitrate is not directly released into the atmosphere, but is a secondary product (Seinfeld and Pandis, 1998; Paerl et al., 2000).



Other emission sources for nitrate, besides fossil fuel combustion from automobiles and industries, include biomass burning and other natural fixation processes (Paerl, 2002). Ammonia and ammonium are derived from agricultural waste, fertilizers, industrial emissions, and decomposition (Paerl, 2002). NH_3 is directly released into the atmosphere and can be transformed to NH_4^+ through atmospheric reactions (see reactions 5 through 7 below) (Seinfeld and Pandis, 1998; Aneja et al., 2001).



Less is understood about organic nitrogen. It can derive from a wide range of natural and anthropogenic sources, be composed of multiple compounds including urea and amino acids, and can be transported in the atmosphere over long distances (Scudlark et al., 1998; Cornell et al., 2003; Whitall et al., 2003). There are often large uncertainties in organic nitrogen determinations related to sampling methods, treatment after collection, and analytical techniques. In addition, due to the instability of dissolved organic nitrogen, only a limited number of experiments were conducted to obtain dissolved organic nitrogen concentrations (Scudlark et al., 1998; Meyers et al., 2000; Cornell et al., 2003). A large portion of the atmospheric nitrogen input to coastal waters is in the form of inorganic nitrogen, mainly nitrate (NO_3^-) and ammonium (NH_4^+); however, organic nitrogen has been recently recognized as another significant component of the total nitrogen and should be included when determining the total atmospheric nitrogen input (Peierls and Paerl, 1997).

1.3. Atmospheric Nitrogen Deposition

Atmospheric N deposition is defined as the “flux of nitrogen from the atmosphere to land and water surfaces” (Sustainable Biosphere Initiative Project Office, 1997).

Nitrogen can reach the surface waters by two main processes: dry deposition and wet deposition, either directly or indirectly. Wet deposition is carried out by precipitation. It is usually an episodic and high-level source of atmospheric nitrogen. Dry deposition is the sedimentation and impaction of particles and gases of nitrogen onto surfaces. This tends to be a chronic, low-level source of nitrogen (Voldner et al., 1986; Paerl, 1995; Russell, 2000; Paerl et al., 2002; Valiela and Bowen, 2002). Certain forms of atmospheric-derived nitrogen can be readily used by marine plants and microorganisms, and thus can contribute significantly to the accelerated rates of primary production seen in eutrophied systems (Glibert et al., 1991).

As stated previously, atmospheric nitrogen deposition is an important source of “new” nitrogen to coastal waters, especially since it can affect a large regional area (Valigura et al., 2000; Paerl et al., 2002). Most of this nitrogen is the result of human activities, which have led to more than a 6 to 8-fold increase in atmospherically-deposited nitrogen to coastal waters in the northeast (Holland et al., 1999). Since population growth of coastal areas is increasing, atmospheric nitrogen deposition is also projected to increase and become an even greater cause of environmental concern. In ten estuaries studied off the east coast of the United States, atmospheric inputs accounted for 15-42% of the total nitrogen input, with an average value of 24% (Castro and Driscoll, 2002). Most of the estuaries in the northeast and mid-Atlantic regions of the United States receive ~10-30% of their total nitrogen input from atmospheric deposition (Fisher and

Oppenheimer, 1991; Hinga et al., 1991; Valigura et al., 1996; Paerl, 1997; Stacey et al., 2000). The mid-Atlantic region may receive the highest input of atmospheric nitrogen in the United States due to the eastward transport of nitrogen emissions from agriculture and industry/urbanization in the Ohio Valley and elsewhere (Galloway et al., 1984; Scudlark and Church, 1993).

A study conducted at Cape Cod, Massachusetts indicated that atmospheric nitrogen deposition has increased over the past century at a rate of about $0.26 \text{ kg N ha}^{-1}$ per decade. The values for wet deposition of $\text{NO}_3\text{-N}$ were $0.90 \text{ kg N ha}^{-1} \text{ year}^{-1}$ in 1925 and increased to approximately $4.0 \text{ kg N ha}^{-1} \text{ year}^{-1}$ in 1980, resulting in eutrophication (Bowen and Valiela, 2001). At Waquoit Bay, Cape Cod, Massachusetts, atmospheric deposition accounted for 37% of the total nitrogen input to the bay in 1990 and remains the largest single source of nitrogen to the watershed (Bowen and Valiela, 2001). New nitrogen input to North Carolina coastal waters from atmospheric deposition was calculated to range from 36 to 80%. A total of 10 to 20% of the daily primary production in these waters was ascribed to this atmospheric deposition (Paerl and Fogel, 1994).

Atmospheric nitrogen input represents 15 to 55% of the total nitrogen input to the Neuse River Estuary in North Carolina, which has been experiencing eutrophication as noted above (Whitall et al., 2003). Atmospheric deposition is also a major source of nitrogen to the Chesapeake Bay region, accounting for 43% of the total nitrogen input. Increased nitrogen deposition has resulted in accelerated primary production and a steady decline of the bay's water quality (Fisher and Oppenheimer, 1991; Smith et al., 1992; Russell et al., 1998; Scudlark et al., 1998).

Many coastal waters are experiencing toxic and harmful algal blooms due to enhanced atmospheric deposition rates. Studies conducted in the Gulf of Mexico and along the Atlantic coast, for example, have demonstrated conclusively a connection between atmospheric nitrogen deposition and the presence of algal blooms. Areas of high atmospheric nitrogen deposition have been usually associated with frequent harmful algal blooms (Duce, 1991; Paerl, 1995; Valigura et al., 1996; Paerl and Whitall, 1999). It is apparent that in the United States, particularly along the east coast, increased atmospheric nitrogen deposition poses a threat to many coastal waters and estuaries, mainly due to overenrichment of nitrogen. "Globally it is estimated that atmospheric nitrogen deposition accounts for approximately 40 Tg N/year, compared to 30 Tg N/year from rivers, 10 Tg N/year from groundwater, and 20 Tg N/year from biological nitrogen fixation" (Paerl and Whitall, 1999, p.307).

1.4. Atmospheric Nitrogen Deposition to New Jersey Coastal Waters

The state of New Jersey has a densely populated coastline which spans a distance of ~1,800 miles. Major industries such as tourism, ports, fishing, shellfishing, and recreation are dependent upon coastal resources and comprise a significant amount of New Jersey's revenue (National Oceanic and Atmospheric Administration, 2004). Not only are New Jersey's coastal waters impacted by the coastal population but also by its densely populated inland areas. It is a major industrial and chemical producing state as well. These inland and coastal populations have the potential to affect water quality by increasing the amount of nutrients released to New Jersey's coastal waters. The National Oceanic and Atmospheric Administration (NOAA) conducted an eutrophication survey for the Mid-Atlantic region in 1997 and found high and hypereutrophic concentrations of

chlorophyll *a* in a number of estuarine systems such as the Hudson-Raritan Bay, Barnegat Bay, Delaware Inland Bays, and the Delaware Bay (Figure 2) (National Oceanic and Atmospheric Administration, 1997).

Barnegat Bay, located along the central New Jersey coastline, is a shallow, lagoon-type estuary with a variety of habitats that support rich planktonic, benthic, and nektonic communities, including endangered species (Kennish, 2001). This estuary is sensitive to external changes because of its location near or downwind of urban and industrial areas exposing the estuary to pollution emissions and because it is shallow with restricted circulation. Since the late 1980's, "brown tides" and other phytoplankton blooms have occurred frequently during the summer. Benthic macroalgal blooms have also become more frequent in summer. Due to the increased plant growth, especially algae, the water quality has been greatly affected (Gao, 2002). In 1995, Barnegat Bay was accepted into the National Estuary Program because it was recognized "as an estuary of national significance threatened by pollution, development and overuse" (Clement et al., 2001; U.S. Environmental Protection Agency, 2004). At the southern end of New Jersey is the Delaware Estuary. This estuary's water quality has been improving, but is still threatened by human development and non-point source pollution. Nutrient levels were found to be highest along the coast, "indicating that anthropogenic activities are a likely significant contributor to the excess nutrient load" found in the estuary (New Jersey Department of Environmental Protection, 1999; Partnership for the Delaware Estuary, 2002). The New York – New Jersey Harbor Estuary is surrounded by heavily populated areas, especially the metropolitan complex of New York City, resulting in major water quality problems and the occurrence of harmful algal blooms.

Contamination from organic and inorganic toxins and anthropogenic input of nutrients are high due to sewage treatment plants, wastewater, and fossil fuel combustion. This high input of nutrients has resulted in eutrophic conditions (Gao et al., 2002; Steinberg et al., 2004).

Atmospheric nitrogen deposition rates along New Jersey's coastal waters are high compared to those in other states of the Mid-Atlantic and Northeast regions of the country (Meyers et al., 2000). Nationwide, New Jersey's coastal waters exhibit some of the highest nitrogen inputs from atmospheric deposition, especially in Barnegat Bay (Castro et al., 2000). The elevated chlorophyll *a* concentrations observed along the coast of New Jersey may be due to the increased nitrogen input from atmospheric sources derived from human activities in New Jersey as well as other inland states.

1.5. Eutrophication

Eutrophication is a process by which a body of water becomes enriched with organic matter (Nixon, 1995; National Research Council, 2000). The availability of nutrients influences biological productivity in coastal waters. An overabundance of nutrients can lead to eutrophication, increasing the primary productivity and greatly affecting water quality (Gao, 2002). Other detrimental effects from eutrophication include changes in biodiversity and trophic structure, hypoxia or anoxia, the presence of harmful or toxic algal blooms, and the die-off of plants and animals (Sustainable Biosphere Initiative Project Office, 1997; Paerl and Whitall, 1999). Primary symptoms of eutrophication include increased levels of chlorophyll *a*, epiphytes, and/or macroalgae, while secondary symptoms include low dissolved oxygen levels, loss of submerged aquatic vegetation, and toxic blooms (Clement et al., 2001). The coastal waters that are

most susceptible to eutrophication are shallow systems with poor water circulation, low freshwater input, and a limited tidal range (Kennish, 1992).

Human activities such as fertilizer production, fossil fuel combustion, industrial emissions, and agriculture have resulted in increased nutrient inputs to coastal waters which can lead to eutrophication (Hinga, 1991). Nitrogen is the major nutrient contributing to eutrophication of estuarine and coastal marine systems worldwide (Hicks et al., 1995). During the past century it has been estimated that human activities have doubled the amount of nitrogen available to plants and animals especially along coastal waters (Sustainable Biosphere Initiative Project Office, 1997). Some sources of nitrogen, mainly fertilizer production, fossil fuel combustion, and nitrogen-fixing agricultural crops have increased three-fold from 1960 to 1990 and continue to grow (National Research Council, 2000). Land-use changes such as urbanization can also affect water quality and lead to eutrophication because of an increased input of land-derived nitrogen (Bowen and Valiela, 2001).

Nitrogen is considered a crucial element for many coastal waters because it is usually the primary limiting nutrient for primary productivity/ biomass accumulation (Ryther and Dunstan, 1971; Vitousek and Howarth, 1991; Nixon, 1995; Paerl, 1995; Paerl and Whitall, 1999; Rabalais, 2002; Driscoll et al., 2003; Galloway et al., 2003). When nitrate and other forms of nitrogen enter an estuarine system, they are removed by the primary producers for growth and other functions. The phytoplankton will either die and recycle the nitrogen back into the water or will be consumed by other organisms that will excrete the nitrogen as waste or recycle it back into the water when they die (Sverdrup et al., 2003). However, excessive nutrient loading can affect water quality.

Primary producers are the first to respond to increased loading by increasing their biomass (Rabalais, 2002). As stated previously, one of the primary symptoms of eutrophication is increased levels of chlorophyll *a*, a measure of plant biomass. The rapid growth of phytoplankton and benthic macroalgae over a short time period can generate blooms that are usually harmful to the environment. Toxic algal blooms occur because some algae produce toxins; these blooms have the potential to harm or kill fish and shellfish as well as adversely affecting marine mammals and humans (National Research Council, 2000; Rabalais, 2002; Driscoll et al., 2003). Subsequently, when these primary producers die, bacterial decomposition depletes dissolved oxygen, resulting in hypoxia or anoxia. This process degrades water quality and causes myriad problems, such as fish kills and the loss of submerged aquatic vegetation (Nixon, 1993; Russell et al., 1998; Sverdrup et al., 2003).

Eutrophication has become a major problem throughout the United States especially along the east coast (e.g., Neuse River Estuary, NC; Chesapeake Bay, VA; and Barnegat Bay-Little Egg Harbor Estuary, NJ). Nitrogen loading in the Neuse River Estuary has increased by at least 30% over the past three decades leading to hypoxia and other impacts (Stanley, 1988; Dodd et al., 1993; Paerl et al., 1998; Whitall et al., 2003). The Chesapeake Bay, the largest estuary in North America, has also been altered due to increased loading of nutrients, dissolved oxygen depletion, and a reduction of submerged aquatic vegetation (Cooper and Brush, 1991; Boesch et al., 2001; Bratton et al., 2003). Kiddon et al. (2003) assessed the ecological condition of Mid-Atlantic estuaries, focusing on four main systems: the Chesapeake Bay, Delaware River Estuary, Maryland and Virginian coastal bays, and Albemarle-Pamlico estuarine system. Overall, about 20-50%

of all four systems showed signs of eutrophication. Eutrophication is now considered the most widespread water quality problem in the United States (Nixon, 1995; Carpenter et al., 1998). According to Boland et al. (1993), “perhaps the most pressing problem in many estuarine and marine systems today is that of nutrient enrichment leading to eutrophication.”

1.6. Statement of the Problem

The future condition of coastal waters depends on proper management and continuous monitoring, especially as the population of coastal areas is increasing. It has been estimated that the “populations of coastal counties in the USA are increasing three times faster than the U.S. population as a whole” (Culliton et al., 1989). Accelerated population growth and development in coastal areas can lead to elevated nitrogen emissions to the atmosphere, thereby potentially increasing atmospheric nitrogen deposition on estuarine and nearshore ocean waters (Pryor and Barthelmie, 2000). More intensive research is necessary to gain a better understanding of atmospheric nitrogen deposition and how it may affect coastal waters, especially since east coast regional studies indicate that atmospheric deposition is a major source of nitrogen entering these waters (Paerl et al., 2000). Conducting more research in this area will provide essential data for the development of accurate nutrient budgets to assess ecosystem function and condition for coastal management programs.

Few monitoring stations exist along the coast that focus on the input of nitrogen from the atmosphere (National Research Council, 2000). At the Mullica River-Great Bay Estuary in southern New Jersey, water column nutrient data are being continuously collected by the Jacques Cousteau National Estuarine Research Reserve, but there has

been little data collected on atmospheric nitrogen deposition to this region. Therefore, the effects of atmospherically-derived nitrogen on the estuary are not known.

2. OBJECTIVES

2.1. Research Objectives

The main goal of this project is to quantify the atmospheric nitrogen input, mainly inorganic nitrogen, and to determine its potential effects on the Mullica River-Great Bay ecosystem. Specific objectives have been established to achieve this goal:

- 1) Obtain time series measurements for atmospheric concentrations of nitrate and ammonium in aerosols and precipitation.
- 2) Determine atmospheric deposition fluxes using atmospheric dry and wet deposition models with incorporation of the in situ measurement data.
- 3) Identify sources of atmospheric nitrogen by using air mass back trajectory analysis techniques.
- 4) Examine the relationship between elevated nitrogen input and the occurrence of high chlorophyll *a* concentrations in the estuary by applying remotely sensed ocean color imagery.

3. STUDY SITE

3.1. Site Selection

Not all of New Jersey's coastal waters are experiencing a degradation of water quality and eutrophication. Previous research has shown that the Mullica River-Great Bay Estuary, located within the Jacques Cousteau National Estuarine Research Reserve

(JCNERR), exhibits little degradation (Kennish, 2004). It is considered “one of the most pristine and least impacted estuarine systems in the densely populated urban corridor of the northeastern United States” (Durand, 1988; Able et al., 1992, 1999). This estuary, therefore, can serve as an excellent reference location to assess the health of impacted coastal ecosystems in New Jersey. Research and monitoring has been ongoing in the Mullica River-Great Bay Estuary. Extensive water column data is being collected through a System-Wide Monitoring Program (SWMP) at the reserve. There are four SWMP sites in the estuary, covering a distance of about 30 km, with two locations in the Mullica River (Lower Bank and Chestnut Neck) and two in Great Bay (Buoy 126 and Buoy 139). Grab samples are collected each month at the sites and analyzed for nutrients (nitrate, ammonium, and phosphate) as well as chlorophyll *a* concentrations. YSI data loggers (Yellow Springs Instrument 6-series, models 6000 and 6600) are also located at these sites, and they record water quality parameters every thirty minutes. Recorded parameters include temperature, salinity, dissolved oxygen, water level, pH, and turbidity (Kennish et al., 2004). Monitoring of these parameters is important, in part, for characterizing the environmental health of the estuary (Able and Hoden, 2002; Kennish et al., 2004).

This project is the first to focus on determination of atmospheric nitrogen input to this estuary, and the results can be combined with the water column nutrient data collected by the JCNERR to better understand potential nitrogen impacts on the system. In addition, the data can be further utilized for developing a nutrient budget for the region. The generated data can also be used to compare this estuary with other estuaries

along the east coast of the United States and to help coastal management programs address water quality problems coastwide.

3.2. Estuary and Characteristics

The Mullica River-Great Bay Estuary is located along the southern New Jersey coastline, approximately 14 kilometers north of Atlantic City (Kennish et al., 2004). This area has a temperate climate with a seasonal variation characteristic of the mid-Atlantic region (Kennish and O'Donnell, 2002). Precipitation averages 100-122 cm/yr and is usually evenly distributed year-round. However, about 50% of the total precipitation is lost to evapotranspiration, and only about 5% discharges into Great Bay due to the porous, sandy soils of the watershed (Psuty et al., 1993; Rhodehamel, 1998).

The Mullica River-Great Bay Estuary extends from Lower Bank (freshwater/saltwater interface) in the Mullica River to Little Egg Inlet (polyhaline) (Figure 3). It consists primarily of open estuary bordered by salt marshes (Kennish et al., 2004). The Mullica River watershed drains a surface area of 1,475 km² (Figure 4). The depth of the Mullica River ranges from five to nine meters and has a dark color due to tannins and humic compounds that originate from the Pine Barrens. These substances also cause low pH levels in the river. Due to the dark color and the depth of the river, light transmission and nutrient utilization are low (Able and Hoden, 2002). The Mullica River winds eastward for approximately 65 km, emptying into Great Bay. It has an average runoff of 83.8 cm a year and contributes the largest volume of freshwater to the bay (Durand, 1998; Kennish et al., 2004).

Great Bay has a surface area of 41.6 km² and a mean depth of about two meters. The bay is more productive than the Mullica River because of increased light penetration

which enables greater nutrient uptake by autotrophs (Able and Hoden, 2002). Nutrients enter the bay mainly from the river. The Pine Barrens are extremely nutrient poor, but upriver farmlands and urban areas represent important sources of nitrogen and other nutrients (Durand and Nadeau, 1972). Besides the Mullica River, a minor fraction of nutrients enter the bay from the ocean through Little Egg Inlet.

Semi-diurnal tides also influence the bay waters, which have an average salinity range of 10 to 32 ‰ and a temperature range of 0 to 30 °C (Kennish et al., 2004). A counterclockwise circulation pattern exists in the bay. During ebb tides, fresh water discharged from the Mullica River flows along the south side of the bay, while seawater from Little Egg Inlet flows along the north side during flood tides. This current pattern causes a counterclockwise gyre to form in the center of the bay (Durand, 1988; Kennish et al., 2004).

Overall, the Mullica River-Great Bay Estuary is a highly productive system. The surrounding coastal watershed supports a variety of habitats such as pineland forests, coastal plain, salt marshes, and barrier islands (Kennish and O'Donnell, 2002; Kennish et al., 2004). Upland forest areas consist of pine-oak and oak-pine forests, while the lowland areas support cedar swamps, bogs, and the Atlantic white cedar. The salt marshes, which are found on the coast and along the lower Mullica River, are mainly comprised of salt meadow grass, saltwater cordgrass, and spike grass, while the barrier islands consist primarily of dune grass, bayberry, heather, and marsh elder. Due to the diversity of habitats, it has become a major migratory stop for waterfowl, shorebirds, and raptors. In the winter, there may be as many as 70,000 individual waterfowl in the Mullica River-Great Bay area. It also supports more than 60 species of finfish along with

diverse shellfish, amphibian, plankton, and reptile populations. Some endangered species take refuge here such as bald eagles, peregrine falcons, swamp pink plants, and timber rattlesnakes, along with several other endangered plants and marine mammals (Jacques Cousteau National Estuarine Research Reserve, 2004).

3.3. Environmental Conditions

The lower Mullica River watershed primarily consists of forested land and marshes with developed land concentrated in Tuckerton and Mystic Island (Durand, 1998). The waters in this region have traditionally been undisturbed and clean with little human impact (Kennish et al., 2004). Most of the Mullica River watershed is sheltered from anthropogenic input because the upstream portions are part of the New Jersey Pinelands National Reserve, while the downstream portions are surrounded by federal and state wildlife refuges (Psuty et al., 1993; Zampella et al., 2001).

