ATMOSPHERIC DEPOSITION OF NITROGEN: IMPLICATIONS FOR NUTRIENT OVER-ENRICHMENT OF COASTAL WATERS

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Left Running Head: H. W. Paerl, R. L. Dennis, D. R. Whitall

Right Running Head: Atmospheric N deposition to coastal waters

ABSTRACT

Atmospheric deposition of nitrogen (AD-N) is a significant source of nitrogen enrichment to N-limited estuarine and coastal waters downwind of anthropogenic emissions. Along the U.S. East coast and eastern Gulf of Mexico, AD-N currently accounts for 10 to over 40% of "new" N loading to estuaries. Extension of the regional acid deposition model (RADM) to coastal shelf waters indicates that 11, 5.6, and 5.6 kg-N ha^{-1} may be deposited on the continental shelf areas of the Northeastern U.S. Coast (NE), Southeast U.S. Coast (SE) and Eastern Gulf of Mexico (East Gulf), respectively. AD-N approximates or exceeds riverine N inputs in many coastal regions. From a spatial perspective, AD-N is a unique source of N enrichment to estuarine and coastal waters because, for a receiving water body, the airshed may exceed the watershed by 10-20 fold or greater. Thus, AD-N may originate far outside the of currently-managed watersheds. AD-N impacts waters downstream of the oligo- and mesohaline estuarine "nutrient filters" where large amounts of terrestrially-supplied N are assimilated and/or denitrified. Therefore, AD-N may increase in importance as a "new" N source downstream of these regions and in adjacent coastal waters. Regionally and globally, N deposition associated with urbanization (NO_x, PAN) and agricultural expansion (NH_4^+ and possibly organic N) has increased in coastal airsheds. Recent growth and intensification of animal (poultry, swine, cattle) operations in the midwest and Mid-Atlantic regions have led to increasing amounts of NH_4^+ emission and deposition, according to a 3 decadal analysis of the National Acid Deposition Program (NADP) network. In Western Europe, where livestock operations have dominated agricultural production for the better part of this century, NH_4^+ is the most abundant form of AD-N. AD-N deposition in the U.S. is still

dominated by oxides of N (NO_x) emitted from fossil fuel combustion; however, annual NH_4^+ deposition is increasing, and in some regions is approaching total NO_3 deposition. In receiving estuarine and coastal waters, phytoplankton community structural and functional changes, associated water quality, trophic and biogeochemical alterations (i.e., algal blooms, hypoxia, food web and fisheries habitat disruption) are frequent consequences of N-driven eutrophication. Increases in and changing proportions of various new N sources regulate phytoplankton competitive interactions, dominance and successional patterns. These quantitative and qualitative aspects of AD-N and other atmospheric nutrient sources (e.g., Fe) may promote major biotic changes now apparent in estuarine and coastal waters, including the proliferation of harmful algal blooms, with cascading impacts on water quality and fisheries. Because of its relatively large contribution to total new N loading and potential biogeochemical and ecological importance, AD-N requires attention from regional air/watershed nutrient budgeting and management perspectives.

INTRODUCTION

Human population growth, urban, industrial and agricultural expansion have profoundly impacted the quantities and composition of nitrogen (N)-containing pollutants released to the environment (Vitousek et al. 1997). In particular, man's encroachment on the coastal zone has been accompanied by a precipitous rise in land-based N nutrients released as either point sources (i.e., wastewater, industrial discharges, stormwater overflow discharges) or diffuse non-point agricultural, urban and rural discharge. A strong and direct relationship between human expansion and accelerating riverine N inputs to coastal waters testifies to this impact (Peierls et al. 1991; Howarth et al. 1996). Diverse studies in a broad range of estuarine and coastal waters receiving anthropogenic N enrichment have shown these waters to be N-limited; namely, N supply controls the rate of primary production (Dugdale 1967; Ryther and Dunstan 1971; D'Elia et al. 1986; Nixon 1986, 1995). It follows that N enrichment has been linked to accelerated primary production, or eutrophication, in these waters (Nixon 1986, 1995). N-enhanced eutrophication may be manifested as increased frequencies, magnitudes and persistence of suspended algal (phytoplankton) blooms (Richardson 1997). Phytoplankton blooms may be toxic and/or accumulate as large masses of ungrazed organic matter in the sediments, fueling excessive oxygen consumption in the form of hypoxia (<4 mg L^{-1} O_2) and anoxia (no detectable O_2), conditions that are stressful or fatal to resident finfish and shellfish communities (Winn and Knott 1992; Justic et al. 1993; Diaz et al. 1995; Paerl et al. 1998; Rabalais et al. 1999).