Several studies were conducted on primary productivity and nutrients in the Mullica River-Great Bay Estuary from 1961 to 1977. These studies found that development had a minimal impact. The watershed at that time consisted primarily of undisturbed pineland and farmland. Low concentrations of nitrogen were characteristic of the waters draining the undisturbed pineland areas. Higher nitrogen concentrations occurred upriver in the waters draining the agricultural and urban areas. Nitrogen was found to be the principal limiting nutrient in this region. Primary production increased down-estuary in response to increased nitrogen input from the river, although, low nitrogen levels usually limited primary productivity, especially in Great Bay (Durand and Nadeau, 1972; Durand, 1998). Wenner et al. (2001) reviewed water quality data from the JCNERR and 43 other National Estuarine Research Reserve sites across the United States

from 1996 to 1998. For that time period, their analysis showed that all of the reserves in the Mid-Atlantic region, except the JCNERR, showed signs of hypoxia. The two sampling sites used in the JCNERR for this study were at Lower Bank in the Mullica River and Buoy 126 in Great Bay. The same results were also found in 1999 and 2000 (Kennish and O'Donnell, 2002). In 2001, the Pinelands Commission released a report on the status of the Mullica River watershed, focusing on the landscape and selected aquatic and wetland resources. The commission noted that only 15% of the Mullica River watershed was developed or farmed, with most of the area still forested (~85%). The forested areas were relatively undisturbed with little land use, and the streams that drained these minimally impacted areas had low levels of nutrients (Zampella et al., 2001). These studies demonstrate the high water quality of the Mullica River-Great Bay Estuary through time.

4. METHODS

4.1. Sampling Collection

Atmospheric samples, precipitation and aerosol, were collected at Rutgers University Marine Field Station in Tuckerton, New Jersey (39.59° N, 74.34° W) from March 2004 to March 2005. This field station is located at the southern tip of a salt marsh peninsula across from the Little Egg Inlet in the Mullica River-Great Bay Estuary (Figure 5). The samplers used for collecting the atmospheric samples were bolted onto a wooden platform located near the field station and adjacent to the water. This platform was built off a walkway that runs from the field station to a meteorological tower abutting the shoreline. The wooden platform was considered the best location to place the

samplers because there was minimal contamination from the surrounding environment. The cleaning and assembling of the equipment used for precipitation and aerosol sampling were conducted in the Atmospheric Chemistry Laboratory at Montclair State University. A clean-room operation procedure was followed.

4.1.1. Precipitation

Precipitation sampling involved the use of a MIC wet-only automatic precipitation sampler controlled by an onsite rain sensor (MIC Company, Richmond, Ontario, Canada). Samples were collected for event-based rain showers throughout the year (March 2004 to March 2005). Collection was carried out with plastic reservoir sets that were previously cleaned. Cleaning consisted of placing the plastic reservoir sets in 1 N HCl for two to three days and then rinsing them thoroughly four times with distilled water (Millipore Elix 3 System, Millipore Corporation, Molsheim-France). They were then dried under a laminar flow bench (Enviroco Corporation, Albuquerque, New Mexico) and sealed in plastic bags until use.

To carry out the procedure for precipitation collection, the top cover of the sampler was manually opened. With gloves on, a plastic funnel-reservoir set was placed in the precipitation sampler. Information such as the sample number, date, weather conditions, and notes were logged into the precipitation log in a binder. During a rain event, the sampler automatically opened to collect the precipitation and automatically closed when no more precipitation was detected on the rain sensor. A rain gauge measured the rainfall and retained a record of the precipitation for up to nine days (Oregon Scientific Inc., Portland, Oregon, USA). This rain gauge data were also recorded in the precipitation log, including how much rain was collected each day. After

the precipitation sample was collected, the cover was manually opened. With gloves on, the plastic funnel-reservoir set was taken out. The bottle was disconnected from the funnel. The bottle was then labeled with the sample number and the date with a permanent marker and sealed tightly in a plastic bag. The bag with the unfiltered sample was then frozen until analyzed. The remaining information was logged into the precipitation log (i.e., date taken out, weather conditions, notes, and the total amount of rainfall for the sample). The above procedure was then repeated for each precipitation sample. Duplicate samples were taken from time to time to verify the accuracy of the results. The used funnels were placed in plastic bags and taken back to Montclair State University to be cleaned. They were never reused without first being recleaned.

4.1.2. Aerosols

Aerosol samples were collected using a Model 500EL high-volume aerosol sampler (Aquaero Tech, Miami, Florida, USA) following the method outlined in the instruction manual provided by Aquaero Tech. The flow rate averaged $\sim 1 \text{ m}^3 \text{ min}^{-1}$. Whatman 41 or 48 filter paper was used to collect the samples, and the sampling duration lasted between 6 and 24 hours. The sampling volume ranged from 354.24 m^3 to 930.60 m^3 depending on the sampling duration and the flow rate during each sample collection. The sampling frequency was around once per week from March 2004 to May 2004. To prepare for aerosol sampling, the aerosol filter holder was first rinsed with distilled water and allowed to dry under the flow bench. Subsequent to drying the filter holder, cleaned forceps were used to place the filter paper in it. The aerosol filter holder was then double-bagged and placed in a case until used.

The filter holder was loaded at Rutgers University Marine Field Station in the first week of sampling. No clean room flow bench was available at the station during that time; therefore, a filter blank was taken by exposing the filter paper for about one minute to the air in the room where the loading was taking place. The filter paper was then folded, labeled, placed in a plastic bag, and frozen. The filter blank was used to account for any existing particles in the air that might skew the results. For the remaining aerosol sampling period, loading of the filter holder took place under a clean room flow bench in the lab at Montclair State University prior to sampling.

When ready for use, gloves were used to place the aerosol filter holder into a plastic box attached to the aerosol sampler. After the aerosol filter holder was secured, the aerosol sampler was started. The sampling date, time, pressure reading, and the weather (i.e., temperature, humidity, and the conditions that day) were recorded. The sampler was run for about 6 to 24 hours. After collecting the sample, the time, pressure reading, and weather conditions were recorded. The sampler was then turned off. All of this information was subsequently entered into a spreadsheet.

Clean forceps were used to remove the sample filter from the holder. The filter paper was folded in half, making sure the corners matched up as close as possible to ensure that the sample was not exposed. The filter paper was then placed in a zipped plastic bag and labeled with a permanent marker, noting the date, sample number, and the type of filter paper used (Whatman 41 or 48). The sample was then placed in the freezer until analysis. The above procedure was repeated for each aerosol sample. A clean-room operation procedure was followed.

4.2. Laboratory Sample Preparation

4.2.1. Precipitation

To prepare precipitation samples for analysis, the frozen samples were first thawed at room temperature. The pH of each sample was then taken with the SevenEasy pH meter (Mettler Toledo, Germany). Each sample was subsequently filtered to remove any particulate matter using a polycarbonate filter of 0.45 μm pore size along with a 250 ml Nalgene filtration system. Before filtration, the 0.45 μm polycarbonate filters were rinsed with distilled water every 20-30 minutes for several hours, and the filtration system was cleaned with 1 N HCl. It was then rinsed thoroughly with distilled water to ensure no contamination would affect the results. Once the sample was filtered, the filtered solution was then poured into two separate, clean-labeled vials: one vial for nitrate (anion) and one for ammonium (cation) analysis, if there was enough sample. The nitrate vials were then refrigerated, and the ammonium vials were frozen until they were ready for analysis. Any excess filtered solution was placed in a clean, labeled bottle and frozen. The used polycarbonate filters were placed in a clean, labeled petri dish and allowed to dry under the flow bench. Once dried, the petri dishes were placed in the freezer (approximately -20°C) for storage. After each filtration, the filtration system and forceps were rinsed with distilled water, a new polycarbonate filter was used, and the above procedure was repeated.

4.2.2. Aerosols

To prepare aerosol samples for analysis, a sample was removed from the freezer. A clean exacto blade was used to cut one-fourth of the filter-paper sample, which was then placed in a clean, labeled bottle. The remainder of the filter paper (three-fourths)

was again folded so that no sample was exposed. It was then placed back in the sampling bag and frozen. A total of 100 ml of distilled water was added to the bottle to leach the sample filter. After the water was added, the bottle was placed in an ultrasonic bath for one hour, making sure the distilled water in the bottles was below the tap-water level of the bath. Three of the aerosol samples were cut in half (the quarters were cut in half) to make duplicates so only 50 ml of distilled water were added to six bottles.

After the ultrasonic bath, the samples were filtered to remove any particulate matter. The same procedure used for the precipitation filtration was employed for filtering the aerosol samples. Rinsed 0.45 μm polycarbonate filters were used with a 250 ml Nalgene filtration system. The filtered solution was split between two clean, labeled vials, one for nitrate and one for ammonium analysis. The nitrate vials were then refrigerated, and the ammonium vials were frozen until they were ready to be analyzed. Any excess filtered solution was placed in a clean, labeled bottle and frozen. The used polycarbonate filters were placed in a clean, labeled petri dish and allowed to dry under the flow bench. Once dried, they were frozen. After each filtration, the filtration system and forceps were rinsed with distilled water, a new polycarbonate filter was used, and the above procedure was repeated.

4.3. Chemical Analysis

4.3.1. Analytical Procedure

The analysis of nitrate and other anions in the prepared precipitation and aerosol samples was conducted in the Atmospheric Chemistry Laboratory at Montclair State University with a Dionex 2500 Ion Chromatograph (IC) (Dionex Corporation). The IC system was equipped with an IonPac AG11-HC 4mm guard column and an IonPac AS18

4mm analytical column for anions such as nitrate. An eluent mixture of 50% w/w sodium hydroxide (NaOH) and distilled water was used to elute nitrate and the other anions at a flow rate of 1 ml min^{-1} . When ready for analysis, the nitrate samples were taken out of the refrigerator and placed at room temperature for about two hours. The samples were then transferred to 5 ml vials specific for the IC and run along with the prepared standards (Figure 6). The remaining sample was placed back in the refrigerator. The amount of nitrate and other anions in the samples was then measured (mg L^{-1}) (Figures 7 and 8). If any of the peaks for the anions were too high based on the standards range, especially for the aerosol samples, the samples were diluted by taking 2 ml of the sample and 2 ml of distilled water until the peaks dropped back within the range of the standards. The IC detection limit for nitrate was determined to be 0.05 mg L^{-1} . This concentration gave a signal three times the standard deviation of the background noise on the IC. Gao (2002) found the detection limit for nitrate to be 0.05 mg L^{-1} when using a Dionex DX-100 IC. The relative standard deviation was also calculated by running one precipitation sample four times on the IC to determine the accuracy of the nitrate measured. The standard deviation was 0.088.

The analyses of ammonium and other cations in the prepared precipitation and aerosol samples were conducted at the Rutgers Pineland Field Station in New Lisbon, New Jersey. The ammonium vials were taken out of the freezer and thawed at room temperature before their analysis at the field station. The field station's IC detection limit for ammonium was 0.05 mg L^{-1} .

4.3.2. Interlaboratory Comparison

Five precipitation samples were also taken to Rutgers Pineland Field Station for anion analysis to conduct an interlaboratory comparison (Table 1). The detection limit for nitrate from the IC at the field station was 0.03 mg L^{-1} . The same standards were used for both analyses at Montclair State and the field station. The anion concentrations obtained at Montclair State's laboratory were consistently higher than the concentrations obtained at Rutgers Pineland Field Station. The average percent difference between the nitrate concentrations from the two laboratories was 14.97%. A paired samples t-test was run for the nitrate concentrations from the two laboratories and the significance value was 0.022, indicating that the results are significantly different. The samples were stored for around two weeks longer at the field station before analysis and may be a contributing factor to the difference in concentrations due to a chemical change in composition over time. Some of the inorganic nitrogen could have been converted into organic nitrogen resulting in lower concentrations; however, this probably accounts for a very small loss. There could also be a difference in results due to the age of each of the laboratory's IC's column and suppressor as well as different standard operating procedures and quality assurance practices established for each laboratory.

5. RESULTS AND DISCUSSION

5.1. Atmospheric Concentrations

5.1.1. Nitrate and Ammonium Concentrations in Precipitation

The results indicate that nitrate concentrations for precipitation are almost always higher than ammonium concentrations (Figure 9). The molar ratios of nitrate to

ammonium in the atmosphere are depicted in Figure 10, with an average ratio of 4.6. These ratios reflect the influence from biological activity in the soil related to nitrification and denitrification. Biological activity is another source of nitrogen but is not an aspect of this research project; these molar ratios are mentioned for possible future applications. Figure 11 shows the distribution of the concentrations for nitrate and ammonium in precipitation. Each box displays the 10th, 25th, 50th, 75th, and 90th percentiles of the concentrations. Any values above the 90th or below the 10th percentiles are shown as open circles. The average nitrate and ammonium concentrations for precipitation samples collected from the Mullica River-Great Bay Estuary in this study are 2.3 mg L⁻¹ and 0.42 mg L⁻¹, respectively, which gives a nitrate-to-ammonium ratio of 5.5. The nitrate and ammonium concentrations in precipitation appear to be significantly correlated with an R² value of 0.74 (Figure 12). This may be due to both species originating from anthropogenic sources and undergoing certain atmospheric reactions such as the one described by Equation 7. More detailed information can be found in Appendix 1.

These results are comparable to other studies conducted along the east coast (Table 2). Gao (2002) also showed that the concentration of ammonium was almost always lower than nitrate concentrations for precipitation samples collected at Barnegat Bay, New Jersey. Gao found that the average nitrate concentration for precipitation was 1.8 mg L⁻¹ and the average ammonium concentration was 0.33 mg L⁻¹, with a nitrate-to-ammonium ratio of 5.5. Along the Connecticut coastline of Long Island Sound, Luo et al. (2002) indicated that nitrate concentrations were higher than ammonium concentrations in precipitation. In their study, the mean nitrate concentration was 0.70

mg L⁻¹, and the mean ammonium concentration was 0.47 mg L⁻¹ (nitrate-to-ammonium ratio: 1.5). The same results were found in the Chesapeake Bay system, with the volume-weighted average concentrations of nitrate and ammonium from wet deposition being 1.3 and 0.24 mg L⁻¹, respectively, giving a nitrate-to-ammonium ratio of 5.4 (Russell et al., 1998). The similar nitrate-to-ammonium ratios in precipitation over coastal southern New Jersey and the Chesapeake Bay may suggest a regional signature of atmospheric nitrogen.

There are certainly slight variations in the results for the above studies. The results are not expected to be exactly the same, and this is because precipitation collection methods varied between studies, with collections being conducted on a daily, weekly, bi-weekly, or event basis for a period ranging from 6 months to 4 years. The equipment used to collect the precipitation also differed. Some studies used an automated sampler with a bucket lined with a Teflon bag or a stainless steel bucket, while other studies, including this one, used plastic funnel reservoir sets in an automatic sampler. Also, the sampling location (whether it was near an urban or rural site), the strength and source of emissions, and the precipitation rate could all affect the amount of nitrate and ammonium deposited onto these coastal waters.

The pH of individual precipitation samples is shown in Figure 13. The monthly precipitation pH values are given in Table 3, ranging from 4.0 to 4.8, with an average value of 4.3, indicating an acidic nature. More detailed information can be found in Appendix 2. These values are fairly close to the precipitation pH measured by Gao (2002) at Barnegat Bay, New Jersey with an average value of 4.5. The cause of this acidity is likely the result of anthropogenic emissions from the combustion of fossil fuels

which release nitrogen oxides and sulfur dioxide into the atmosphere. These gas pollutants are the primary sources for acid deposition because they are later transformed into nitric and sulfuric acids which increase the acidity of precipitation (Seinfeld and Pandis, 1998). When the relationship between pH and nitrate and ammonium concentrations in precipitation was investigated, it was determined that high nitrate and ammonium concentrations were related to low pH values (Figure 14). Acidic rainfall combined with high inorganic nitrogen concentrations could increase primary productivity when compared to more neutral rain (Paerl, 1985).

5.1.2. Nitrate and Ammonium Concentrations in Aerosols

Nitrate concentrations in the aerosol samples also appear to be higher than ammonium concentrations for this region during the spring (Figure 15). The distribution of values for nitrate and ammonium concentrations in aerosols is depicted in Figure 16. The average nitrate and ammonium concentrations for aerosol samples collected from this region were $3.7 \mu\text{g m}^{-3}$ and $1.6 \mu\text{g m}^{-3}$, respectively. More detailed information can be found in Appendix 3. These concentrations are a little higher when compared to other areas along the east coast (Table 4). At Barnegat Bay, New Jersey, Gao (2002) also found ammonium concentrations to be lower than nitrate concentrations for the collected aerosol samples, with average concentrations of $2.0 \pm 0.89 \mu\text{g m}^{-3}$ for nitrate and $0.50 \pm 0.28 \mu\text{g m}^{-3}$ for ammonium. However, at Long Island Sound, the mean aerosol concentration of ammonium was higher than the mean nitrate concentration with values of $1.0 \mu\text{g m}^{-3}$ and $0.18 \mu\text{g m}^{-3}$, respectively. This difference could be the result of an increase in the gas-to-particle conversion of NH_3 to NH_4^+ because of elevated

concentrations of strong acids and water vapor in the atmosphere at this location (Nadim et al., 2001; Luo et al., 2002).

5.2. Atmospheric Deposition

5.2.1. Atmospheric Flux Calculations

Atmospheric flux can be defined as the deposition of nitrogen from the atmosphere to the surface of the water per unit area per unit time (Gao, 1990). Based on the in situ measurements of nitrate and ammonium, the atmospheric flux via wet and dry deposition can be calculated using wet and dry deposition models for the Mullica River-Great Bay Estuary. Wet deposition involves the removal of atmospheric substances within clouds and below the cloud base mainly by precipitation (Pryor and Barthelmie, 2000). The wet deposition flux, F_w , can be calculated by the following equation:

$$F_w = 10 C_r * P \quad (8)$$

where,

C_r = concentration of nitrate or ammonium in precipitation (mg L^{-1})

P = precipitation rate (cm/month)

10 = unit conversion factor

The precipitation rate was determined by using the available meteorological data collected from the United States Geological Survey's (USGS) summary of monthly hydrologic conditions at Atlantic City, New Jersey (Figure 17). There are uncertainties related to the wet deposition flux calculations since the precipitation rates used were not for Rutgers University Marine Field Station (RUMFS) but for Atlantic City, a site located ~14 km south. There was a rain gauge located at RUMFS and the monthly precipitation rates were similar to USGS's values but not exactly the same. Occasionally, there were

malfunctions on the RUMFS's rain gauge which is why the USGS's precipitation rates are used in the calculations. Since precipitation is not evenly distributed over an area, one location might receive more or less precipitation than another. Also, there are uncertainties concerning the nitrate concentrations in precipitation since there was around a 15% difference when an interlaboratory comparison was conducted. Therefore, these concentrations can only serve as a first approximation. There is an uncertainty of $\pm 20\%$ associated with the wet deposition fluxes.

Dry deposition can be defined as the "removal of gaseous and particulate species from the atmosphere without precipitation" (Gao, 1990). It is affected by such factors as wind, the chemical and physical properties of the species, and the nature of the surface. Solubility and reactivity play an additional role in the dry deposition of gaseous species. Molecular diffusion, impaction, and gravitational settling play an additional role in the dry deposition of particles; the dry deposition process depends primarily on the particle size. Diffusion typically transports small particles due to their random motion from constant bombardment. During impaction, particles cannot adjust to the change in the direction of airflow, and their inertia results in their deposition to the surface. Gravitational settling occurs when the gravitational force exceeds the drag force for large particles (Seinfeld and Pandis, 1998; Pryor and Barthelmie, 2000). The atmospheric flux via dry deposition (aerosol), F_d , can be calculated by the following equation:

$$F_d = (2.592 \times 10^4) * C_{air} * V_d \quad (9)$$

where,

C_{air} = concentration of nitrate or ammonium in the air (mg/L)

V_d = dry deposition velocity (cm/s)

$$2.592 \times 10^4 = \text{unit conversion factor}$$

The volume of each aerosol sample was calculated by multiplying the flow rate ($\text{m}^3 \text{min}^{-1}$) with the total sampling time (minutes). The flow rate was determined by using the calibration curve provided by the manufacturer of the aerosol sampler which took into account the pressure (inches H_2O) recorded from the sampler. The sampling volume was then used to calculate the air concentration. The concentration from the IC was converted into the mass per filter, and this mass was then divided by the sampling volume to obtain the air concentration. The dry deposition velocity was derived from the Slinn and Slinn model (Slinn and Slinn, 1980). Since the velocity is related to particle size, different dry deposition velocities were determined for aerosol nitrate and aerosol ammonium: 0.34 cm/s and 0.19 cm/s, respectively. Extensive details for determining these dry deposition velocities can be found in Gao (2002). It is difficult to accurately measure the dry deposition velocity because many factors affect the result, such as meteorological conditions, the properties of the species under study, and transport processes. Consequently, there is an uncertainty of $\pm 50\%$ associated with the abovementioned values for the dry deposition velocities of nitrate and ammonium. Thus, the calculated values can only serve as first approximations (Gao, 2002).

5.2.2. Seasonal Patterns of Atmospheric Nitrogen Deposition

Tables 5 and 6 show the seasonal and monthly values for the wet and dry deposition of nitrate and ammonium, respectively. Total wet deposition (nitrate + ammonium) appears to be highest in the spring for the Mullica River-Great Bay Estuary, with the average rate being $0.42 \text{ g m}^{-2} \text{ month}^{-1}$, which accounts for $\sim 42\%$ of the total wet deposition. However, the summer and winter seasons also had relatively high wet

deposition fluxes, $0.25 \text{ g m}^{-2} \text{ month}^{-1}$ for the summer and $0.21 \text{ g m}^{-2} \text{ month}^{-1}$ for the winter (Figure 18). Precipitation was high in the summer and was above normal during January and February of 2005, which could increase the amount of nitrogen deposited.