Management of coastal eutrophication has focused on identifying and reducing excessive N inputs to these N-sensitive waters (Environmental Protection Agency 1989;

1998; National Research Council 2000). Both point and non-point land-based sources have been identified as targets for N input controls and a variety of land-based nutrient reduction and/or mitigation strategies have evolved to tackle the problem. When identifying key external or "new" N sources responsible for over-enrichment of N sensitive waters, it has become evident that land-based sources are not the only culprits. Among anthropogenic sources of "new" N to estuarine and coastal waters, atmospheric deposition of N (AD-N) is now recognized as highly significant and increasingly-important (Paerl 1985, 1995; Fisher and Oppenheimer 1991, Chesapeake Bay Program 1994; Valigura et al. 1996; Jaworski et al. 1997; Ecol. Soc. Amer. 1998; EPA 1999) (Fig. 1). In the past century alone, anthropogenically-mediated atmospheric N emissions have increased by nearly 10-fold (Howarth 1998). It is estimated that from 10 to over 40% of "new" N supplied to these waters is of atmospheric origin (Valigura et al. 1996, 2000). In some regions (e.g., mid-Atlantic and Northeast, Tampa Bay), the atmosphere is now the single largest source of new N (Valigura et al. 1996). This underscores the need to better quantify AD-N inputs on local and regional scales, and to understand ecosystem-level biogeochemical, trophic, water quality and habitat responses to this growing N source. AD-N is also an emerging "new" N source in developing nations experiencing urban, agricultural and industrial expansion in coastal regions.

Because of its large scale and magnitude, AD-N plays a central role in coastal N budgets, biogeochemical, trophodynamic, water quality and habitat changes in downwind waters. Specifically, we must clarify; 1) the spatiotemporal linkage of AD-N emissions, transport and fate on local, regional and larger (ocean basins, global) scales, 2) the absolute and relative (to land-based sources) roles AD-N plays as a "new" N source, 3)

the "sphere of influence" of AD-N as a "new" N source in N sensitive estuaries and coastal regions, 4) the chemical constituents in AD-N, and 5) the biological availability and ecological roles of these AD-N constituents, as they pertain to mechanisms of eutrophication, algal and higher plant composition, including harmful algal bloom species.

In this contribution, we examine and synthesize information pertinent to the roles of AD-N in coastal nutrient over-enrichment, biogeochemical and trophic change. We will attempt to integrate knowledge of the sources, composition, deposition and ecological responses over scales ranging from ecosystem- to regional levels. Lastly, we address requirements and options for managing this growing and evolving source of "new" N in coastal waters.

Atmospheric N Composition and Sources

Atmospherically-deposited N may be either "wet" in origin (if N is dissolved in precipitation such as rain or snow), or "dry" (the settling of N-containing particles and gases to land and water surfaces). Atmospherically-derived N deposited in wet or dry forms may be deposited directly, or it may take an indirect route if it enters the estuary via runoff and groundwater from the surrounding watershed. The majority of atmospheric N exists as inorganic N in two principal forms: oxidized N and reduced N.

Oxidized N is found in the form of gaseous nitric acid (HNO_3), nitrogen dioxide (NO_2) and aerosol nitrate (NO_3). Contributions from NO_2 are minimal and will not be further considered. Nitric acid is the parent form of oxidized N. It is a termination product of the oxidation of nitrogen oxide ($NO_X = NO + NO_2$) and volatile organic

compounds as part of atmospheric photochemistry (EPA 1996; Seinfeld and Pandis 1998). Aerosol nitrate exists as ammonium nitrate; it results from the partitioning of a fraction of HNO_3 into particulate form in the presence of ammonia (NH_3). (Seinfeld and Pandis 1998). The principal source of nitric acid and aerosol nitrate in North America is the combustion of fossil fuels (e.g. by coal and oil-fired powerplants, automobiles and other forms of transportation) that produces precursor emissions of NO_X, primarily NO.

Reduced N in the atmosphere exists in the form of gaseous ammonia (NH_3) and aerosol ammonium (NH_4). NH_4 results from chemical reactions involving sulfuric acid droplets, nitric acid, and ammonia that partitions a fraction of NH_3 into fine particulates: ammonium sulfate, ammonium bisulfate, ammonium nitrate and other complex aerosol mixtures (Seinfeld and Pandis 1998). The majority of NH_3 is directly emitted into the atmosphere from agricultural sources such as fertilizer application and confined animal operations.

Organic nitrogen (ON) is also an important fraction of AD-N (Correll and Ford 1982; Timperley et al. 1985; Mopper and Zika 1987). The sources and composition of atmospheric ON are not well understood, although rainfall in agricultural areas tends to be relatively enriched in dissolved organic nitrogen (DON) (c.f. Timperley et al. 1985). DON accounts for ~15 to 30% of wet N deposition in coastal and open ocean waters (Correll and Ford 1982; Cornell et al. 1995; Peierls and Paerl 1997; Russell et al. 1998).