Total dry deposition seems to increase from March to May, with $0.026 \text{ g m}^{-2} \text{ month}^{-1}$ for March, $0.040 \text{ g m}^{-2} \text{ month}^{-1}$ for April, and $0.051 \text{ g m}^{-2} \text{ month}^{-1}$ for May, approximately a 20-30% increase per month (Figure 19). This suggests that the formation of nitrate and ammonium in the atmosphere could be promoted by increased air temperature and solar radiation intensity. Many studies have found that atmospherically deposited nitrogen varies seasonally, with the highest concentrations and deposition fluxes occurring during the warmer seasons. Maximum concentrations of wet nitrogen species were highest in the spring and summer in Virginia and North Carolina (Trivette et al, 2001; Whitall et al., 2003). For the Chesapeake Bay, nitrate and ammonium monthly precipitation concentrations and wet deposition fluxes peaked in the spring and early summer. On average, the spring and summer contributed 39 and 28% of the total annual nitrogen deposited to the Chesapeake Bay, while fall and winter only contributed 16 and 17% (Russell, et al., 1998; Sheeder et al., 2002). High concentrations of nitrogen species in aerosols and precipitation, as well as high wet and dry deposition fluxes, occurred during the warm seasons, especially in the summer at Long Island Sound (Luo et al., 2002). At Barnegat Bay, New Jersey, Gao (2002) found the highest values for wet deposition of nitrate and ammonium during the spring and summer. High dry deposition of nitrate and ammonium were also associated with the warmer seasons for this region.

These seasonal patterns could also be the result of a seasonal variation in the emission of nitrogen species into the atmosphere and with removal processes such as precipitation scavenging (Gao, 2002; Sheeder et al., 2002). Ammonium concentrations tend to peak during the warmer seasons because it is the onset of the growing season, and there is an increase in animal excreta emissions. Increases in nitrate concentrations during the warmer seasons, in turn, are possibly due to increased soil or industrial emissions or increased automobile use (Scudlark and Church, 1993; Russell et al., 1998). The direction from which an air mass originates can also play a role in affecting the deposition of nitrogen species, i.e. inland or coastal, agricultural or urban origin (Whitall et al., 2003). For the Mullica River-Great Bay Estuary, there does not appear to be a seasonal precipitation pattern, rather precipitation fluctuates throughout the year (Figure 17). This suggests that other factors, such as the variation in emission source strength and the origin of the air mass, influence the seasonal variation of nitrate and ammonium for this area.

5.2.3. Back Trajectory Analysis

A trajectory is the path of a hypothetical air mass moving in space through time. Air mass trajectory calculations are based on the assumption that this air mass is large enough to retain its identity for at least a few days, and it is a qualitative analysis. Back trajectory analysis is becoming a widely used and accepted approach for tracing backwards in time the path that an air mass followed as it traveled from its origin (Wallace and Hobbs, 1977). Many studies have used back trajectory analysis because it can help to identify air transport patterns and potential sources for such compounds as ammonium, nitrate, reactive nitrogen oxides, black carbon, and dust. This information

can then be used to help explain the variations in atmospheric composition and deposition for the location under study (Gao, 1990; Russell et al., 1998; Boudries et al., 2004; Tong et al., 2005).

A common model used for back trajectory analysis is the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model which was developed by the National Oceanic and Atmospheric Administration's Air Resource Laboratory. For this project, Version 4.7 of the HYSPLIT model was used to calculate and plot back trajectories to illustrate the long-range transport of air masses to the Mullica River-Great Bay Estuary (Draxler and Rolph, 2003). These back trajectories can help to identify possible sources of nitrogen to this region and to determine if the origin of the air masses influences the seasonal variation of nitrogen deposition. The trajectories were calculated by using the HYSPLIT model together with the Eta Data Assimilation System (EDAS) 40 km archived meteorological dataset. The total run time was 48 hours from the date and UTC time selected, and a new trajectory was displayed every 6 hours with starting heights of 500, 200, and 50 meters above ground level. A representative trajectory was then chosen for a high and a low atmospheric nitrogen deposition event.

Figure 20(a) represents a high atmospheric nitrogen deposition event that occurred during the spring of 2004. This air mass trajectory illustrates that the air masses originated inland, particularly from the northwest. Increased amounts of anthropogenic emissions from industries or large urban areas in this region could have delivered a high amount of nitrogen, leading to increased atmospheric nitrogen deposition to the Mullica River-Great Bay Estuary. Figure 20(b) represents a low atmospheric nitrogen deposition event that occurred in the fall of 2004. For this trajectory, the air masses originated from

the northeast and the south, mainly over the Atlantic Ocean, although some also passed over the New England states. The Atlantic Ocean is characterized by low nitrogen emissions, resulting in low concentrations of nitrogen delivered to the Mullica River-Great Bay Estuary (Prospero et al., 1996). These back trajectories suggest that atmospheric nitrogen deposition to the Mullica River-Great Bay Estuary is related to the origin of the air mass; continental origins provide a greater source of nitrogen than marine origins. Also, the origin of the air mass appears to play a role in influencing the seasonal variation of nitrogen species for this area. The high atmospheric nitrogen deposition event which occurred during the spring had an inland origin, while the low atmospheric nitrogen deposition event that occurred during the fall had primarily a marine origin. As mentioned previously, this seasonal variation may also be due to changes in emission source strength.

5.2.4. Annual Atmospheric Nitrogen Deposition

The total wet deposition of nitrate and ammonium to the Mullica River-Great Bay Estuary is $3.2 \text{ g m}^{-2} \text{ month}^{-1}$, and the total dry deposition is $0.47 \text{ g m}^{-2} \text{ month}^{-1}$ (Table 8). Thus, wet deposition, especially of nitrate, appears to be the main contributor of atmospheric nitrogen deposition to the Mullica River-Great Bay Estuary, accounting for 87% of the total deposition. However, this observation only applies to the three months when aerosol samples were collected. If aerosol sampling continued throughout the year, the dry deposition estimate may have been different which could slightly change the proportion of dry deposition in the total deposition estimate. Nevertheless, there is agreement here with other studies conducted within the mid-Atlantic and northeast

regions, where wet deposition was significantly greater than dry deposition (Meyers et al., 2000; Gao, 2002; Sheeder et al., 2002).

Based on the average monthly deposition rates (Table 7), the annual wet deposition flux for nitrate and ammonium are $2.7 \text{ g m}^{-2} \text{ year}^{-1}$ and $0.49 \text{ g m}^{-2} \text{ year}^{-1}$, respectively. The dry deposition flux for nitrate and ammonium in the spring, based on the average monthly deposition rates (Table 6), are $0.095 \text{ g m}^{-2} \text{ month}^{-1}$ and $0.022 \text{ g m}^{-2} \text{ month}^{-1}$, respectively. However, these values only reflect the dry deposition of nitrogen for the spring. Assuming that there is no seasonal change for the remainder of the year, the annual dry deposition is roughly estimated to be $0.38 \text{ g m}^{-2} \text{ year}^{-1}$ for nitrate and $0.087 \text{ g m}^{-2} \text{ year}^{-1}$ for ammonium. There are uncertainties related to these values since the dry deposition was not directly measured for the entire year, and the dry deposition is likely to change with season. Therefore, these estimates may involve certain degrees of uncertainty. The total annual atmospheric deposition flux for nitrate is then $3.1 \text{ g m}^{-2} \text{ year}^{-1}$ and $0.58 \text{ g m}^{-2} \text{ year}^{-1}$ for ammonium to the Mullica River-Great Bay Estuary (Table 8). Therefore, nitrate deposition is the dominant fraction, accounting for ~ 84% of the total inorganic nitrogen deposition to this estuary. More detailed information can be found in Appendices 4 and 5.

The surface area of the Mullica River-Great Bay Estuary is 41.6 km^2 (Kennish et al., 2004). Therefore, the total atmospheric inorganic nitrogen (nitrate and ammonium) directly deposited to this estuary is estimated to be $15 \times 10^7 \text{ g year}^{-1}$. An estimate of the total atmospheric inorganic nitrogen deposited to the Mullica River's watershed is determined to be $5.5 \times 10^9 \text{ g year}^{-1}$, based on the area of the watershed ($1,475 \text{ km}^2$) (Zampella et al., 2001). However, as mentioned previously, not all of this nitrogen will

enter the estuary due to retention, utilization, or denitrification during transport through the watershed. Table 9 compares the nitrogen flux and the total nitrogen deposition to the watershed and water surface of the Mullica River-Great Bay Estuary with other coastal waters in the mid-Atlantic region. All of the studies listed in the table focused on inorganic nitrogen deposition, i.e. nitrate and ammonium. Most of the results are comparable and fall within the same range. There are some differences though depending on the sizes of the waterbodies and watersheds studied. Also, the proximity of the site to the emission sources could affect the deposition. Variations in methodologies to determine the atmospheric nitrogen input, as well as differences in the values used to calculate the nitrogen loading such as the dry deposition velocity, could also cause differences in deposition between study sites. This inorganic nitrogen only represents a portion of the total atmospheric nitrogen deposition because organic nitrogen is likewise considered to be an additional significant component of the total atmospheric nitrogen input.

5.3. Estimate of Atmospheric Organic Nitrogen Deposition

The main focus of this research has been inorganic nitrogen, but previous studies have shown that dissolved organic nitrogen is also an important component because it can increase the total nitrogen input to coastal waters, as well as the estimated total atmospheric nitrogen deposition values that were previously based only on inorganic nitrogen (Cornell et al., 1995; Peierls and Paerl, 1997; Cornell et al., 2003).

Dissolved organic nitrogen can be calculated by subtracting the total dissolved inorganic nitrogen from the total dissolved nitrogen, $DON = TDN - TIN$, or it can be estimated by taking 25% of the total wet nitrogen deposited (Scudlark et al., 1998;

Meyers et al., 2000). In North Carolina, the annual atmospheric dissolved organic nitrogen was ~26% of the total wet atmospheric nitrogen, and at Lewes, Delaware, a site that has been considered to be generally representative of the northeast United States, the annual dissolved organic nitrogen input accounted for 23% of the total nitrogen in precipitation (Peierls and Paerl, 1997; Scudlark et al., 1998). Seitzinger and Styles (unpublished) found that organic nitrogen accounted for 19% of the total wet nitrogen deposition to New Jersey while Gao (unpublished) found that organic nitrogen accounted for 20-30%. Based on this previous research and using the range of 20-30% of the total wet atmospheric nitrogen deposited, dissolved organic nitrogen is estimated to contribute an additional 0.65 to 0.97 g m⁻² year⁻¹ to the Mullica River-Great Bay Estuary.

5.4. Remote Sensing

Periods of high nitrogen deposition can be identified from the calculated atmospheric flux via wet deposition. The runoff from the Mullica River may also contribute to a high nutrient discharge into Great Bay, especially when there is considerable precipitation. High input of nutrients from the atmosphere and from the Mullica River into the estuary may contribute enough nitrogen to induce increased levels of chlorophyll *a*, an indicator of plant biomass. Increased precipitation in coastal North Carolina waters was associated with an increase in chlorophyll *a* concentrations (Paerl et al., 1995). When the monthly runoff from the Mullica River into Great Bay was plotted with the total wet atmospheric deposition, a strong pattern appeared. The peaks for total wet deposition corresponded to the peaks for river runoff (Figure 21). Therefore, an accelerated input of nutrient nitrogen to the estuary by precipitation may promote the

growth of phytoplankton in these coastal waters. The relationship between increased nitrogen input and primary productivity is investigated by using remotely sensed data.

Remote sensing can be defined as the use of electromagnetic radiation to obtain information about the ocean, land, or atmosphere without being in physical contact with the area under study (Martin, 2004). It is becoming a widely used field of science because it can provide global coverage, high repeat rates, and consistent, continuous data for atmospheric and oceanic studies. Oceanic remote sensing variables include sea surface temperature, winds, waves, salinity, and ocean color. Ocean color is useful in determining biooptical properties of the ocean, such as the presence and concentration of phytoplankton, sediments, and dissolved organic matter (Shen et al., 2001). Oceanic waters can be divided into two categories based on their optical properties: Case 1 and Case 2 waters. Case 1 waters are usually located in the open ocean and are waters for which phytoplankton and their associated materials (such as debris, heterotrophic organisms and bacteria, excreted organic matter) control optical properties. The optical properties for Case 2 waters are dominated by inorganic suspended matter, organic particles, and colored dissolved organic matter as a result of river runoff and anthropogenic activities. Case 2 waters are waters not classified as Case 1 and are typically coastal waters or inland seas (Morel and Prieur, 1977). The Mullica River-Great Bay Estuary would be classified as Case 2 water.

When focusing on primary productivity, remotely sensed ocean color data is used to derive chlorophyll concentrations (Martin, 2004). The remotely sensed ocean color data for this project was obtained from the Moderate Resolution Imaging Spectroradiometer (MODIS), which is aboard the Aqua (EOS PM) satellite launched by

NASA in 2002 (*MODIS*, 2005). It is a cross-track scanner, meaning that this instrument scans at right angles to the satellite's path, and has a swath width of 2,300 km. MODIS also provides global coverage with a revisit time of 1-2 days. One of the primary objectives of MODIS is to observe ocean color and to provide data products that include chlorophyll *a* concentrations (Cracknell et al., 2001). MODIS uses spectral bands 8 through 16 for ocean color observations, which cover the wavelengths from 412 nm (visible light) to 865 nm (near infrared) (Martin, 2004).

In this study, 8-day interval chlorophyll *a* data are processed for the same time period that the atmospheric nitrogen is measured for the spring of 2004, when total atmospheric nitrogen deposition is at its highest (Figure 22 a-g). Quantitative analysis of the remotely sensed images is then used to characterize the relationship between the atmospheric nitrogen input and chlorophyll *a* concentrations for the Mullica River-Great Bay Estuary (Figure 23). Wet deposition was used in this figure instead of total deposition because it contributes the majority of atmospheric nitrogen to this region. Chlorophyll *a* concentrations appear to increase in response to increased atmospheric wet deposition. The phytoplankton may not respond immediately to this input which is why a lag time is seen. When wet deposition fluxes decreased, chlorophyll *a* concentrations eventually decreased as well. Figure 22 (d) shows a high chlorophyll *a* concentration of 8.0 mg m^{-3} during the time period of March 15 to March 22, 2004 in response to an increase in atmospheric wet deposition ($0.84 \text{ g m}^{-2} \text{ month}^{-1}$) around two weeks before. Figure 22 (f) shows a lower chlorophyll *a* concentration of 4.0 mg m^{-3} as a result of a steady decline in atmospheric wet deposition after the time period of March 22 to March 29, 2004. However, other sources of nitrogen, such as runoff from the Mullica River,

may also influence chlorophyll *a* concentrations. The nutrients in the runoff may not be immediately available for use due to transport processes that take place before reaching the estuary so an increase in chlorophyll *a* concentration may not be seen right away after a precipitation event. Overall, the chlorophyll *a* concentrations for the spring ranged from 4.0 to 8.0 mg m⁻³. Clark and Kremer (2004) state that chlorophyll *a* concentrations between 10-30 mg m⁻³ may be considered algal blooms. The Mullica River-Great Bay Estuary appears to still have relatively pristine waters, at least during the spring when the highest deposition fluxes occur, although the chlorophyll *a* concentrations did increase following high wet deposition fluxes of atmospheric nitrogen.

6. CONCLUSIONS

This project was the first to quantify the atmospheric nitrogen input for the Mullica River-Great Bay Estuary. The average concentration of nitrate and ammonium in the precipitation samples are 2.3 mg m⁻³ and 0.42 mg m⁻³, respectively. The nitrate-to-ammonium ratio in precipitation is 5.5, similar to the one obtained in the Chesapeake Bay. This may suggest a regional signature of atmospheric inorganic nitrogen. The average concentration of nitrate in the aerosol samples is 3.7 µg m⁻³ and 1.6 µg m⁻³ for ammonium in the spring. Nitrate concentrations were higher than ammonium concentrations for both the precipitation and aerosol samples. Atmospheric deposition fluxes were then calculated based on wet and dry deposition models and the concentration data. Based on an annual period of sampling, the average wet deposition fluxes for nitrate and ammonium are determined to be 0.21 g m⁻² month⁻¹ and 0.040 g m⁻² month⁻¹, respectively, while the average dry deposition fluxes for nitrate and ammonium

are determined to be $0.035 \text{ g m}^{-2} \text{ month}^{-1}$ and $0.0080 \text{ g m}^{-2} \text{ month}^{-1}$, respectively, based on a spring period of sampling. Total dry deposition seems to increase approximately 20-30% per month in the spring, suggesting that atmospheric nitrate and ammonium formation could be promoted by increased air temperature and solar radiation intensity. Atmospheric nitrogen wet deposition appears to vary with season with the highest fluxes occurring during the spring, with an average value of $0.42 \text{ g m}^{-2} \text{ month}^{-1}$, accounting for ~42% of the total annual wet deposition. This seasonal deposition could possibly be influenced by the variation in emission source strength and the origin of the air mass. Back trajectory analysis illustrated that high atmospheric nitrogen deposition events during the spring are associated with air masses originating inland, particularly from the northwest, increasing nitrogen emissions due to industries and urban areas in that region. During the fall when low atmospheric nitrogen deposition events took place, the air masses had a marine origin, which is characterized by low nitrogen emissions.

Overall, wet deposition appears to be the main contributor to atmospheric nitrogen deposition for the Mullica River-Great Bay Estuary, accounting for 87% of the total deposition. The total annual atmospheric deposition flux for nitrate is $3.1 \text{ g m}^{-2} \text{ year}^{-1}$ and $0.58 \text{ g m}^{-2} \text{ year}^{-1}$ for ammonium to the Mullica River-Great Bay Estuary. Assuming that there is no seasonal change for the remainder of the year, the annual dry deposition fluxes for nitrate and ammonium are roughly estimated. As stated previously, these values can only serve as first approximations. Nitrate deposition is the dominant source of N, accounting for ~84% of the total inorganic nitrogen deposition to the Mullica River-Great Bay Estuary. Based on the total annual atmospheric deposition fluxes for nitrate and ammonium, the total atmospheric inorganic nitrogen directly

deposited to this estuary and to the Mullica River watershed is then estimated to be $15 \times 10^7 \text{ g year}^{-1}$ and $5.5 \times 10^9 \text{ g year}^{-1}$, respectively. Applying a previous result that dissolved organic nitrogen accounts for ~ 20-30% of the total wet nitrogen deposition, dissolved organic nitrogen is estimated to contribute 0.65 to $0.97 \text{ g m}^{-2} \text{ year}^{-1}$ to the Mullica River-Great Bay Estuary.

The remotely sensed ocean color data demonstrates that atmospheric nitrogen deposition does influence chlorophyll *a* concentrations. When wet deposition is high ($0.84 \text{ g m}^{-2} \text{ month}^{-1}$), phytoplankton and macroalgae eventually respond by increasing their biomass and therefore, chlorophyll *a* concentrations increase (8.0 mg m^{-3}). When wet deposition decreases ($0.12 \text{ g m}^{-2} \text{ month}^{-1}$), so does plant biomass and chlorophyll *a* (4.0 mg m^{-3}). However, the chlorophyll *a* concentrations never exceeded 8.0 mg m^{-3} for the spring of 2004, indicating that the Mullica River-Great Bay Estuary still has relatively pristine waters even when atmospheric nitrogen deposition is high.

Now that the atmospheric nitrogen input is known for this estuary, an accurate nutrient budget can be produced when combined with data from other sources (i.e. water column data) to assess ecosystem function and condition for coastal management programs. It will be important to continue monitoring this estuary because the Mullica River-Great Bay Estuary is not immune to the threat of increasing anthropogenic alterations in the future. Atmospheric nitrogen deposition cannot be ignored when developing coastal management plans. Reducing atmospheric nitrogen deposition rates in the future will be important for improving the water quality of our coastal and estuarine waters.

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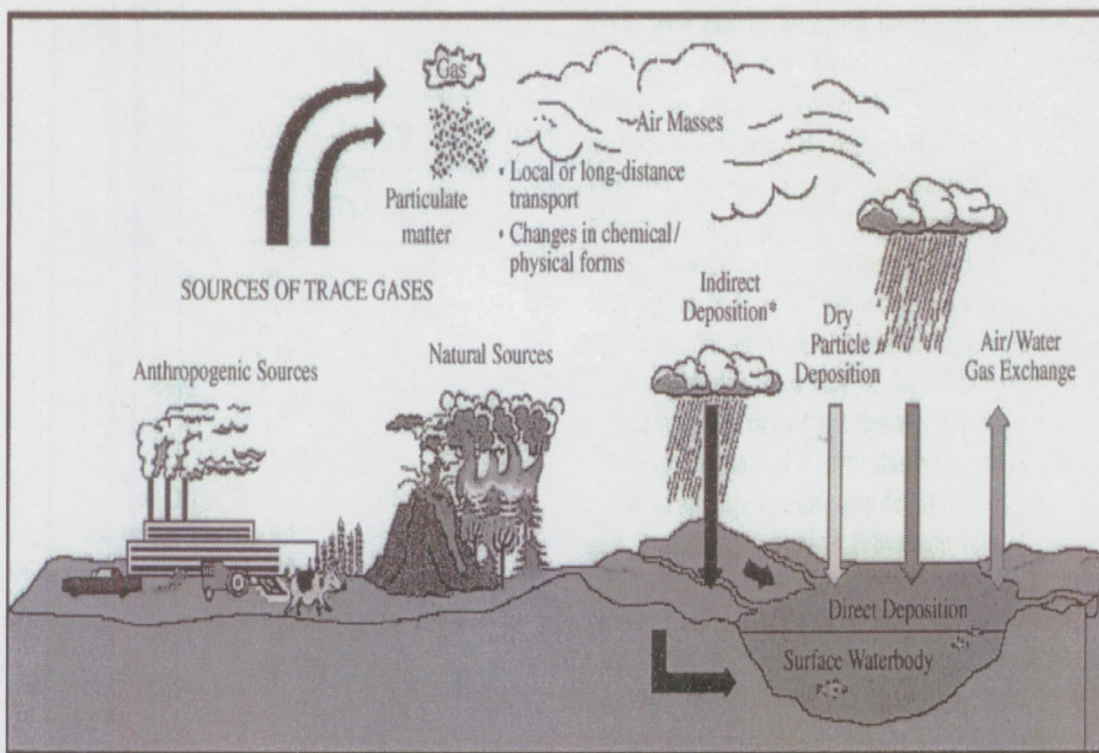
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* Indirect deposition is direct deposition to land followed by runoff or seepage through groundwater to a surface waterbody.

Figure 1. Illustration showing nitrogen sources and transport processes affecting coastal water bodies (Aneja et al., 2001).

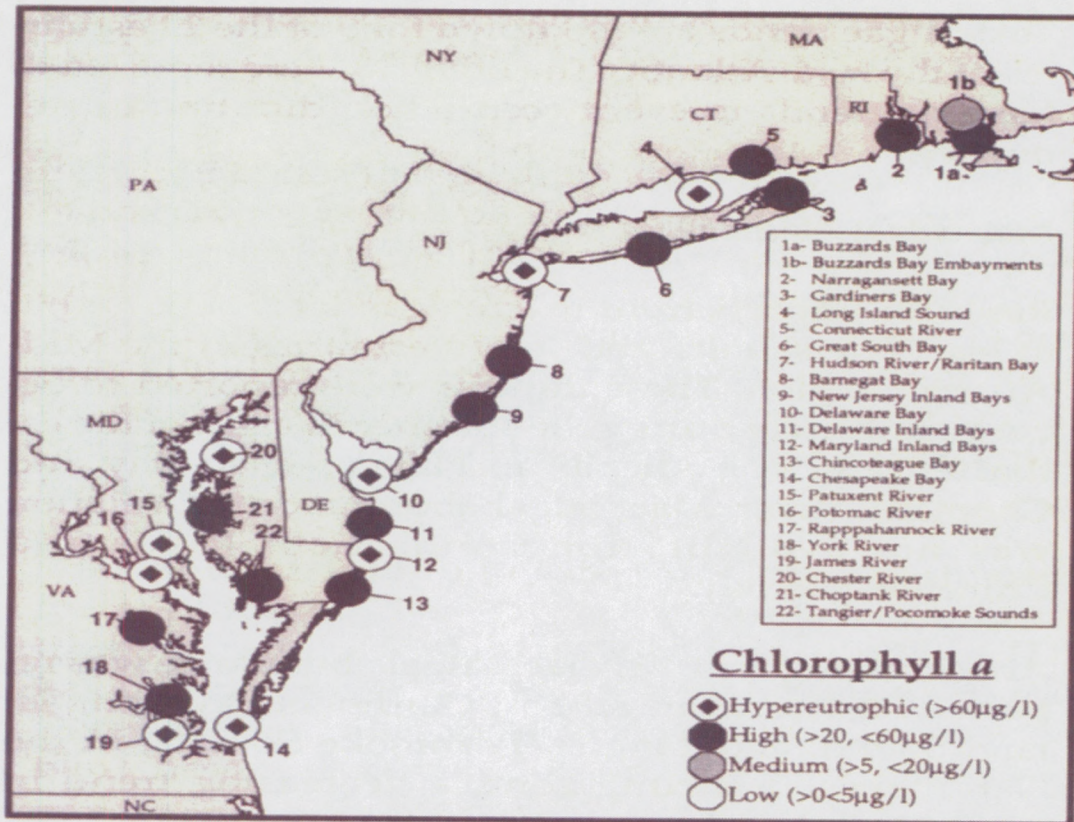


Figure 2. Chlorophyll *a* concentrations recorded by NOAA's Eutrophication Survey for the mid-Atlantic region (NOAA, 1997).

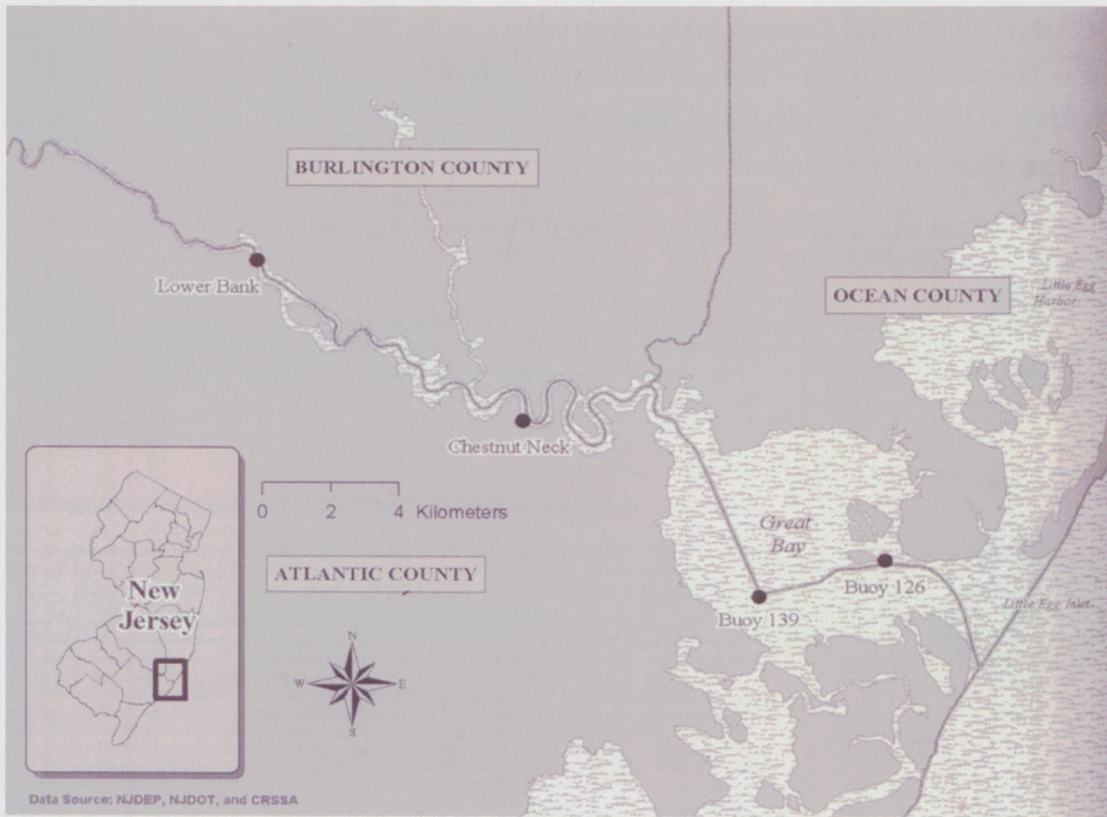


Figure 3. Map of the Mullica River-Great Bay Estuary displaying system-wide monitoring sites (closed circles) of the Jacques Cousteau National Estuarine Research Reserve. Inset shows location of the estuary with respect to the state of New Jersey (Kennish et al., 2004).



Figure 4. Illustration of the Mullica River-Great Bay watershed depicting the major river basins which drain an area of 1,475 km² (New Jersey Department of Environmental Protection, 2004).

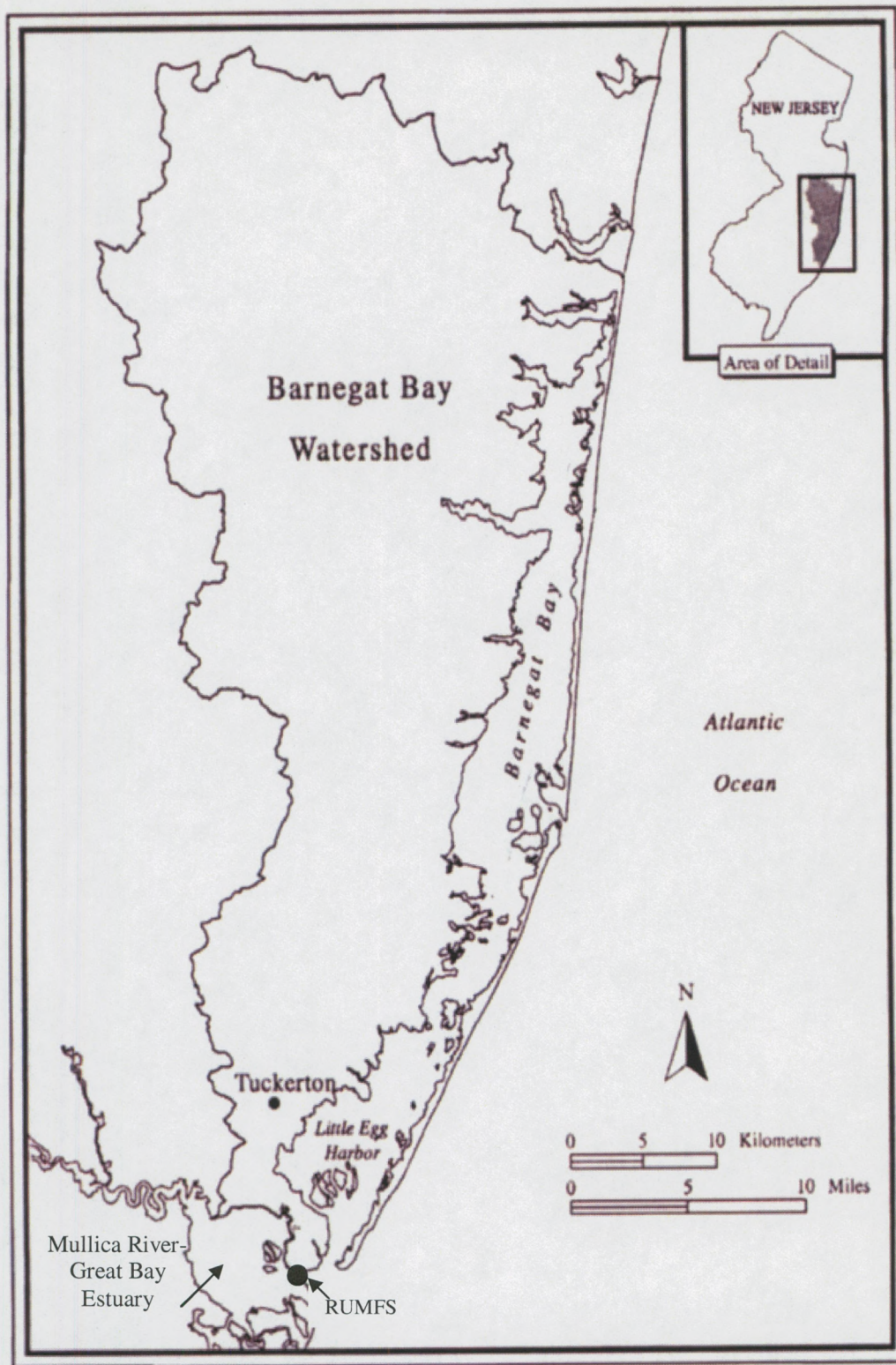


Figure 5. Map of the study area showing the site of atmospheric sampling at the Rutgers University Marine Field Station (RUMFS) (Gao, 2002).

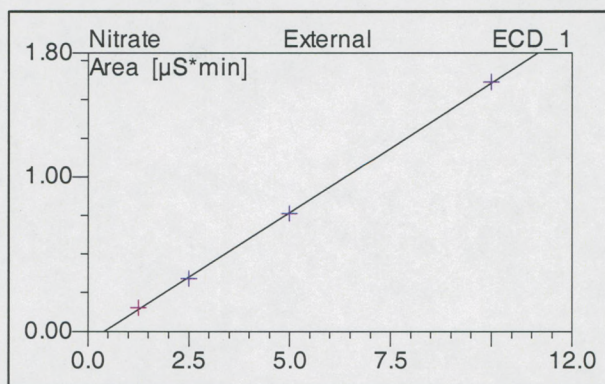
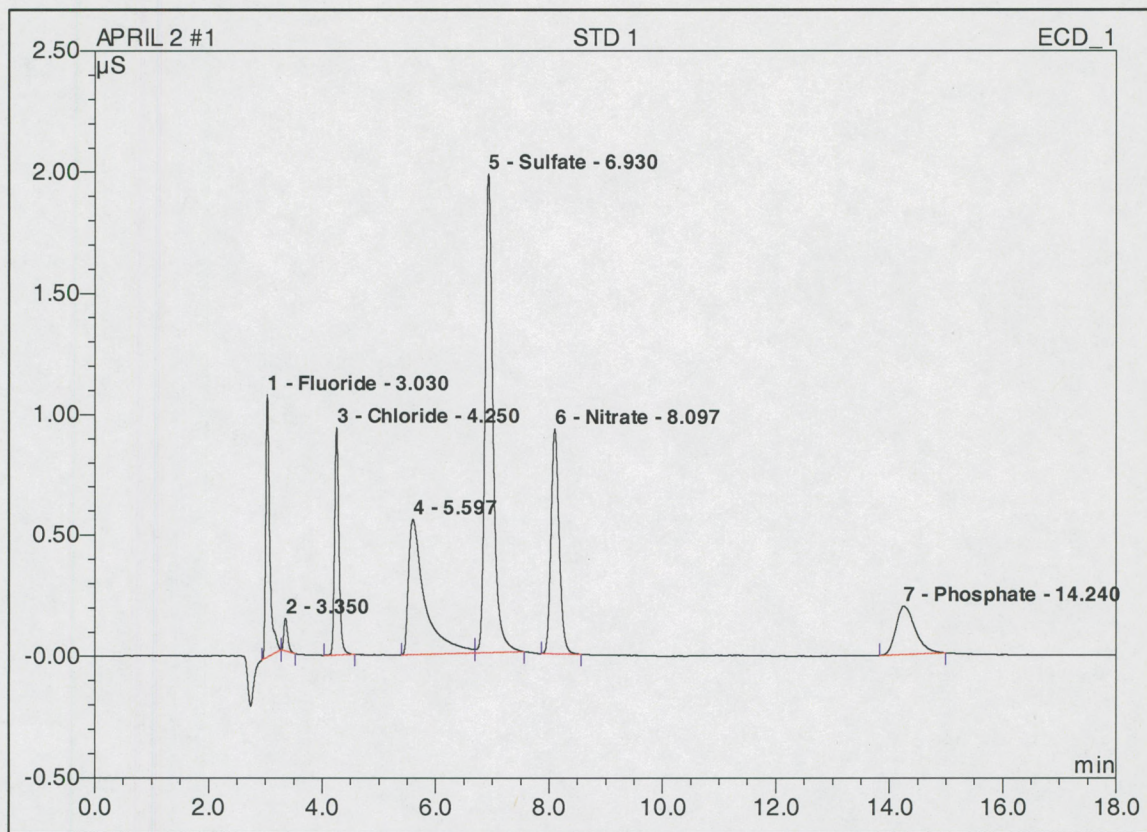
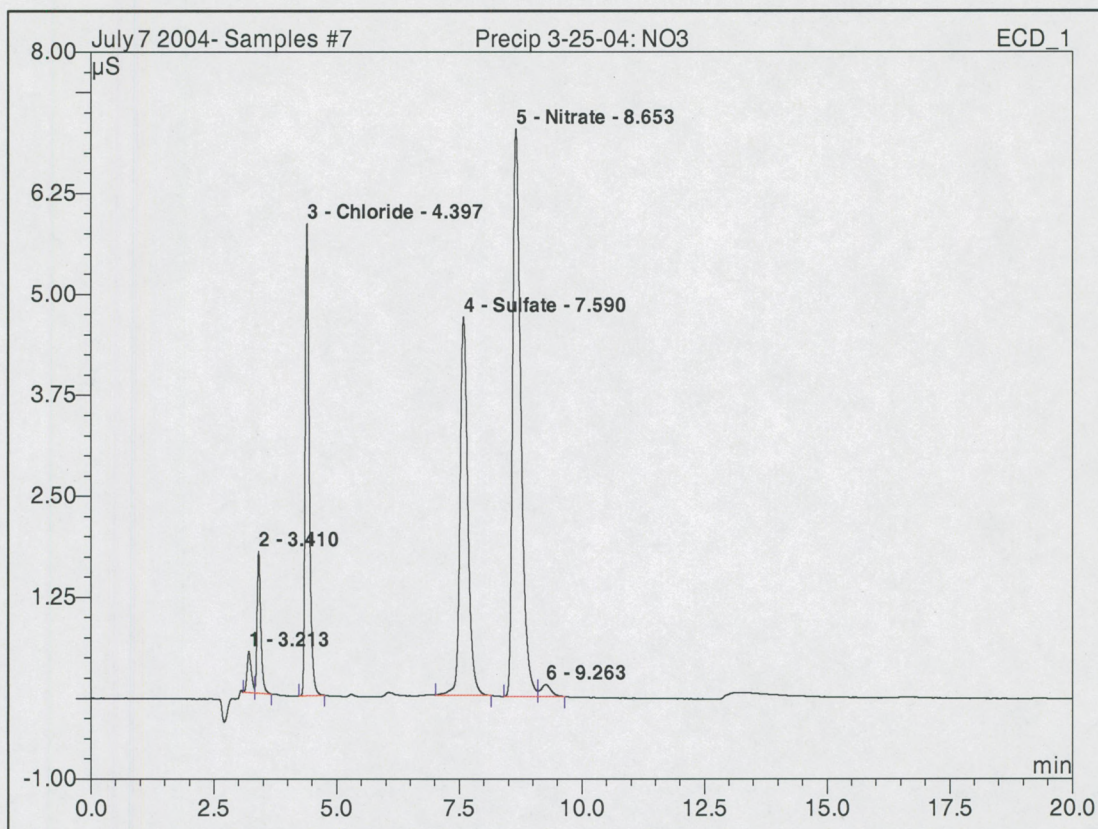
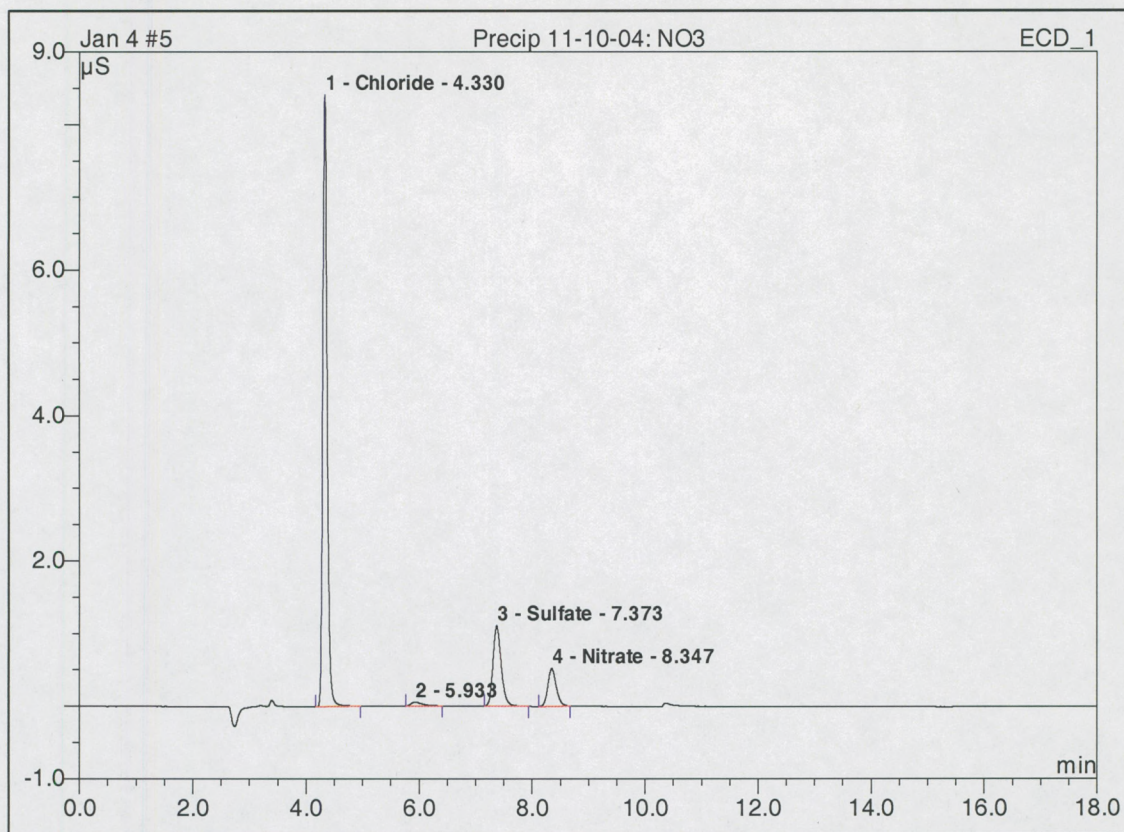


Figure 6. Diagram displaying the ion species (fluoride, chloride, sulfate, nitrate, and phosphate) in the standards used for analysis on the Ion Chromatograph. The figure below shows the regression line for nitrate in standards 1 through 4.



| No. | Ret.Time min | Peak Name | Height μS | Area μS*min | Rel.Area % | Amount | Type |
|---------------|-----------------|-----------|--------------|----------------|---------------|--------|------|
| 1 | 3.21 | n.a. | 0.512 | 0.051 | 1.67 | n.a. | BM |
| 2 | 3.41 | n.a. | 1.754 | 0.153 | 5.00 | n.a. | MB |
| 3 | 4.40 | Chloride | 5.842 | 0.571 | 18.65 | 1.937 | BMB |
| 4 | 7.59 | Sulfate | 4.685 | 0.871 | 28.43 | 3.988 | BMB |
| 5 | 8.65 | Nitrate | 7.032 | 1.379 | 45.03 | 8.455 | BM |
| 6 | 9.26 | n.a. | 0.152 | 0.038 | 1.23 | n.a. | MB |
| Total: | | | 19.978 | 3.063 | 100.00 | 14.381 | |

Figure 7. Peak heights and retention times of the anions detected in a spring precipitation sample analyzed on the Ion Chromatograph. The table also provides pertinent information from the analysis, especially the amount (mg L^{-1}) of each anion species.



| No. | Ret.Time min | Peak Name | Height μS | Area μS*min | Rel.Area % | Amount | Type |
|---------------|-----------------|-----------|--------------|----------------|---------------|--------|------|
| 1 | 4.33 | Chloride | 8.421 | 0.758 | 72.31 | 2.618 | BMB |
| 2 | 5.93 | n.a. | 0.055 | 0.013 | 1.27 | n.a. | BMB |
| 3 | 7.37 | Sulfate | 1.107 | 0.187 | 17.83 | 1.255 | BMB |
| 4 | 8.35 | Nitrate | 0.520 | 0.090 | 8.59 | 0.929 | BMB |
| Total: | | | 10.103 | 1.049 | 100.00 | 4.802 | |

Figure 8. Peak heights and retention times of the anions detected in a fall precipitation sample analyzed on the Ion Chromatograph. The table also provides important information from the analysis, especially the amount (mg L^{-1}) of each anion species.