Atmospheric N Deposition Processes

All forms of inorganic N are very water-soluble and not influenced significantly by aqueous chemistry; thus all forms wet deposit equally well. In contrast, dry deposition

is significantly influenced by the form of the inorganic N and the physical characteristics of the surface to which it is deposited. Dry deposition flux depends on both the ambient concentration and the chemical's affinity for deposition (deposition velocity). Gaseous HNO_3 deposition velocities exceed those of NH_3, but at moderate to high concentrations of NH_3 they are the same order of magnitude (Meyers, et al. 1998; Duyzer et al. 1994; Fowler et al. 1998). At low concentrations of NH_3 there is a compensation point and plants can become a source of NH_3 rather than a sink (Langford and Fehsenfeld 1992; Duyzer et al. 1994; Fowler et al. 1998; Wyers and Erisman 1998). Over land, gaseous NH_3 and HNO_3 are very sticky (high deposition velocity), whereas, the small (<0.5 μm) inorganic N particles are much less likely to deposit (low deposition velocity). The gaseous deposition velocity is an order of magnitude higher than the small particulate deposition velocity. Also, for both gases and aerosols, the deposition velocity to open, fresh water surfaces, is roughly 2 to 5 times lower than to terrestrial surfaces. In contrast, over salt water, sea salt aerosol will preferentially and efficiently partition interstitial HNO_3 gas to NO_3 aerosol associated with supermicron particles (1-5 μm and greater) (Keene and Savoie 1998). This shift in aerosol size from 0.1-0.5 μm over land, a size not affected by gravity, to the order of 2-5 μm over salt water, a size significantly affected by gravity, will increase the particle NO_3 deposition velocity by more than an order of magnitude (Slinn 1982; Davidson and Wu 1990; Pryor et al. 1999; Torseth and Semb 1998). Thus, over open salt water particle NO_3 deposition will dominate dry deposition and it can be the same order as NO_3 wet deposition. On the other hand, the thermodynamic and phase partitioning relationships do not favor ammonia partitioning to supermicron particles and it tends to be found principally on the fine particles <0.5μm.

Due to the large difference in gaseous and fine particulate deposition velocities, dry deposition rates of oxidized and reduced N to land are different. These, in turn, affect ratios of wet to dry deposition for the two types of inorganic N. Modeling analysis with the Extended Regional Acid Deposition Model (Extended RADM) indicates that the partitioning of ambient concentrations of nitric acid and ammonia into the fine particulate species of nitrate and ammonium is basically reversed with respect to one another for the land areas of coastal states of the eastern U.S. (Mathur and Dennis 2000). The fractions of $NO_3/(NO_3 + HNO_3)$ and $NH_4/(NH_4 + NH_3)$ have medians of 0.23 and 0.74, respectively, over the eastern and Gulf Coast estuaries. This same pattern is observed in Northern Europe (Sorteberg et al. 1998) and in CASTNet data for oxidized N in the eastern U.S. (Clark et al. 1997). Hence, the dry deposition of oxidized N will be significantly larger than that of reduced N, whereas wet deposition is hardly or not at all influenced by the differences in partitioning. Model analyses suggest that wet and dry deposition to terrestrial surfaces of oxidized forms of N will be roughly comparable on a long-term annual basis. They suggest that wet and dry deposition of reduced forms of N to land surfaces will be unequal, with wet deposition, in general, being roughly a factor of 2 to 3 larger on an annual basis. Over salt water wet and dry deposition of oxidized forms of N are also expected to be comparable on an annual basis. But for reduced forms of N wet and dry deposition over salt water will be unequal, with wet deposition being much larger. Over estuaries with a fresh-to-salt water gradient at the surface, there will be a gradient in the dry deposition of oxidized-N, tracking the increase with increasing salinity of nitrate attached to supermicron-sized particles.

Because dry deposition velocities for open, fresh water are lower than those for land, the delivery of direct AD-N to estuaries is expected to be dominated by wet deposition, even on an annual basis. National Acid Deposition Program (NADP) data show that while more oxidized-N than reduced nitrogen was being deposited in the 1980's, the reduced fraction is increasing with time (Fig. 2). Now about the same mass of oxidized and reduced nitrogen is being deposited to coastal areas. Wet deposition is an acute or episodic form of AD-N, while dry deposition is a chronic, low-level source of AD-N. If ammonia emissions sources are large and nearby, as has been shown for hog operations in North Carolina (Aneja 2000, Whitall et al in preparation) then the dry deposition of reduced N may be much larger than indicated here, possibly comparable to the wet deposition. The exact relationship between wet and dry reduced and oxidized N needs to be locally established for individual airsheds and watersheds with the help of both measurements and modeling. The terrestrial release of atmospherically deposited N to the rivers is most likely to be in the form of oxidized N (Stoddard 1993). Thus, the major source of atmospherically deposited ammonia is likely to be direct deposition to the estuary surface.