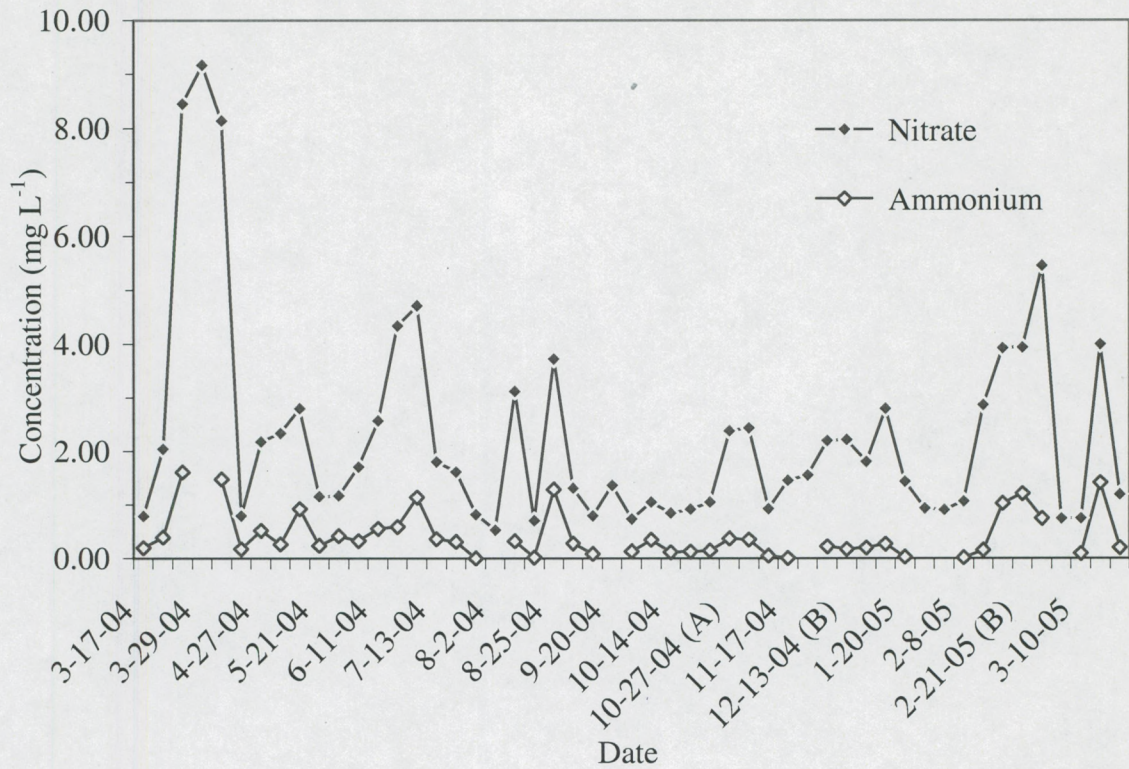


Figure 9. Concentrations of nitrate and ammonium in precipitation samples collected at RUMFS from March 2004 to March 2005. (A) and (B) indicate that duplicate samples were taken for a precipitation event. A missing value indicates that ammonium was not detected for that sample.

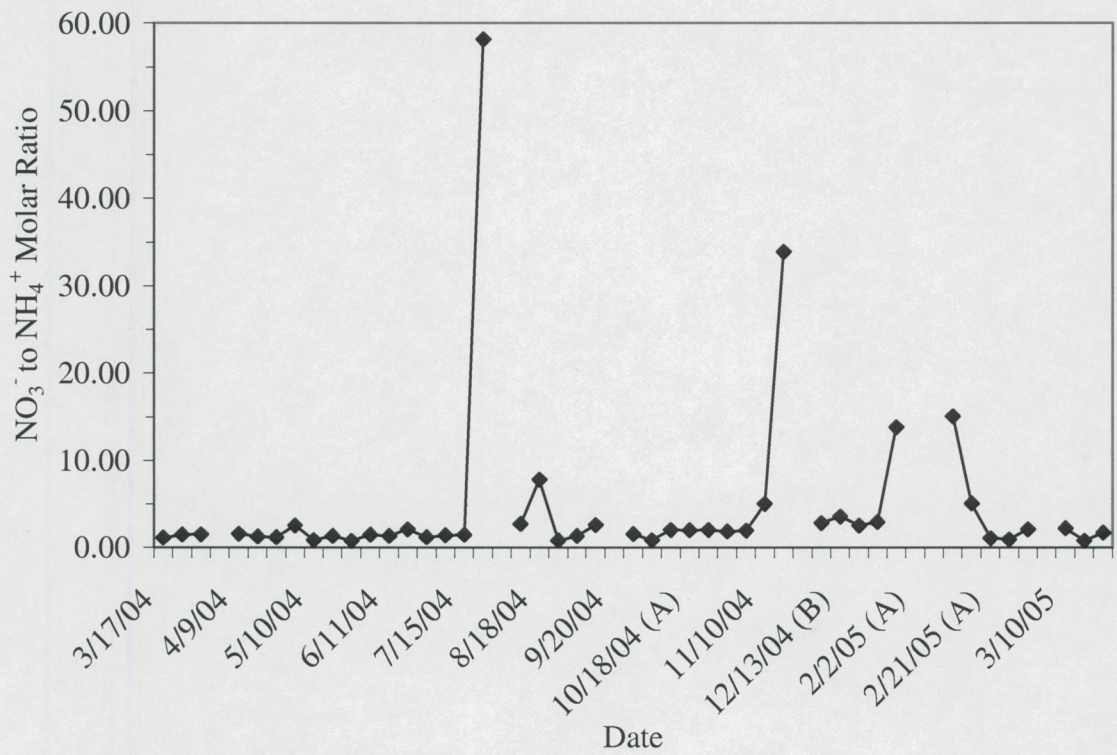


Figure 10. Nitrate to ammonium molar ratios in precipitation samples collected at RUMFS from March 2004 to March 2005. (A) and (B) indicate that duplicate samples were taken for a precipitation event. A missing value indicates that ammonium was not detected for that sample.

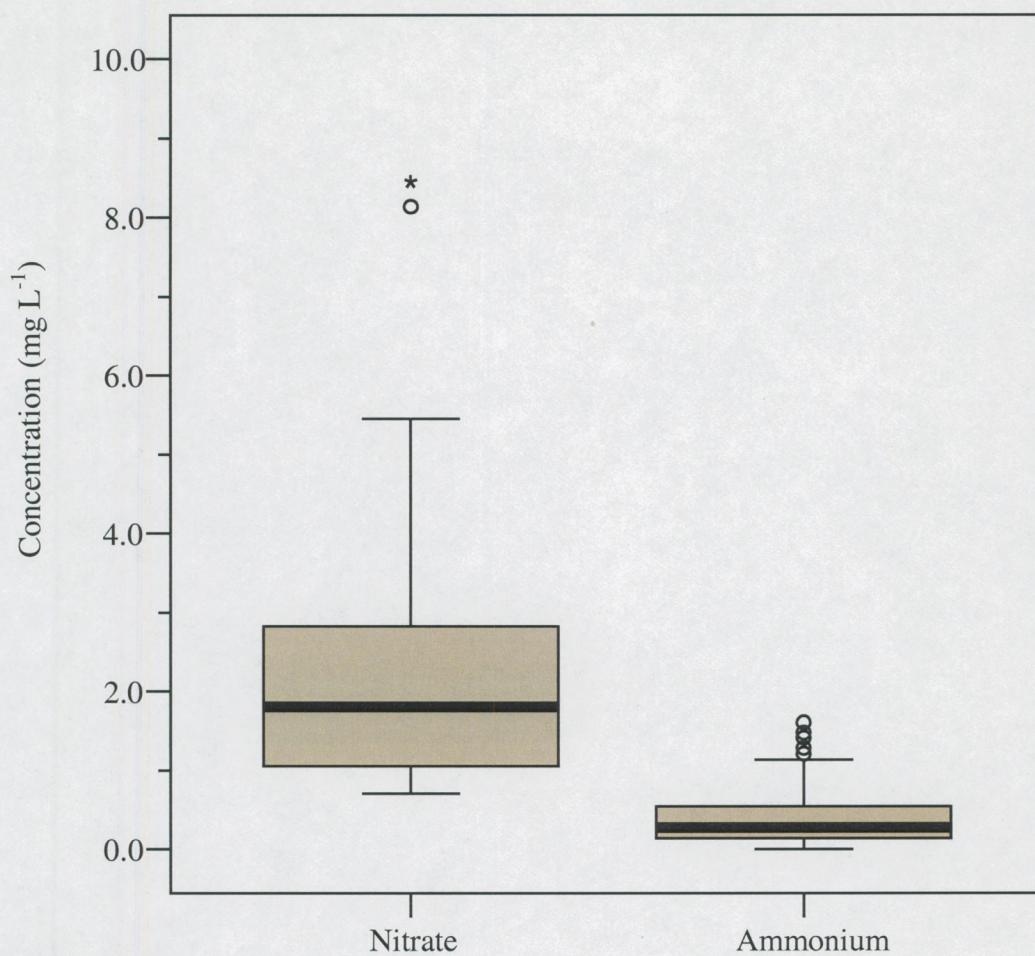


Figure 11. Box plot displaying the 10th, 25th, 50th, 75th, and 90th percentiles for nitrate and ammonium concentrations for precipitation samples. Any values above the 90th or below the 10th percentiles are shown as open circles.

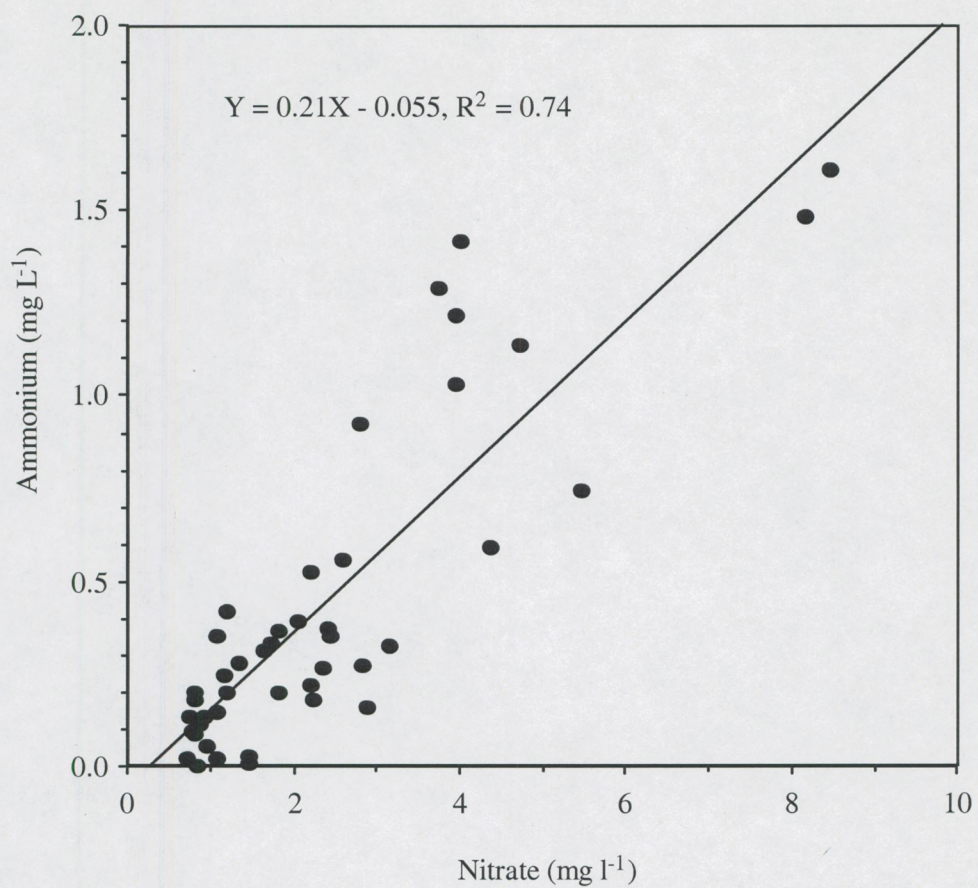


Figure 12. Nitrate and ammonium concentration correlation for precipitation samples collected from March 2004 to March 2005.

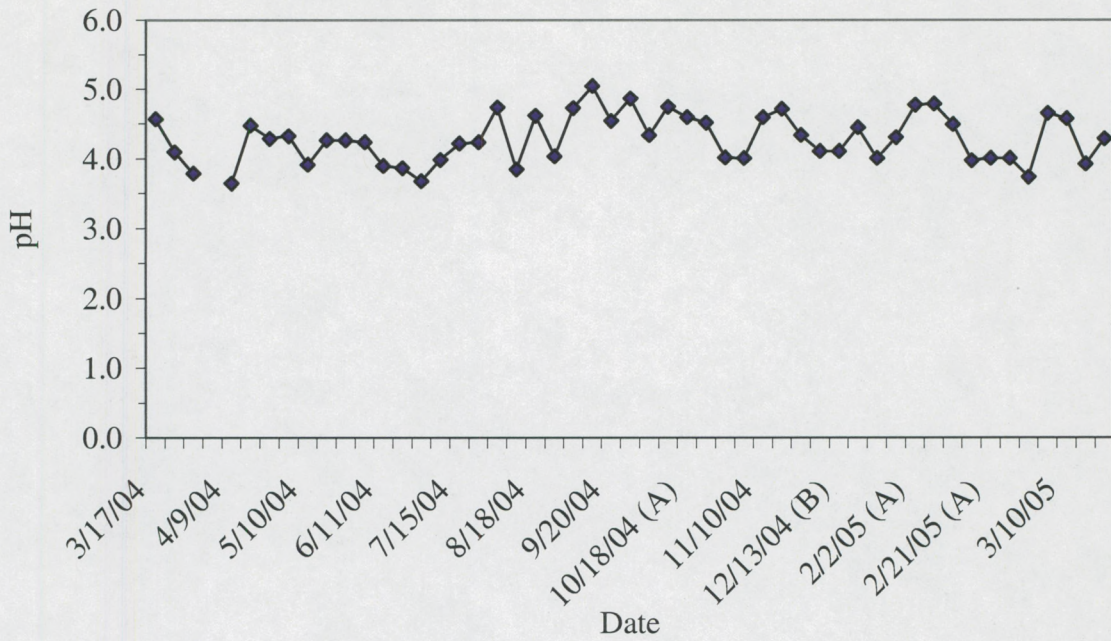


Figure 13. pH in precipitation samples collected at RUMFS from March 2004 to March 2005. (A) and (B) indicate that duplicate samples were taken for a precipitation event.

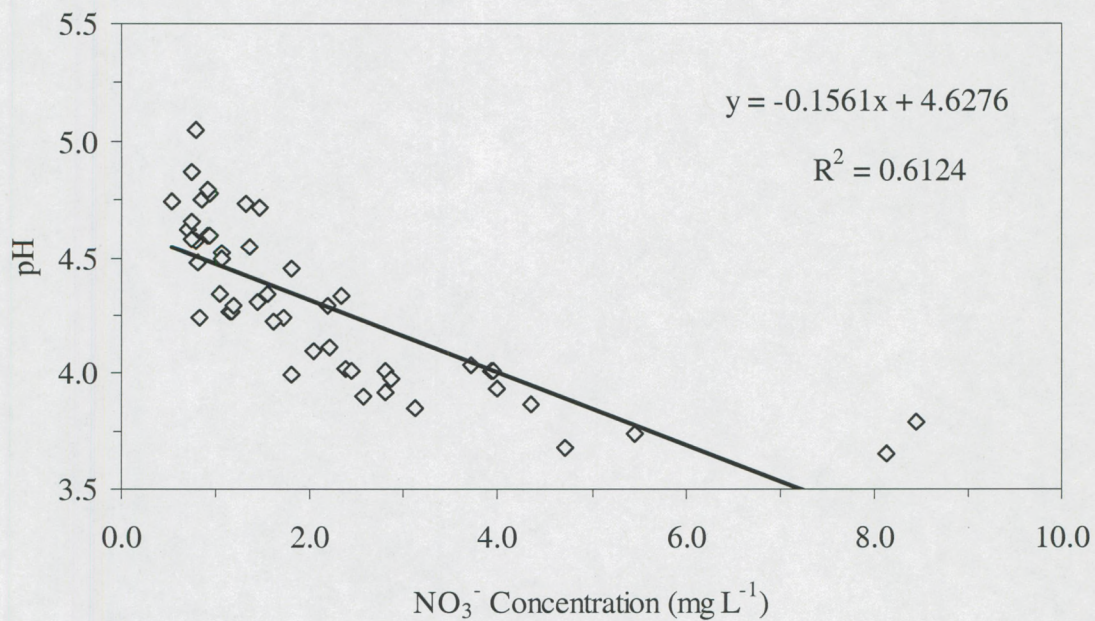
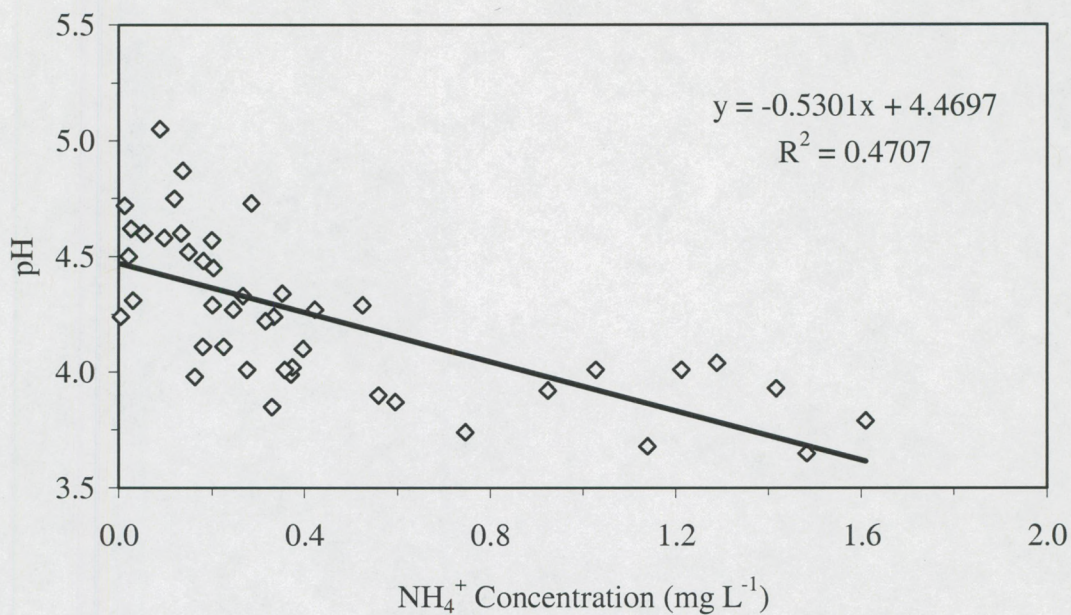


Figure 14. Relationship between pH and nitrate and ammonium concentrations in precipitation (March 2004 to March 2005).