The N Airshed for Estuaries

To address AD-N contributions to the estuaries, it is necessary to establish a sense of the sources of the AD-N. From where and from how far away is it coming? This can be accomplished through the concept of an airshed. However, the atmosphere does not have a lateral boundary and the flow of atmospheric chemicals to an estuary does not have a well-defined beginning as does the flow of surface waters. The boundary can be

defined in terms of the relative climatological range of the majority of the deposition from a source and in terms of deposition efficiency. The concept of a normalized range of influence of a source region has been quantified to produce a prescription for constructing principal airsheds for watersheds (Dennis 1997; Dennis and Mathur 2001). The distance at which the accumulated deposition from a source region encompasses 1/e of its total continental deposition, roughly the 65% contour of accumulation, is taken as the source's normalized range of influence. The RADM (Chang et al. 1987) and the Extended RADM (Mathur and Dennis 2000) have been used to define the range of influence of over 100 source regions across the Eastern U.S. The normalized range of influence of annual oxidized-N deposition from NO_X emissions for the Eastern U.S. is approximately 400-600 km in the prevailing direction of transport. The distance is shorter in a direction that opposes the prevailing wind. The normalized range of influence of annual reduced-N deposition from NH_3 emissions for the Eastern U.S. is approximately 75% of the range for oxidized-N or 300-450 km. The modeling approach used to develop annual averages (Dennis et al. 1990; Brook et al. 1995a; 1995b) gives a climatological average representative of at least 10 years of meteorology, not a single specific year. These ranges are consistent with a residence time for N compounds in the lower atmosphere, controlled by deposition loss processes, of approximately 1 and ? days for oxidized-N and about 1 day for reduced-N. The atmospheric lifetime measured by deposition will be slightly shorter than the typical lifetime of the chemicals in the atmosphere, because the lifetimes in the upper troposphere, which are longer, are being ignored. Precipitation "scavenging" plays an important role in determining the deposition lifetimes for the Eastern U.S.

Interpretation of model evaluation results (e.g. Cohn and Dennis 1994) suggests that most likely the size of the oxidized-N range of influence is biased short. Overprediction of wet deposition by 20% on average for both oxidized-N and reduced-N is a defining evaluation result. Evaluation results for reduced-N are mixed. Errors suggest biases in both directions that potentially offset each other. The range of influence for reduced-N appears to be a reasonable best estimate. In modeling studies for Northern Europe the range for oxidized-N is somewhat longer than for the Eastern U.S. and the difference in the transport range between oxidized-N and reduced-N is larger (Hov et al. 1994; Hov and Hjøllo 1994). The higher ammonia emissions in Europe and the drier north, together with the judgments about the effect of biases on oxidized-N ranges, are the most likely explanations for the differences. Hence, the differences in transport range reflect differences in emissions and climatology between the two continents. Oxidized-N principal airsheds have been defined and characteristics developed for 20 watersheds along the U.S. East Coast and Gulf Coast. Oxidized-N airshed characteristics are given in Table 1 for all of the watersheds and are summarized in Table 2.

The airsheds are large compared to watersheds, even though only the area over the continent is counted. Example airsheds for the East Coast and Gulf Coast are shown in Figures 3 and 4, respectively. Most of the airsheds are from 15 - 200 times larger than the drainage area of the watersheds receiving the N-deposition. The variation in size representative of the distribution of airsheds, defined by the span between the 20th and 80th percentiles of the rank-ordered sizes, is about a factor of two, from 475,000 km^2 to 900,000 km^2 (Table 2). The size of the airshed is influenced by variations in the climatological range across the Eastern U.S. and the size of the watershed, but the

variation in airshed size is much smaller than that for watershed area because the atmospheric range of influence is large. The airshed for Tampa Bay is unusually small because of its location relative to the geography of Florida. The NO_X emissions from within the airshed boundary explain from 47% to 76% of the oxidized-N deposition to the watershed drainage area. For slightly more than half of the watersheds, the emissions from the airshed explain between 60 and 70% of the deposition. When the percent explained is 70% or higher, emissions within or close to the watershed are important. When the percent explained is ~55% or lower, then long-range transport of the oxidized-N from outside the airshed to the watershed is very important.

Characteristics of reduced-nitrogen airsheds have been developed for three watersheds along the East and Gulf Coasts. These are given in Table 3. The airsheds are shown in Figure 5. The reduced-N airsheds are smaller than those for the oxidized-N, although they are still much larger than the watersheds. The two reduced-N airsheds in the mid-Atlantic region are 61% and 64% as large as the oxidized-N airsheds, whereas, the Gulf Coast reduced-N airshed is 71% as large as the oxidized-N airshed. In the Southeast, where there is more rainfall, the two airsheds appear closer in size. Surprisingly, the percent of the reduced-N deposition explained by the NH_3 emissions from the airshed is smaller than for oxidized-N, even though the range of influence for reduced-N is shorter. The percent explained for reduced-N ranges from 49-60%. The fact that as much of the reduced-N deposition is accounted for by a much smaller fraction of the Eastern North American NH_3 emissions compared to the fraction for the NO_X emissions indicates that local deposition is indeed important. However, transport is three-dimensional, and because most of the reduced-N deposition is in the form of wet

deposition, very long-range transport of small, diffuse concentrations collectively can have an important depositional impact. In addition, emissions in the central part of the continent are generally high, adding to the importance and size of a diffuse background of reduced-N entering coastal regions.