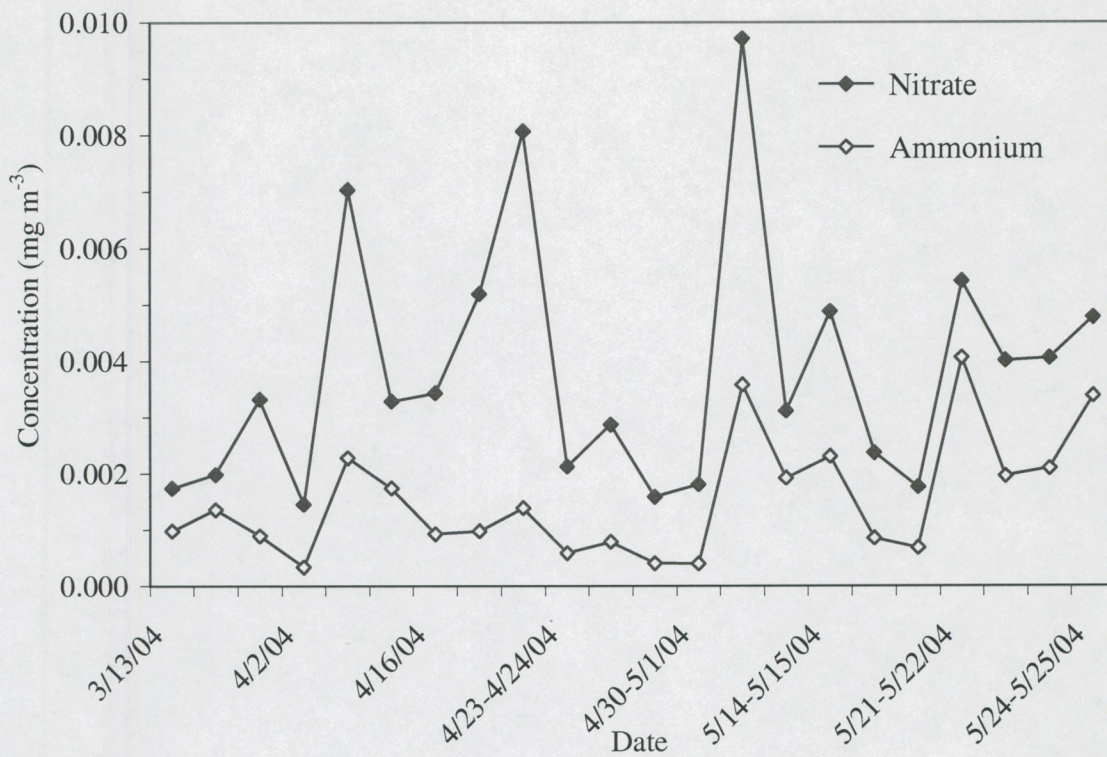


Figure 15. Concentrations of aerosol nitrate and ammonium for samples collected at RUMFS from March to May 2004.

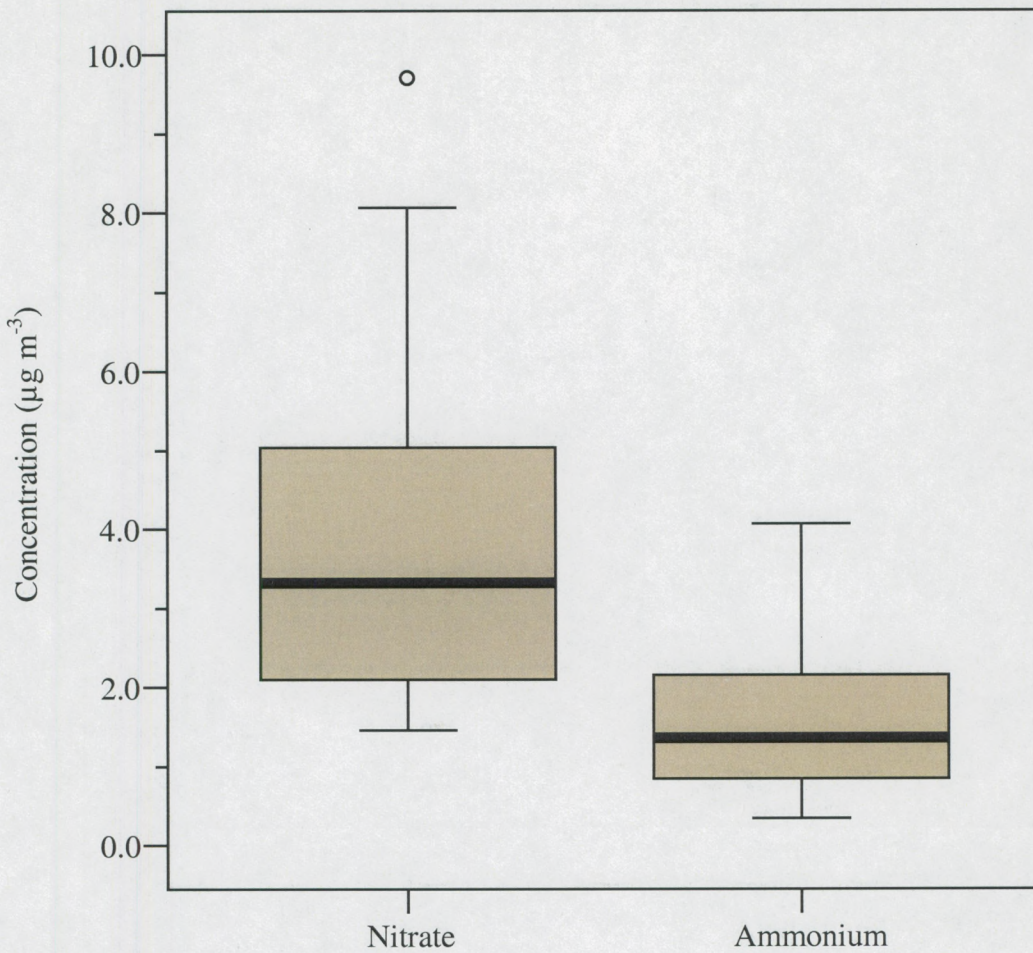


Figure 16. Box plot displaying the 10th, 25th, 50th, 75th, and 90th percentiles for nitrate and ammonium concentrations for aerosol samples. Any values above the 90th or below the 10th percentiles are shown as open circles.

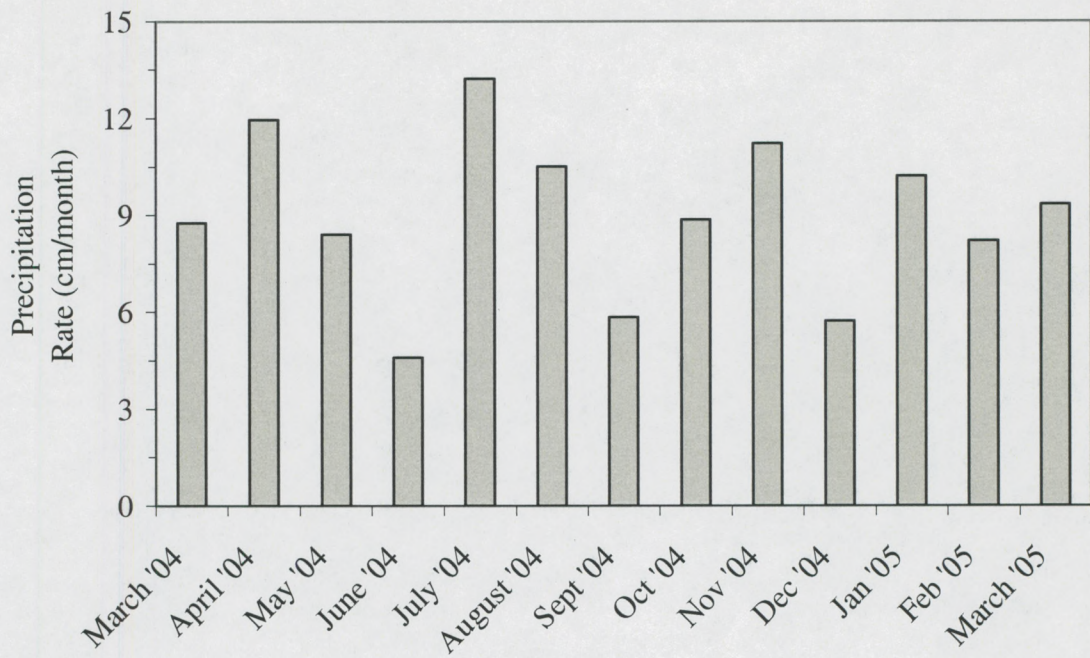


Figure 17. Monthly precipitation rate at the RUMFS site for the March 2004 to March 2005 sampling period.

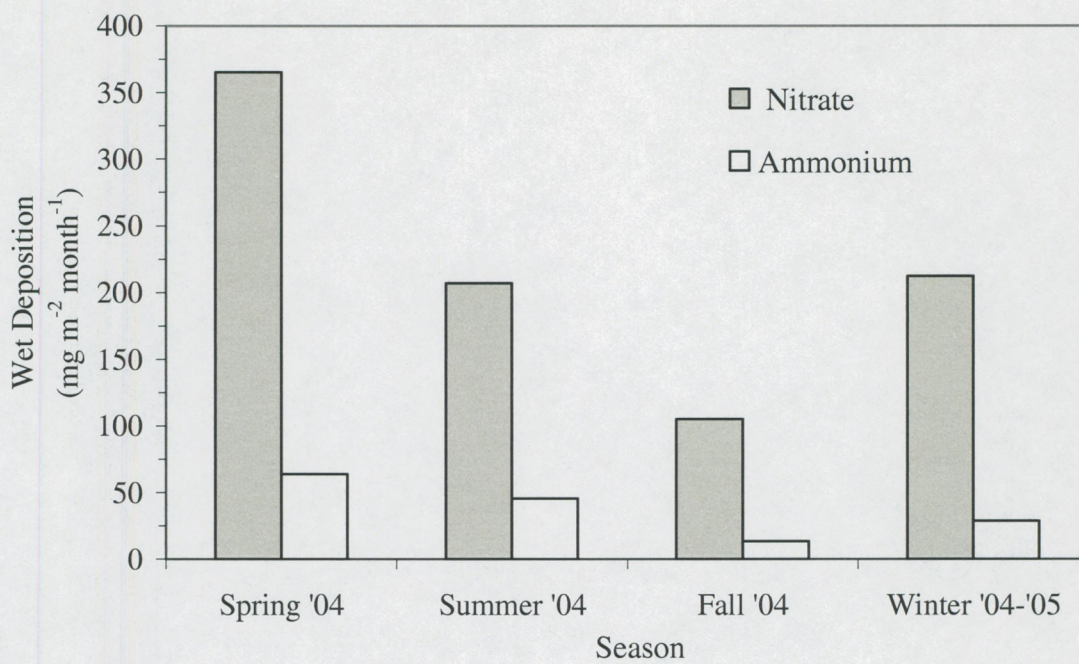


Figure 18. Seasonal wet deposition of nitrate and ammonium at the RUMFS site from March 2004 to March 2005.

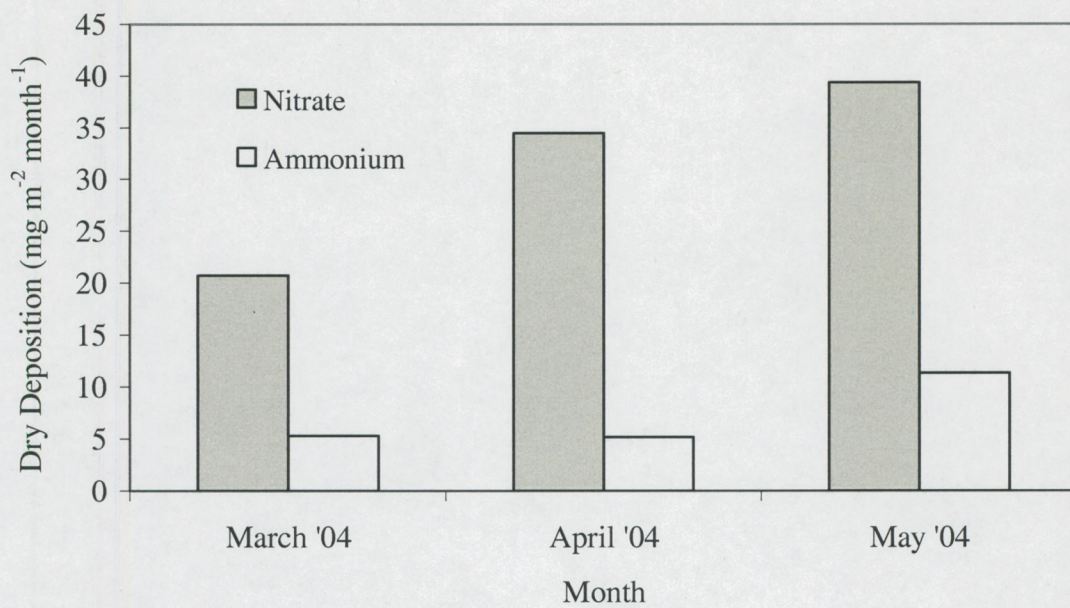


Figure 19. Monthly dry deposition of nitrate and ammonium for the spring of 2004 at the RUMFS site.

Backward trajectories ending at 12 UTC 09 Apr 04
EDAS Meteorological Data

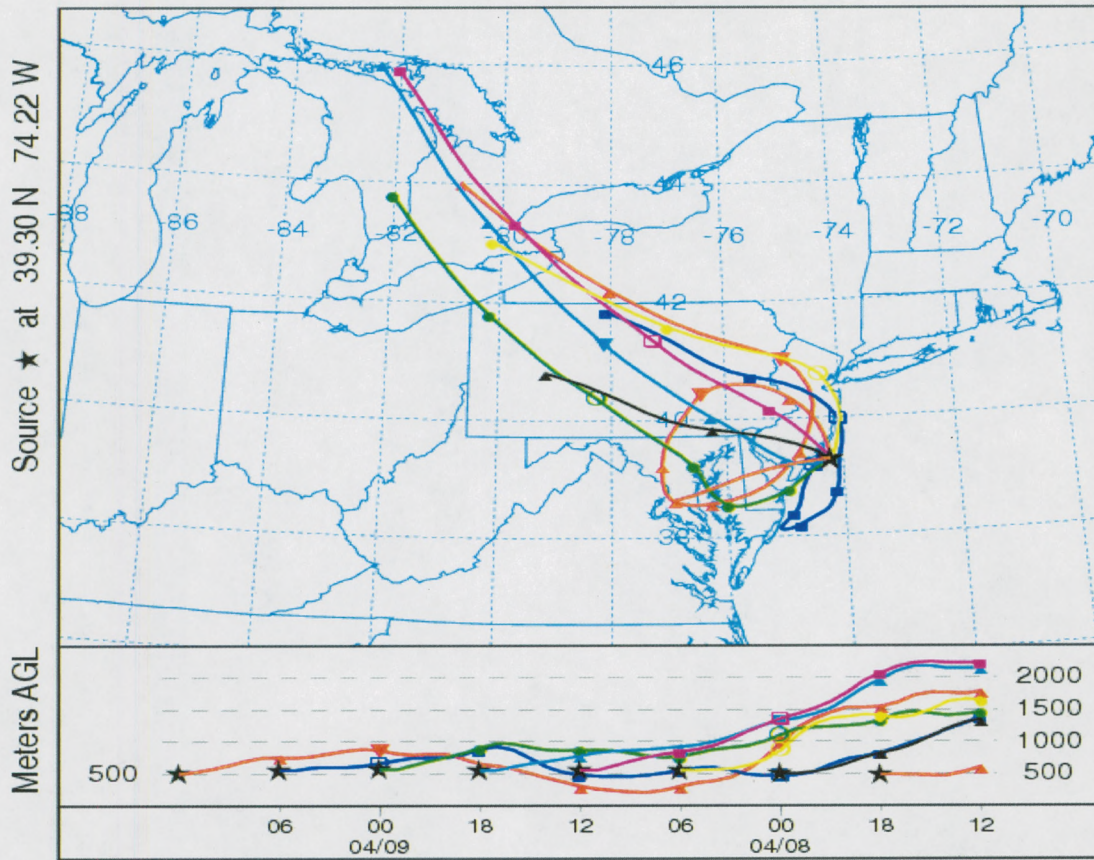


Figure 20(a). Back trajectory analysis for a high nitrogen deposition event occurring in the spring.

Backward trajectories ending at 12 UTC 30 Sep 04
EDAS Meteorological Data

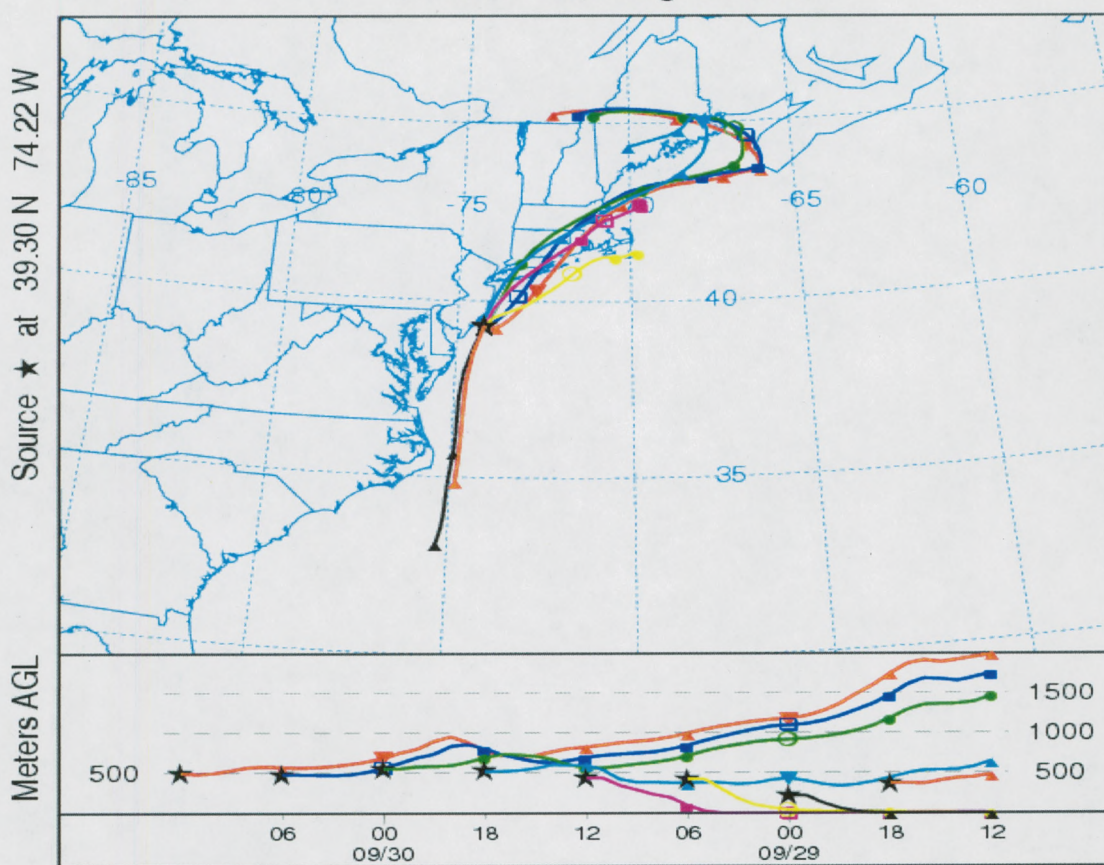


Figure 20(b). Back trajectory analysis for a low nitrogen deposition event occurring in the fall.