The principal airsheds provide perspective regarding the geographic source of the majority of the inorganic N-deposition to the estuaries. The emissions from within the airsheds explain a clear majority of the oxidized-N deposition and at least half of the reduced-N deposition to the watersheds. Long-range transport to the watersheds of inorganic N from hundreds of km away is clearly important for both forms of AD-N. Long-range transport is especially important for reduced-N, a conclusion somewhat contrary to conventional wisdom; but modeling sensitivity studies are consistent with observed trends in North Carolina discussed above (Dennis and Mathur 2001). Hence, conclusions based on these modeling results seem reasonable.

Biogeochemical, Trophic and Water Quality Impacts of AD-N on Estuarine and Coastal Ecosystems

Sensitivity and response of a receiving estuary to specific N inputs are dependent on interacting hydrologic, morphologic and biogeochemical characteristics. Surface area, volume and depth, combined with hydrologic throughput (flushing) determine water residence time; a key factor controlling nutrient concentrations, loading rates and biological response to N inputs. In addition, the estuary's response varies along its longitudinal salinity gradient, which strongly affects plant and animal community composition and activity. In an estuary's predominantly fresh headwaters, riverine

(terrigenous) discharge dominates new N inputs. Further downstream, in mesohaline segments of the estuary, significant fractions of the terrigenous N load are assimilated by phytoplankton and benthic flora, or microbially denitrified to biologically unreactive N_2 gas (Kennedy 1983; Nixon 1986; Seitzinger 1986; Boynton et al. 1995). Inputs of N that result from direct deposition, however, can by-pass this estuarine N "filter" (Kennedy 1983; Paerl 1995, 1997). As such, AD-N assumes an increasingly important role as a new N source in lower estuarine, sound and coastal waters below the biological N filtering zone (Fig. 1). Because of a scarcity of direct measurements, there is a great deal of uncertainty as to how the relative importance of AD-N increases beyond this zone. At present, we must rely on modeling efforts based on meteorology and the known behavior of AD-N constituents. Development and evaluation of appropriately scaled coastal depositional models and their requirements for field verification are discussed below.

The Role of AD-N in Estuarine and Coastal N Budgets

There are efforts underway to quantify wet and dry deposition at near-shore and offshore locations worldwide (GESAMP 1989; Duce 1986, 1991; ESA 1998). These efforts address estuarine and coastal systems along geographic and trophic gradients. In the U.S., gradients range from the highly impacted Northeast and Mid-Atlantic to less-impacted Gulf of Mexico and Pacific coastal regions (Castro et al. 2000). Included are systems varying in size, water residence time and trophic state, enabling researchers and managers to make comparisons of the relative importance of AD-N in N budgets, water quality and trophodynamics. The relative importance of AD-N as a "new" N source in select estuarine and near-shore coastal systems varies from ~5% in waters most heavily

impacted by terrigenous (relative to atmospheric) N inputs (e.g., Mississippi plume region of the northern Gulf of Mexico), to over 30% in waters heavily dominated by AD-N inputs (e.g., Baltic, W. Mediterranean, mid-Atlantic and Northeast US/Canadian Atlantic coastal regions). A summary of representative N-sensitive waters for which adequate data are available is provided in Table 4.

The Extended RADM was used to develop estimates of the flux of total (wet + dry) oxidized- plus reduced-N from the atmosphere to the coastal ocean over the continental shelf. The model does not include sea salt, so its influence was incorporated in a post-processing step. Assuming recent estimates of the mean diameter of sea salt aerosol of 2-5 µm for the East Coast of the U.S. are correct and apply to the Gulf Coast as well, then a reasonable assumption is that wet and dry deposition of oxidized nitrogen will be approximately equal. Dry deposition from the Extended RADM was adjusted accordingly. The results indicate that sea salt influence is clearly important to the overall flux. Deposition rates of 11, 5.6, and 5.6 kg-N ha^{-1} were calculated for the continental shelf areas of the Northeastern U.S. Coast (NE), Southeast U.S. Coast (SE) and Eastern Gulf of Mexico (East Gulf), respectively. The average rate was computed for the shelf area out to a 200 m depth isopleth. Several known model biases are expected to roughly cancel out, but there is uncertainty. These rates are considered best estimates with a likely uncertainty of ±30%. They are in the same range, but overall somewhat higher than those of Prospero et al. (1996), being 60% higher for the NE, 25% higher for the SE and the East Gulf is expected to be higher by the same percentage as for the SE. For the area covering the continental shelf from 0-200 m depth, the best estimate for annual total N flux from atmospheric deposition of inorganic N to the coastal ocean is 20 x 10^9 moles of

N, 5.5 x 10^9 moles of N, and 10 x 10^9 moles of N for the NE, SE and East Gulf, respectively. The uncertainty of ±30% applies to these estimates as well. These annual fluxes are similar to but somewhat larger than those given in Nixon et al. (1996). The flux from the atmosphere is comparable to the flux from the land (estuaries) to the continental shelf given in Nixon et al. (1996) for the NE and it is about half the flux from the land for the SE and East Gulf areas, although it is difficult to extract a precise Nixon et al. (1996) estimate for the East Gulf. Thus, the atmosphere is estimated to contribute a sizable flux of new N to the U.S. continental shelf on the Atlantic side.

The Neuse River Estuary/Pamlico Sound, NC: A Case Study of the Role of AD-N as an Estuarine "new" N Source

The Neuse River Estuary and Pamlico Sound, located in eastern North Carolina, USA (Fig. 6) are representative of shallow N-sensitive estuarine and coastal waters under the influence of growing N inputs and accelerating eutrophication (Copeland and Gray 1991; Bricker et al. 1999). The Pamlico Sound system and its subestuaries are the 2nd largest estuarine complex in the US (5,300 km^2), and represent a major fisheries nursery supporting approximately 80% of the mid-Atlantic coastal commercial and sports fisheries (Copeland and Gray 1991). Efforts are under way to examine the role of AD-N in the nutrient budgets and eutrophication dynamics of these waters.

The Neuse and other subestuaries of Pamlico Sound exhibit widespread and chronic N-limitation (Hobbie and Smith 1975; Kuenzler et. al. 1979; Copeland and Gray 1991; Paerl 1983; Rudek et al. 1991). Anthropogenic N enrichment to these estuaries has been closely linked to eutrophication, algal blooms, hypoxia/anoxia and associated

declines in water quality and fisheries resources (Copeland and Gray 1991; Christian et al. 1991; Paerl et al. 1995, 1998). The Neuse Estuary receives N inputs from a mosaic of upstream and upwind agricultural, urban and industrial sources. Fossil fuel combustion and agricultural and industrial N emissions represent a significant and growing source of new N to this system (Paerl and Fogel 1994), reflecting national and worldwide trends (Duce 1986; Luke and Dickerson 1987; Asman 1994; Paerl 1995; Holland et al. 1999). Depending on the relationship between watershed-estuary surface areas, degree of watershed N-retention, and proximity of atmospheric sources, an important fraction of atmospherically-derived N is directly deposited on the estuary (Paerl et al. 1995).

The Neuse River Estuary has been the focus of a 3 year (1996-1999) study comparing the terrigenous point and non-point sources with wet AD-N flux measurements (NH_4^+, NO_3^- and organics) from 6 sampling locations in the watershed. This AD-N study used a N retention model (Table 5) and an in-stream degradation model (Table 6) to estimate the amount of indirect N deposition reaching the estuary. This value, combined with measured direct deposition fluxes allowed for the comparison of the total (indirect + direct) AD-N flux to the total “new” N flux to the estuary. This study has shown that wet AD-N contributes between 15 and 32% of the “new” or external N flux to the estuary on an annual basis (Table 7), with direct deposition to the estuary alone accounting for 5% of the total “new” N flux. Deposition is fairly evenly distributed between NH_4^+, NO_3^- and organic N. This AD-N flux varies seasonally with the highest fluxes occurring during the summer months, which may be driven by seasonal changes in emissions (Whitall 2000; Whitall and Paerl submitted).

The Neuse R. Estuary supplies approximately 30% of the Sound's freshwater inflow. Downstream of the Neuse's mesohaline N stripping zone, AD-N may represent as much as 40% of new N inputs to the open Pamlico Sound (Paerl and Fogel 1994; Paerl et al. 1995; Whitall and Paerl submitted).

In the context of ecosystem function, AD-N inputs must be integrated into the overall scheme of N cycling and resultant productivity/eutrophication responses (Fig. 7). This means that we must consider impacts of AD-N contemporaneously and contiguously with internal N cycling (i.e., sediment-water column exchange and regeneration of N), which is known to play a significant role in controlling N availability, productivity and resultant trophic state of this and other shallow estuaries (Neilson and Cronin 1981; Nixon 1981; Christian et al. 1991; Rizzo et al. 1992).