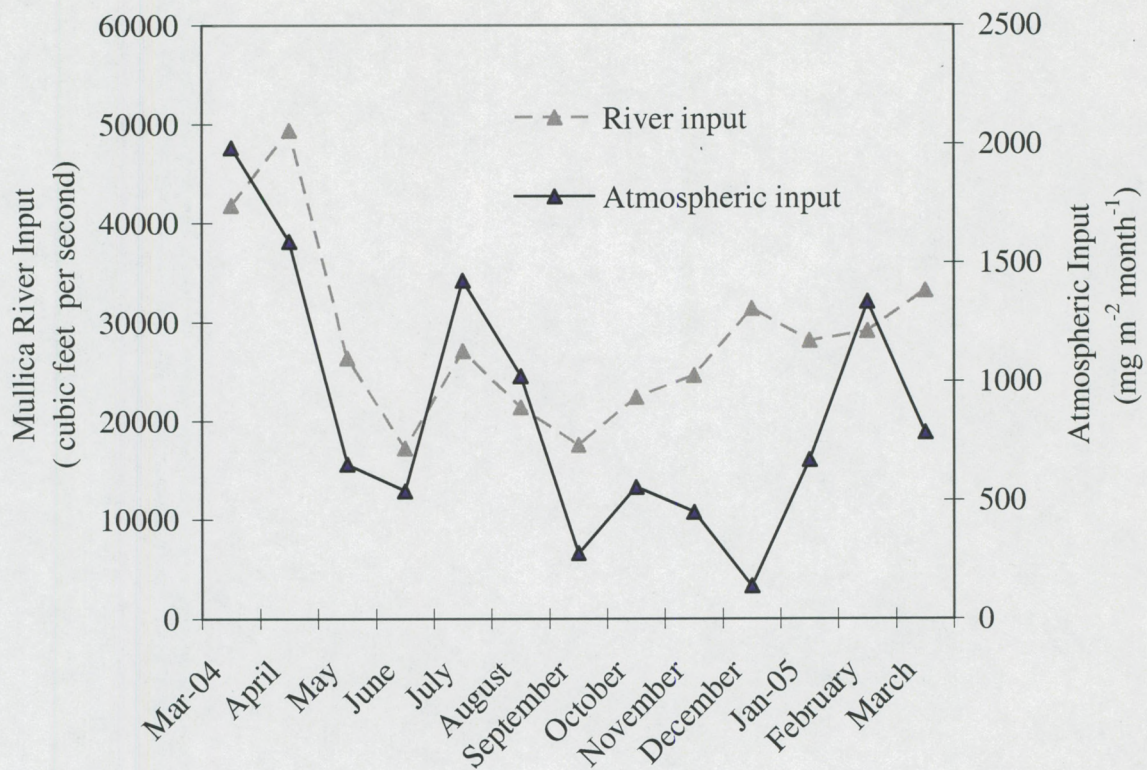
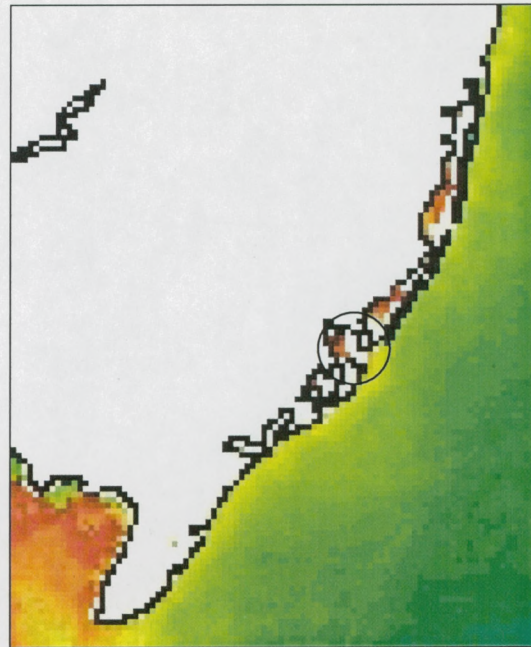
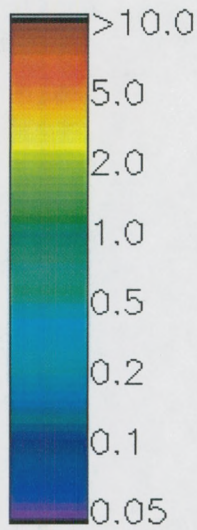
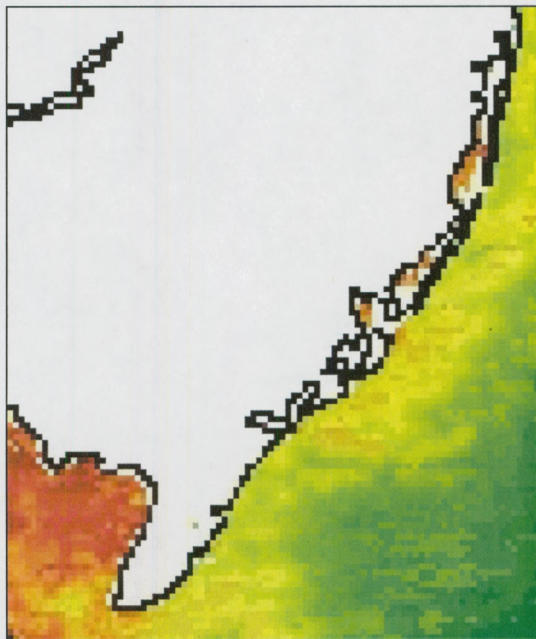


Figure 21. Nutrient input from atmospheric wet deposition and runoff at the mouth of the Mullica River to the Mullica River-Great Bay Estuary from March 2004 to March 2005.

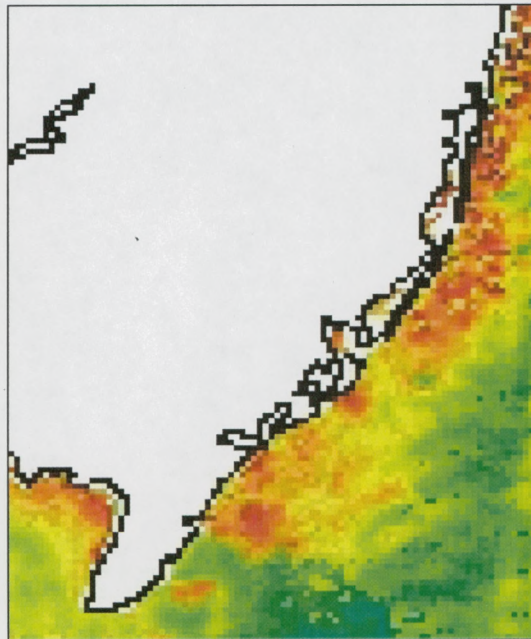
chlor_a mg/m³



(a) 3/14/04 to 3/21/04

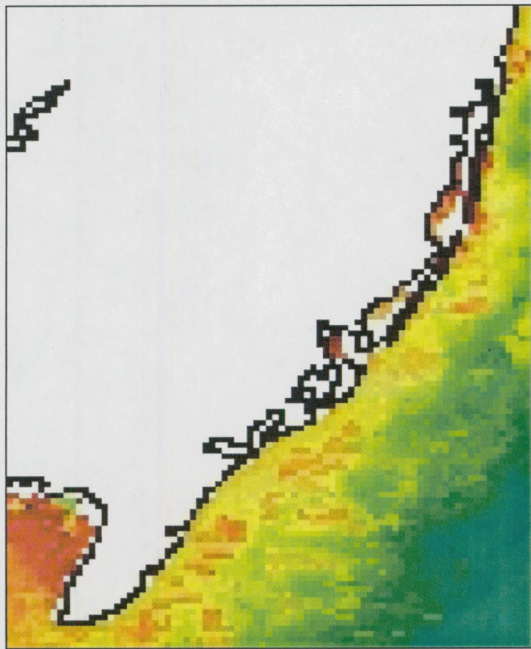


(b) 3/22/04 to 3/29/04

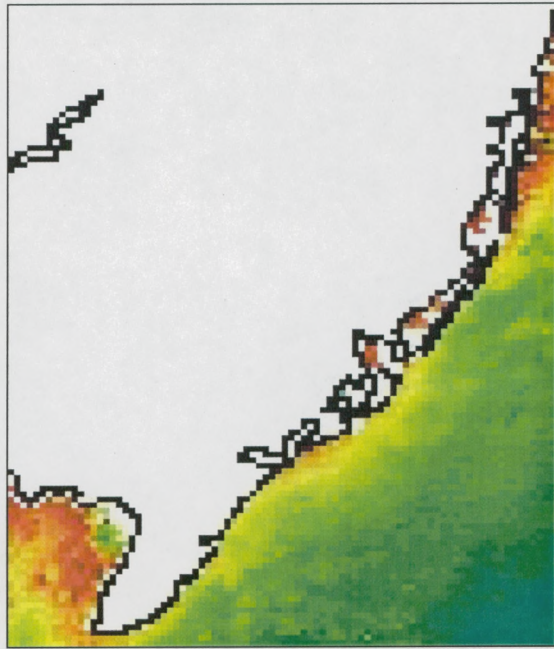


(c) 4/7/04 to 4/14/04

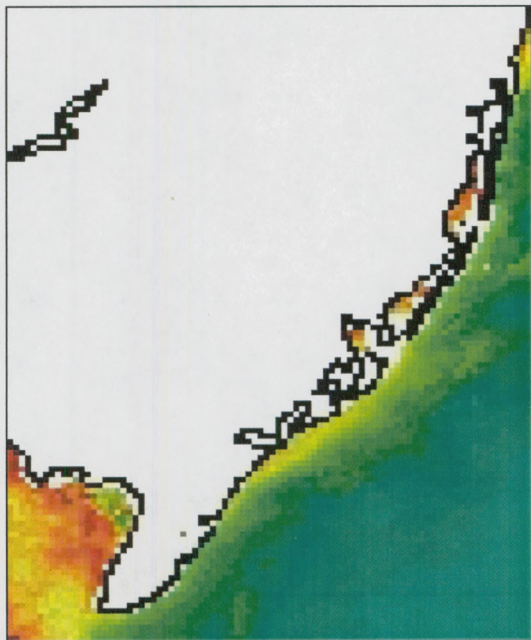
Figure 22 (a-c). MODIS Aqua 8-day chlorophyll *a* satellite images for the Mullica River-Great Bay Estuary from March to April 2004. This area is circled in (a). (NASA Goddard Space Flight Center DAAC)



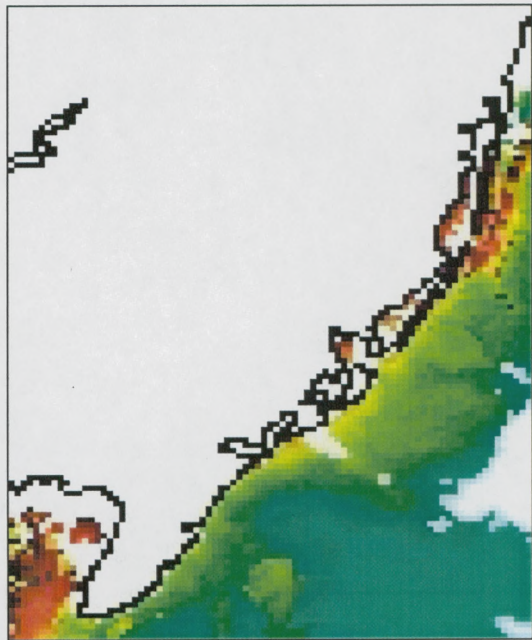
(d) 4/15/04 to 4/22/04



(e) 5/1/04 to 5/8/04



(f) 5/9/04 to 5/16/04



(g) 5/25/04 to 6/1/04

Figure 22 (d-g). MODIS Aqua 8-day chlorophyll *a* satellite images for the Mullica River-Great Bay Estuary from April to May 2004.
(NASA Goddard Space Flight Center DAAC)

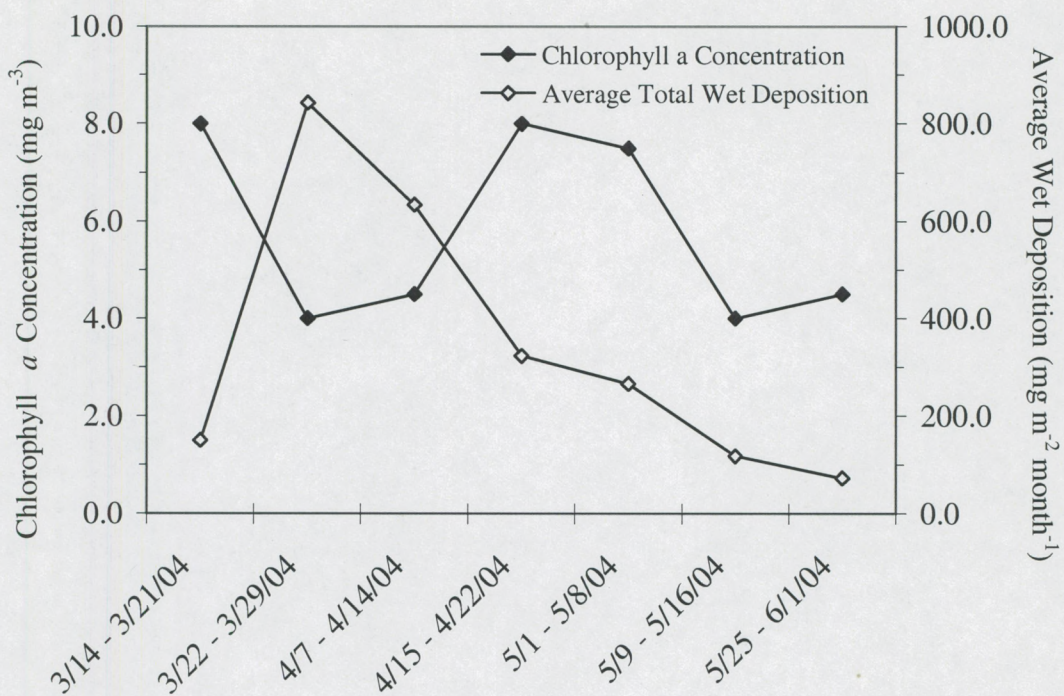


Figure 23. Relationship between chlorophyll *a* concentrations and atmospheric wet deposition for the Mullica River-Great Bay Estuary in the spring of 2004.

Table 1. Interlaboratory comparison anion analyses.

| Date | Montclair | Rutgers | Montclair | Rutgers | Montclair | Rutgers | Montclair | Rutgers |
|------------------|---|---|---|---|--|---|--|--|
| | Concentration Nitrate (mg L ⁻¹) | Concentration Nitrate (mg L ⁻¹) | Concentration Sulfate (mg L ⁻¹) | Concentration Sulfate (mg L ⁻¹) | Concentration Chloride (mg L ⁻¹) | Concentration Sulfate (mg L ⁻¹) | Concentration Chloride (mg L ⁻¹) | Concentration Chloride (mg L ⁻¹) |
| 1-3-05 | 1.80 | 1.65 | 1.82 | 1.56 | 5.71 | 1.56 | 5.71 | 5.96 |
| 1-7-05 | 2.80 | 2.72 | 2.39 | 2.14 | 1.10 | 2.14 | 1.10 | 1.16 |
| 1-20-05 | 1.44 | 1.23 | 1.99 | 1.75 | 3.45 | 1.75 | 3.45 | 3.60 |
| 2-2-05 (A) | 0.94 | 0.63 | 1.24 | 0.95 | 3.15 | 0.95 | 3.15 | 3.15 |
| 2-2-05 (B) | 0.91 | 0.59 | 1.19 | 0.88 | 2.92 | 0.88 | 2.92 | 2.65 |
| Mean | 1.58 | 1.36 | 1.73 | 1.46 | 3.27 | 1.46 | 3.27 | 3.30 |
| STD | 0.78 | 0.88 | 0.51 | 0.54 | 1.65 | 0.54 | 1.65 | 1.75 |
| Avg % Difference | | 14.97% | | 16.93% | | | | 0.91% |

$$\% \text{ difference} = \frac{\text{measured}_1 - \text{measured}_2}{(\text{measured}_1 + \text{measured}_2)} \times 100$$

measured₁ - Montclair
measured₂ - Rutgers

Table 2. Precipitation concentration comparison for the mid-Atlantic and northeast regions.

| Region | Collection Year | NO ₃ ⁻ Precipitation Concentration (mg L ⁻¹) | NH ₄ ⁺ Precipitation Concentration (mg L ⁻¹) |
|---------------------------------|------------------------|--|--|
| Mullica River-Great Bay Estuary | 2004-2005 | 2.33 | 0.42 |
| Barnegat Bay, NJ | 1999-2001 ^a | 1.80 | 0.33 |
| Chesapeake Bay | 1993-1994 ^b | 1.33 | 0.24 |
| Long Island Sound, CT | 1991-1994 ^c | 0.70 | 0.47 |

^a Gao, 2002

^b Russell et al., 1998

^c Luo et al., 2002

Table 3. Average monthly precipitation pH for the Mullica River-Great Bay Estuary.

| Month (2004-2005) | pH |
|----------------------|-------------|
| March 2004 | 4.15 |
| April | 4.14 |
| May | 4.17 |
| June | 4.07 |
| July | 4.03 |
| August | 4.31 |
| September | 4.80 |
| October | 4.37 |
| November | 4.55 |
| December | 4.11 |
| January 2005 | 4.26 |
| February | 4.20 |
| March | 4.37 |
| Average | 4.27 |
| Std Deviation | 0.21 |

Table 4. Aerosol concentration comparison for the mid-Atlantic and northeast regions.

| Region | Collection Year | NO ₃ ⁻ Aerosol Concentration (μg m ⁻³) | NH ₄ ⁺ Aerosol Concentration (μg m ⁻³) |
|---------------------------------|------------------------|---|---|
| Mullica River-Great Bay Estuary | 2004-2005 | 3.66 | 1.62 |
| Barnegat Bay, NJ | 1999-2001 ^a | 2.04 | 0.50 |
| Long Island Sound, CT | 1991-1994 ^b | 0.18 | 1.04 |

^a Gao, 2002

^b Luo et al., 2002

Table 5. Seasonal wet deposition for the Mullica River-Great Bay Estuary for the March 2004 to March 2005 sampling period.

| Season | Average Wet Deposition: Nitrate (mg m ⁻² month ⁻¹) | Average Wet Deposition: Ammonium (mg m ⁻² month ⁻¹) | Average Total (mg m ⁻² month ⁻¹) |
|----------------|---|--|--|
| Spring '04 | 355.91 (41%) | 63.95 (44%) | 419.86 (42%) |
| Summer'04 | 207.31 (24%) | 46.70 (32%) | 254.01 (25%) |
| Fall '04 | 108.80 (13%) | 11.69 (8%) | 120.49 (12%) |
| Winter '04-'05 | 188.61 (22%) | 23.63 (16%) | 212.24 (21%) |

Spring: March to May

Summer: June to August

Fall: September to November

Winter: December to February

Table 6. Monthly dry deposition for the Mullica River-Great Bay Estuary for the spring of 2004.

| Month | Average Dry Deposition: Nitrate (mg m ⁻² month ⁻¹) | Average Dry Deposition: Ammonium (mg m ⁻² month ⁻¹) | Average Total (mg m ⁻² month ⁻¹) |
|-----------|--|---|--|
| March '04 | 20.73 (22%) | 5.32 (24%) | 26.05 (22%) |
| April '04 | 34.45 (36%) | 5.17 (24%) | 39.62 (34%) |
| May '04 | 39.36 (42%) | 11.38 (52%) | 50.74 (44%) |

Table 7. Average monthly wet deposition rates for nitrate and ammonium for the Mullica River-Great Bay Estuary from March 2004 to March 2005.

| Month | Average Wet Deposition: Nitrate (mg m ⁻² month ⁻¹) | Average Wet Deposition: Ammonium (mg m ⁻² month ⁻¹) |
|----------------------|---|--|
| March 2004 | 448.15 | 64.40 |
| April | 443.14 | 87.19 |
| May | 176.43 | 40.27 |
| June | 112.71 | 21.97 |
| July | 296.32 | 60.47 |
| August | 212.91 | 57.65 |
| September | 61.53 | 9.91 |
| October | 117.28 | 21.45 |
| November | 147.59 | 3.70 |
| December | 126.37 | 11.58 |
| January 2005 | 205.80 | 17.30 |
| February | 233.66 | 42.02 |
| March | 156.36 | 53.44 |
| Total | 2,738.25 mg m ⁻² yr ⁻¹ | 491.35 mg m ⁻² yr ⁻¹ |
| Std Deviation | 120.45 | 25.64 |

Table 8. Annual wet and dry deposition rates for nitrate and ammonium for the Mullica River-Great Bay Estuary from March 2004 to March 2005.

| | Wet Deposition (mg m ⁻² yr ⁻¹) | Dry Deposition (mg m ⁻² yr ⁻¹) | Total Deposition (mg m ⁻² yr ⁻¹) |
|------------------------------|--|--|--|
| NO ₃ ⁻ | 2,738.25 (85%) | 378.16 (81%) | 3,116.41 (84%) |
| NH ₄ ⁺ | 491.35 (15%) | 87.48 (19%) | 578.83 (16%) |
| Total | 3,229.6 (87%) | 465.64 (13%) | 3,695.24 |

Table 9. Atmospheric deposition comparison for the mid-Atlantic and northeast regions.

| Region | Collection Year | N Flux to the Watershed (kg ha ⁻¹ yr ⁻¹) | Total N Deposition to the Watershed (10 ⁶ kg yr ⁻¹) | N Flux to the Water Surface (kg ha ⁻¹ yr ⁻¹) | Total N Deposition to the Water Surface (10 ⁶ kg yr ⁻¹) |
|-------------------------|------------------------|---|--|---|--|
| Mullica River-Great Bay | 2004-2005 | | 5.46 | 36.95 | 0.15 |
| Barnegat Bay, NJ | 1982-1996 ^a | 12.3 | 1.72 | 8.69 | 0.16 |
| | 1999-2001 ^c | | 6.00 | 42.56 | 0.71 |
| NJ Inland Bays | 1982-1996 ^a | 12.3 | 4.22 | 8.69 | 0.24 |
| Chesapeake Bay | 1979-1996 ^a | 12.91 | 215.34 | 9.35 | 10.53 |
| | 1984-1996 ^d | | 151.30 | | |
| | 1997 ^b | 10.8 | | | 10.50 |
| Raritan Bay, NY | 1979-1996 ^a | 11.95 | 49.71 | 8.55 | 0.68 |
| | 1997 ^b | 10.2 | | | 0.70 |
| Long Island Sound, CT | 1979-1996 ^a | 10.9 | 45.41 | 8.18 | 2.70 |
| | 1997 ^b | 9.1 | | | 2.70 |
| Delaware Bay | 1982-1996 ^a | 12.65 | 42.07 | 9.04 | 1.87 |
| | 1997 ^b | 10.5 | | | 1.90 |

^a Meyers et al., 2000

^b Castro and Driscoll, 2002

^c Gao, 2002

^d Sheeder et al., 2002

Appendices 1 through 5

Appendix 1. Precipitation concentration data collected at the RUMFS site for the Mullica River-Great Bay Estuary.