AD-N and Phytoplankton Production Dynamics

Atmospheric wet and dry deposition introduce into estuaries a variety of biologically-available inorganic compounds (NO_3^-, NH_4^+; DIN), most of which result from human activities (Likens et al. 1974; Galloway et al. 1994). In addition, organic nitrogen (ON) comprises an additionally significant fraction (from 15 to over 30%) of atmospheric deposition (wet and dry) in coastal watersheds (Correll and Ford 1982; Skudlark and Church 1993; Cornell et al. 1995; Peierls and Paerl 1997; Whitall and Paerl submitted). Although the sources and composition of atmospheric ON are poorly known, recent work (Peierls and Paerl 1997; Seitzinger and Sanders 1999) indicates AD-ON constituents are biologically utilized and hence should be included in eutrophication assessments.

Both phytoplankton productivity and community composition respond to chemically diverse AD-N sources. Various bioassay and field surveys show that enrichment with the major atmospheric N constituents NH_4^+ and NO_3^- at natural dilutions results in enhanced phytoplankton primary production and increased biomass (Paerl 1985, 1995; Willey and Paerl 1991; Paerl and Fogel 1994). NO_3^- and NH_4^+ uptake rates vary spatially and seasonally in the Neuse River, suggesting differential community responses to varying N sources (Boyer et al. 1994). Studies on North Sea phytoplankton communities demonstrated a differential responses to various N sources; providing a mechanism for the structuring of these communities (Stolte et al. 1994). Differential N uptake and growth response to NH_4^+ vs. NO_3^- have been attributed to contrasting energy requirements for the assimilation of these compounds (Eppley et al. 1969; Turpin 1991). Under light-limited conditions encountered in turbid estuaries (Cloern 1987), NH_4^+ may be preferred because the energy requirements for using this reduced N source are less than those for NO_3^- (Syrett 1981; Dortch 1990). In light-limited waters, motile phytoplankton groups (e.g., dinoflagellates, cryptomonads) are capable of migrating to near surface depths, ensuring access to radiant energy needed to reduce NO_3^- to NH_4^+, a critical step for incorporating this oxidized form of N into biosynthetic pathways and growth. In contrast, non-motile taxa must cope with deeper, lower irradiance waters, possibly limiting NO_3^- uptake and thus NH_4^+ uptake. Intrinsic physiological differences in N uptake among different phytoplankton taxa exist (c.f., Eppley et al. 1969; Stolte et al. 1994); these may lead to contrasting taxonomic responses to different N sources (Van Rijn et al. 1986, Collos 1989; Riegman 1998). Under conditions of restricted N

availability, characteristic of many N-limited estuaries, such differences can lead to intense competition for either NH_4^+, NO_3^- or organic N.

Bioassay experiments have shown that major estuarine phytoplankton functional groups (e.g., diatoms, dinoflagellates, cryptomonads, cyanobacteria, chlorophytes) may exhibit different growth responses to varying N sources and mixtures thereof (Harrington 1999). Differential responses are not consistent in time and space however. Other complex environmental factors, including light availability, water column mixing depth, water residence time and temperature interact with phytoplankton community N uptake dynamics and growth rates (Cloern 1987, 1999; Richardson et al. submitted). Peierls and Paerl (1997) and Seitzinger and Sanders (1999) showed that atmospherically-derived DON also stimulated bacterial and phytoplankton growth. Atmospherically derived DON may selectively stimulate growth of facultative heterotrophic and photoheterotrophic phytoplankton taxa (e.g., dinoflagellates and cyanobacteria) (Neilson and Lewin 1978; Antia et al. 1991; Paerl 1991).

Taxa-selective phytoplankton responses to specific N inputs may induce specific changes at the zooplankton, herbivorous fish, invertebrate and higher consumer levels (i.e., bottom up effect). Shifts in phytoplankton community composition may also alter the flux of C, N, P and other nutrients as well as oxygen in the estuary (top down effect). For example, if poorly grazed, bloom-forming phytoplankton species dominate nutrient utilization and growth, their biomass is more likely to be deposited in the sediments than transferred up the food chain. This may enhance sediment oxygen consumption, hypoxia and anoxia (Fig. 8). Conversely, readily consumed (grazed) phytoplankton species will more effectively support production at higher trophic levels. This will promote both

export (via migratory fish) and respiration of their biomass in the water column, thereby reducing sediment oxygen demand. These differential pathways and fates of primary production affect estuarine nutrient cycling, water quality and habitability. For example, inedible, sedimented phytoplankton blooms will, by virtue of exacerbating hypoxia potentials, lead to enhanced N (as NH_4^+), P (as PO_4^{3-}) and other nutrient releases from the sediments (Fig 8). In addition, denitrification potentials may be affected. In poorly flushed estuaries this feedback loop could support bloom persistence by ensuring continuing nutrient regeneration. This scenario is promoted by warm, vertically stratified, long residence time conditions.