| Sample # | Sample Date | Concentration Nitrate (mg L ⁻¹) | Concentration Sulfate (mg L ⁻¹) | Concentration Chloride (mg L ⁻¹) | Concentration Ammonium (mg L ⁻¹) | Concentration Sodium (mg L ⁻¹) | pH |
|----------|--------------|---|---|--|--|--|-------|
| 1 | Filter Blank | 0 | 0 | 0 | 0.0952 | 0.1631 | 5.66 |
| 2 | 3-17-04 | 0.7876 | 2.0338 | 7.9165 | 0.1999 | 3.5226 | 4.57 |
| 3 | 3-22-04 | 2.0463 | 2.4868 | 5.1066 | 0.3966 | 2.2938 | 4.10 |
| 4 | 3-25-04 | 8.4554 | 3.9880 | 1.9372 | 1.6089 | 18.6709 | 3.79 |
| 5 | 3-29-04 | 9.1742 | 10.5460 | 2.1590 | ----- | ----- | ----- |
| 6 | 4-9-04 | 8.1411 | 8.5160 | 0.7190 | 1.4818 | 0.6120 | 3.65 |
| 7 | 4-15-04 | 0.7963 | 1.5947 | 1.7650 | 0.1810 | 1.0827 | 4.48 |
| 8 | 4-27-04 | 2.1780 | 2.4387 | 0.9727 | 0.5242 | 0.5916 | 4.29 |
| 9 | 5-4-04 | 2.3402 | 2.4694 | 2.7613 | 0.2666 | 1.3698 | 4.33 |
| 10 | 5-10-04 | 2.7963 | 4.2154 | 1.2444 | 0.9243 | 0.7071 | 3.92 |
| 11 | 5-21-04 | 1.1569 | 1.5966 | 0.6443 | 0.2454 | 0.4616 | 4.27 |
| 12 | 6-1-04 | 1.1698 | 2.2339 | 1.0396 | 0.4220 | 0.6032 | 4.27 |
| 13 | 6-7-04 | 1.7130 | 2.3451 | 3.5196 | 0.3339 | 1.5376 | 4.24 |
| 14 | 6-11-04 | 2.5757 | 2.3899 | 0.6023 | 0.5590 | 0.3695 | 3.90 |
| 15 | 6-29-04 | 4.3425 | 4.4460 | 4.4137 | 0.5957 | 2.1281 | 3.87 |
| 16 | 7-9-04 | 4.7176 | 10.6800 | 27.1082 | 1.1387 | 3.4806 | 3.68 |
| 17 | 7-13-04 | 1.8042 | 3.5904 | 5.7014 | 0.3700 | 2.5044 | 3.99 |
| 18 | 7-15-04 | 1.6182 | 2.1265 | 1.6340 | 0.3155 | 0.8203 | 4.22 |
| 19 | 7-30-04 | 0.8189 | 1.7697 | 0.9800 | 0.004088 | 0.5006 | 4.24 |
| 20 | 8-2-04 | 0.5334 | 0.8728 | 1.6348 | ND | 0.7771 | 4.74 |
| 21 | 8-11-04 | 3.1278 | 3.8844 | 2.6181 | 0.3293 | 1.2279 | 3.85 |
| 22 | 8-18-04 | 0.7082 | 0.9658 | 0.7701 | 0.02626 | 0.3869 | 4.62 |
| 23 | 8-25-04 | 3.7261 | 6.1475 | 256.1882 | 1.2885 | 5.2254 | 4.04 |
| 24 | 9-8-04 | 1.3154 | 2.1438 | 7.6620 | 0.2847 | 3.2602 | 4.73 |
| 25 | 9-17-04 | 0.7951 | 1.0558 | 3.2464 | 0.08786 | 1.7565 | 5.05 |
| 26 | 9-20-04 | 1.3694 | 3.8320 | 20.9926 | ND | 9.4965 | 4.55 |
| 27 | 9-30-04 | 0.7345 | 1.2728 | 2.6906 | 0.1366 | 1.2969 | 4.87 |
| 28 | 10-7-04 | 1.0499 | 2.0526 | 0.8741 | 0.3520 | 0.3992 | 4.34 |
| 29 | 10-14-04 | 0.8470 | 0.9777 | 0.8719 | 0.1192 | 0.3800 | 4.75 |
| 30 | 10-18-04 A | 0.9201 | 1.2092 | 2.4493 | 0.1334 | 1.0993 | 4.60 |

| Sample # | Sample Date | Concentration Nitrate (mg L ⁻¹) | Concentration Sulfate (mg L ⁻¹) | Concentration Chloride (mg L ⁻¹) | Concentration Ammonium (mg L ⁻¹) | Concentration Sodium (mg L ⁻¹) | pH |
|----------|----------------|---|---|--|--|--|------------|
| 31 | 10-18-04 B | 1.0540 | 1.4089 | 3.4387 | 0.1492 | 1.4821 | 4.52 |
| | Average | 0.9871 | 1.3091 | 2.9440 | 0.1413 | 1.2907 | 4.56 |
| 32 | 10-27-04 A | 2.3853 | 3.5684 | 5.6690 | 0.3737 | 2.6185 | 4.02 |
| 33 | 10-27-04 B | 2.4369 | 3.6100 | 5.6638 | 0.3574 | 1.9034 | 4.01 |
| | Average | 2.4111 | 3.5892 | 5.6664 | 0.3656 | 2.2610 | 4.02 |
| 34 | 11-10-04 | 0.9290 | 1.2550 | 2.6177 | 0.05337 | 1.1706 | 4.60 |
| 35 | 11-17-04 | 1.4562 | 1.1891 | 3.5646 | 0.01247 | 1.6634 | 4.72 |
| 36 | 11-29-04 | 1.5574 | 2.6790 | 10.9083 | ND | 5.0584 | 4.34 |
| 37 | 12-13-04 A | 2.2014 | 2.5935 | 6.3659 | 0.2251 | 3.05895 | 4.11 |
| 38 | 12-13-04 B | 2.2173 | 2.7734 | 7.9355 | 0.1800 | 2.5250 | 4.11 |
| | Average | 2.2094 | 2.6835 | 7.1507 | 0.2026 | 2.7920 | 4.11 |
| 39 | 1-3-05 | 1.8049 | 1.8237 | 5.7133 | 0.2032 | 2.4678 | 4.45 |
| 40 | 1-7-05 | 2.8014 | 2.3877 | 1.0992 | 0.2751 | 0.4092 | 4.01 |
| 41 | 1-20-05 | 1.4408 | 1.9901 | 3.4469 | 0.03017 | 1.6553 | 4.31 |
| 42 | 2-2-05 A | 0.9367 | 1.2411 | 3.1468 | ND | 1.4590 | 4.78 |
| 43 | 2-2-05 B | 0.9089 | 1.1917 | 2.6870 | ND | 1.2919 | 4.79 |
| | Average | 0.9228 | 1.2164 | 2.9169 | ND | 1.3755 | 4.79 |
| 44 | 2-8-05 | 1.0705 | 0.8682 | 1.1040 | 0.02060 | 0.1186 | 4.50 |
| 45 | 2-15-05 | 2.8649 | 1.8918 | 1.1453 | 0.1630 | 0.3292 | 3.98 |
| 46 | 2-21-05 A | 3.9259 | 3.5688 | 4.3445 | 1.0274 | 1.9931 | 4.01 |
| 47 | 2-21-05 B | 3.9411 | 3.9514 | 3.9351 | 1.2121 | 1.7456 | 4.01 |
| | Average | 3.9335 | 3.7601 | 4.1398 | 1.1198 | 1.8693 | 4.01 |
| 48 | 2-26-05 | 5.4558 | 4.0402 | 1.4513 | 0.7461 | 0.6134 | 3.74 |
| 49 | 3-1-05 | 0.7483 | 1.4155 | 6.7036 | ND | 3.1514 | 4.66 |
| 50 | 3-10-05 | 0.7502 | 1.2129 | 2.7473 | 0.09734 | 1.3255 | 4.58 |
| 51 | 3-22-05 | 3.9988 | 4.6475 | 1.3976 | 1.4160 | 0.6521 | 3.93 |
| 52 | 3-29-05 | 1.1918 | 1.9412 | 3.3184 | 0.2013 | 1.5575 | 4.29 |
| | AVERAGE | 2.3342 | 2.8820 | 9.4741 | 0.4228 | 2.0736 | 4.32 |
| | RANGE | 0.5334- 9.1742 | 0.8682- 10.6800 | 0.6023- 27.1082 | 0.0125- 1.6089 | 0.1186- 18.6709 | 3.65- 5.66 |
| | STD | 2.0549 | 2.2371 | 37.5114 | 0.4378 | 3.0143 | 0.401 |

* NOT ENOUGH SAMPLE FOR CATION ANALYSIS FOR 3-29-04 ND= Not Detected

Appendix 2. Precipitation pH for the Mullica River-Great Bay Estuary.

| Date | pH |
|------------|------|
| 3-17-04 | 4.57 |
| 3-22-04 | 4.10 |
| 3-25-04 | 3.79 |
| 3-29-04 | 0 |
| 4-9-04 | 3.65 |
| 4-15-04 | 4.48 |
| 4-27-04 | 4.29 |
| 5-4-04 | 4.33 |
| 5-10-04 | 3.92 |
| 5-21-04 | 4.27 |
| 6-1-04 | 4.27 |
| 6-7-04 | 4.24 |
| 6-11-04 | 3.90 |
| 6-29-04 | 3.87 |
| 7-9-04 | 3.68 |
| 7-13-04 | 3.99 |
| 7-15-04 | 4.22 |
| 7-30-04 | 4.24 |
| 8-2-04 | 4.74 |
| 8-11-04 | 3.85 |
| 8-18-04 | 4.62 |
| 8-25-04 | 4.04 |
| 9-8-04 | 4.73 |
| 9-17-04 | 5.05 |
| 9-20-04 | 4.55 |
| 9-30-04 | 4.87 |
| 10-7-04 | 4.34 |
| 10-14-04 | 4.75 |
| 10-18-04 A | 4.60 |
| 10-18-04 B | 4.52 |
| 10-27-04 A | 4.02 |
| 10-27-04 B | 4.01 |
| 11-10-04 | 4.60 |
| 11-17-04 | 4.72 |
| 11-29-04 | 4.34 |
| 12-13-04 A | 4.11 |
| 12-13-04 B | 4.11 |
| 1-3-05 | 4.45 |
| 1-7-05 | 4.01 |
| 1-20-05 | 4.31 |
| 2-2-05 A | 4.78 |
| 2-2-05 B | 4.79 |

| Date | pH |
|----------------|------|
| 2-8-05 | 4.50 |
| 2-15-05 | 3.98 |
| 2-21-05 A | 4.01 |
| 2-21-05 B | 4.01 |
| 2-26-05 | 3.74 |
| 3-1-05 | 4.66 |
| 3-10-05 | 4.58 |
| 3-22-05 | 3.93 |
| 3-29-05 | 4.29 |
| | |
| Average | 4.32 |
| | |

Appendix 3. Aerosol concentration data collected at the RUMFS site for the Mullica River-Great Bay Estuary.

| Sample # | Sample Date | Air Concentration Nitrate (mg m ⁻³) | Air Concentration Sulfate (mg m ⁻³) | Air Concentration Chloride (mg m ⁻³) | Air Concentration Ammonium (mg m ⁻³) | Air Concentration Sodium (mg m ⁻³) |
|----------|--------------------------|---|---|--|--|--|
| 1 | 3-13-04 HV #1 | 0.0017 | 0.0018 | 0.00065 | 0.00098 | 0.00033 |
| 2 | 3-13-04 HV #2 | 0.0020 | 0.0022 | 0.00065 | 0.0014 | 0.00037 |
| 3 | 3-14-04 | 0.0033 | 0.0023 | 0.0032 | 0.00090 | 0.0016 |
| 4 | 3-14-04: Blank | 0 | 0 | 0 | 0 | 0 |
| 5 | 4-2-04 | 0.0015 | 0.0042 | 0.0026 | 0.00034 | 0.0013 |
| 6 | 4-9-04 HV #1 | 0.0070 | 0.0053 | 0.0014 | 0.0023 | 0.00073 |
| 7 | 4-9/4-10-04 HV #2 | 0.0033 | 0.0053 | 0.00054 | 0.0017 | 0.00025 |
| 8 | 4-16-04 HV #1 | 0.0034 | 0.0024 | 0.0034 | 0.00093 | 0.0018 |
| 9 | 4-16/4-17-04 HV #2 | 0.0052 | 0.0027 | 0.0041 | 0.00098 | 0.0022 |
| 10 | 4-23-04 HV #1 | 0.0081 | 0.0063 | 0.0080 | 0.0014 | 0.0048 |
| 11 | 4-23/4-24-04 HV #2 | 0.0021 | 0.0038 | 0.0045 | 0.00059 | 0.0026 |
| 12 | 4-30-04 HV #1 | 0.0029 | 0.0037 | 0.0035 | 0.00079 | 0.0021 |
| 13 | 4-30/5-1-04 HV #2 | 0.0016 | 0.0024 | 0.0015 | 0.00041 | 0.0012 |
| 14 | 4-30/5-1-04 HV #2 - Dup | 0.0018 | 0.0027 | 0.0018 | 0.00040 | 0.0013 |
| | Average | 0.0017 | 0.0025 | 0.0017 | 0.00040 | 0.0012 |
| 15 | 5-7-04 HV #1 | 0.0097 | 0.0114 | 0.0037 | 0.0036 | 0.0022 |
| 16 | 5-7/5-8-04 HV #2 | 0.0031 | 0.0046 | 0.0028 | 0.0019 | 0.00091 |
| 17 | 5-14-04 HV #1 | 0.0049 | 0.0137 | 0.0023 | 0.0023 | 0.0015 |
| 18 | 5-14/5-15-04 HV #2 | 0.0024 | 0.0035 | 0.0043 | 0.00086 | 0.0022 |
| 19 | 5-14/5-15-04 HV #2 - Dup | 0.0018 | 0.0025 | 0.0033 | 0.00069 | 0.0017 |
| | Average | 0.0021 | 0.0030 | 0.0038 | 0.00077 | 0.0020 |

| Sample # | Sample Date | Air Concentration Nitrate (mg m ⁻³) | Air Concentration Sulfate (mg m ⁻³) | Air Concentration Chloride (mg m ⁻³) | Air Concentration Ammonium (mg m ⁻³) | Air Concentration Sodium (mg m ⁻³) |
|----------|--------------------------|---|---|--|--|--|
| 20 | 5-21-04 HV #1 | 0.0054 | 0.0157 | 0.0043 | 0.0041 | 0.00077 |
| 21 | 5-21/5-22-04 HV #2 | 0.0040 | 0.0066 | 0.0032 | 0.0020 | 0.0013 |
| 22 | 5-21/5-22-04 HV #2 - Dup | 0.0041 | 0.0077 | 0.0034 | 0.0021 | 0.0014 |
| | Average | 0.0040 | 0.0071 | 0.0033 | 0.0020 | 0.0013 |
| 23 | 5-24/5-25-04 | 0.0048 | 0.0122 | 0.0099 | 0.0034 | 0.0038 |
| | AVERAGE | 0.0040 | 0.0058 | 0.0034 | 0.0016 | 0.0017 |
| | RANGE | 0.0015 -0.0097 | 0.0018 -0.0157 | 0.00054 -0.0099 | 0.00034 -0.0036 | 0.00025 -0.0048 |
| | STD | 0.0023 | 0.0043 | 0.0023 | 0.0011 | 0.0012 |

Appendix 4. Precipitation deposition data for the Mullica River-Great Bay Estuary.

| Sample # | Sample Date | Wet Deposition: Nitrate (mg m ⁻² month ⁻¹) | Wet Deposition: Ammonium (mg m ⁻² month ⁻¹) |
|----------|----------------|---|--|
| 1 | Filter Blank | ----- | ----- |
| 2 | 3-17-04 | 68.9938 | 17.5092 |
| 3 | 3-22-04 | 179.2559 | 34.7440 |
| 4 | 3-25-04 | 740.6930 | 140.9413 |
| 5 | 3-29-04 | 803.6599 | ----- |
| 6 | 4-9-04 | 973.6756 | 177.2185 |
| 7 | 4-15-04 | 95.2375 | 21.6481 |
| 8 | 4-27-04 | 260.4888 | 62.6897 |
| 9 | 5-4-04 | 196.8108 | 22.4212 |
| 10 | 5-10-04 | 235.1688 | 77.7353 |
| 11 | 5-21-04 | 97.2953 | 20.6416 |
| 12 | 6-1-04 | 53.8108 | 19.4109 |
| 13 | 6-7-04 | 78.7980 | 15.3594 |
| 14 | 6-11-04 | 118.4822 | 25.7163 |
| 15 | 6-29-04 | 199.7550 | 27.4000 |
| 16 | 7-9-04 | 624.1385 | 150.6516 |
| 17 | 7-13-04 | 238.6957 | 48.9480 |
| 18 | 7-15-04 | 214.0879 | 41.7440 |
| 19 | 7-30-04 | 108.3405 | 0.5408 |
| 20 | 8-2-04 | 56.1137 | |
| 21 | 8-11-04 | 329.0446 | 34.6448 |
| 22 | 8-18-04 | 74.5026 | 2.7630 |
| 23 | 8-25-04 | 391.9857 | 135.5520 |
| 24 | 9-8-04 | 76.8194 | 16.6280 |
| 25 | 9-17-04 | 46.4338 | 5.1311 |
| 26 | 9-20-04 | 79.9730 | |
| 27 | 9-30-04 | 42.8948 | 7.9801 |
| 28 | 10-7-04 | 93.0211 | 31.1864 |
| 29 | 10-14-04 | 75.0442 | 10.5569 |
| 30 | 10-18-04 A | 81.5209 | 11.8230 |
| 31 | 10-18-04 B | 93.3844 | 12.9218 |
| | Average | 87.4527 | 12.3724 |
| 32 | 10-27-04 A | 211.3376 | 32.3601 |
| 33 | 10-27-04 B | 215.9093 | 30.9518 |
| | Average | 213.6235 | 31.6559 |
| 34 | 11-10-04 | 104.3267 | 5.9930 |
| 35 | 11-17-04 | 163.5313 | 1.3999 |
| 36 | 11-29-04 | 174.8960 | |
| 37 | 12-13-04 A | 125.9201 | 12.8757 |
| 38 | 12-13-04 B | 126.8296 | 10.2966 |

| Sample # | Sample Date | Wet Deposition: Nitrate (mg m ⁻² month ⁻¹) | Wet Deposition: Ammonium (mg m ⁻² month ⁻¹) |
|----------|----------------|---|--|
| | Average | 126.3748 | 11.5862 |
| 39 | 1-3-05 | 184.2803 | 20.7438 |
| 40 | 1-7-05 | 286.0229 | 28.0894 |
| 41 | 1-20-05 | 147.1057 | 3.0805 |
| 42 | 2-2-05 A | 76.8094 | |
| 43 | 2-2-05 B | 74.5298 | |
| | Average | 75.6696 | |
| 44 | 2-8-05 | 87.7810 | 1.6890 |
| 45 | 2-15-05 | 234.9218 | 13.3668 |
| 46 | 2-21-05 A | 321.9238 | 84.2502 |
| 47 | 2-21-05 B | 323.1702 | 99.3925 |
| | Average | 322.5470 | 91.8214 |
| 48 | 2-26-05 | 447.3756 | 61.1817 |
| 49 | 3-1-05 | 69.9661 | |
| 50 | 3-10-05 | 70.1437 | 9.1016 |
| 51 | 3-22-05 | 373.8878 | 132.3921 |
| 52 | 3-29-05 | 111.4333 | 18.8177 |
| | | | |
| | AVERAGE | 213.7948 | 39.8263 |
| | RANGE | 42.8948- 973.6756 | 0.5408 – 177.2185 |
| | STD | 207.3820 | 46.2652 |

* NOT ENOUGH SAMPLE FOR CATION ANALYSIS FOR 3-29-04

Appendix 5. Aerosol deposition data for the Mullica River-Great Bay Estuary.

| Sample # | Sample Date | Dry Deposition: Nitrate (mg m ⁻² month ⁻¹) | Dry Deposition: Ammonium (mg m ⁻² month ⁻¹) |
|----------|-----------------------------|---|--|
| 1 | 3-13-04 HV #1 | 15.3530 | 4.8376 |
| 2 | 3-13-04 HV #2 | 17.5331 | 6.7089 |
| 3 | 3-14-04 | 29.2889 | 4.4157 |
| 4 | 3-14-04: Blank | 0 | 0 |
| 5 | 4-2-04 | 12.8523 | 1.6805 |
| 6 | 4-9-04 HV #1 | 62.0215 | 11.2534 |
| 7 | 4-9/4-10-04 HV #2 | 28.9668 | 8.5804 |
| 8 | 4-16-04 HV #1 | 30.2532 | 4.5877 |
| 9 | 4-16/4-17-04 HV #2 | 45.7738 | 4.8284 |
| 10 | 4-23-04 HV #1 | 71.0925 | 6.8505 |
| 11 | 4-23/4-24-04 HV #2 | 18.7845 | 2.9109 |
| 12 | 4-30-04 HV #1 | 25.3255 | 3.8935 |
| 13 | 4-30/5-1-04 HV #2 | 14.0334 | 2.0036 |
| 14 | 4-30/5-1-04 HV #2 – Dup | 15.9728 | 1.9744 |
| | Average | 15.0031 | 1.9890 |
| 15 | 5-7-04 HV #1 | 85.5719 | 17.6371 |
| 16 | 5-7/5-8-04 HV #2 | 27.4879 | 9.4716 |
| 17 | 5-14-04 HV #1 | 43.0334 | 11.3885 |
| 18 | 5-14/5-15-04 HV #2 | 20.9118 | 4.2357 |
| 19 | 5-14/5-15-04 HV #2 – Dup | 15.5805 | 3.3784 |
| | Average | 18.2462 | 3.8071 |
| 20 | 5-21-04 HV #1 | 47.8169 | 20.0294 |
| 21 | 5-21/5-22-04 HV #2 | 35.3695 | 9.6667 |
| 22 | 5-21/5-22-04 HV #2 – Dup | 35.8029 | 10.3441 |
| | Average | 35.5862 | 10.0054 |
| 23 | 5-24/5-25-04 | 42.1238 | 16.6931 |
| | | | |
| | AVERAGE | 35.3744 | 7.9773 |
| | RANGE | 12.852 – 85.572 | 1.680 – 20.029 |
| | STD | 20.2077 | 5.4041 |