A need exists to characterize and quantify sources, routes and fates of AD-N, and their interaction with other essential nutrients, as they impact coastal production, eutrophication and water quality dynamics over varying spatial and temporal scales. Changing (largely increasing) amounts of the biologically available reduced and oxidized forms of N reflect changing land use and human activities, including fossil fuel combustion, biomass burning, generation and application of agricultural wastes, use of N-based synthetic fertilizers. Due to changes in emission sources (i.e., agricultural, urban, industrial), certain forms of AD-N are increasing relative to others. One example is intensive animal (poultry, swine, cattle) operations in Western Europe and the U.S. mid-Atlantic region, which have led to elevated ammonium deposition rates (Holland et al. 1999). In the US, depositional changes are reflected in long-term (since the mid to late ‘70s) data from the network of National Acid Deposition Program (NADP) sites including one located in Sampson County, coastal North Carolina (NC-35), a region supporting a high density of industrial-style hog farms (Fig. 9). This location illustrates a

precipitous rise in annual NH_4^+ deposition. In addition, NH_4^+ deposition has increased relative to NO_3^+ deposition (Fig 9), reflecting a national trend in agricultural regions (e.g., upper Midwest) (Fig. 1). The increasing ratio of in NH_4^+ to NO_3^+ deposition reflects the rapid growth in intensive animal operations and simultaneous controls on NO_x emissions (NADP 2000).

Increases in the ratios of ammonium to nitrate as well as other AD-N sources may result in community compositional changes, because as discussed previously, different forms of N may be differentially utilized by phytoplankton and other microorganisms. Accordingly, we are concerned about both the amounts and composition of AD-N inputs because they can impact algal production and community composition, translating into differential water quality impacts (e.g. harmful vs. non-harmful algal blooms).

It might be argued that the form in which "new" N enters an estuary is irrelevant because it may be transformed via in-system N cycling before it is utilized by phytoplankton. However, in most N-limited estuarine and coastal systems "new" N inputs are very rapidly (within hours in the Neuse R. Estuary) assimilated by resident N-starved phytoplankton (Pinckney et al. 1999). As such, large episodic inputs of "new" N, such as those delivered by rainstorms, may be rapidly utilized by resident phytoplankton (Pinckney et al. 1999). Therefore, the chemical form in which this "new" is delivered may determine phytoplankton community and ecosystem responses.

Harrington (1999) experimentally examined phytoplankton community response at the group level to different forms of nitrogen (N) under different irradiance levels. Bioassays were designed in which water samples from the Neuse R. Estuary were amended with equimolar amounts of N in different forms (ammonium-only, nitrate-only,

urea-only, and combined ammonium, nitrate, and urea) then either incubated at ambient irradiance or shaded to 10% of ambient irradiance. High performance liquid chromatography (HPLC)-based diagnostic photopigment analyses (Millie et al. 1993) were used to characterize phytoplankton community responses, including the relative abundance of major algal groups (diatoms, dinoflagellates, cryptomonads, cyanobacteria, chlorophytes). Bioassays performed in the spring of 1998 show that different forms of N caused community shifts at both 100% and 10% of ambient irradiance, reflecting the range of natural light conditions in the estuary. Results indicated that additions of different forms of N result in shifts in phytoplankton community composition; these shift were also reliant on irradiance regimes (Fig. 10). The implications of such shifts for food web alterations and harmful algal bloom potentials are under further investigation.

In addition, enrichment of N relative to other essential nutrients alters the stoichiometric ratios and availabilities of those nutrients. In the Chesapeake Bay and its tributaries, excessive anthropogenic N loading delivered during spring high runoff "freshet" is a chief causative agent for periods of P limitation and co-limitation (Boynton et al. 1995). In the reduced runoff summer months, when N loading decreases and denitrification assumes an important N loss term, productivity in this system is more exclusively N-limited. Studies in the Mississippi plume region of the northern Gulf of Mexico (Rabalais et al. 1996) demonstrate the impacts of excessive N enrichment from the Mississippi River on eutrophication potentials and availability of other growth-limiting nutrients. In particular, the availability of silicon (Si), which is required by diatoms, has been strongly affected. While N enrichment has closely followed human expansion in the Mississippi basin, Si concentrations have not increased. N-driven

eutrophication has increased demands of Si, much of which is biogenically sedimented. As a result, Si resupply rates have not kept up with productivity demands, causing increased Si limitation and decline in diatom dominance. This impacts grazing and higher trophic levels (fisheries), which are dependent on diatom production. Atmospheric deposition, being enriched in N relative to Si (or P) would have a tendency to exacerbate such specific nutrient limitations and potential phytoplankton community shifts.

Atmospheric deposition may also be enriched with metals, either originating from dust, industrial effluents and volcanism (Church et al. 1984; Duce 1986). Trace metal enrichment (especially iron e.g. Fe) in AD and other anthropogenic sources (dust, industrial emissions) may synergistically interact with N to stimulate coastal production and blooms (Zhuang et al. 1995; Takeda et al.; 1995, Paerl et al. 1999). This synergistic "Geritol" effect may exceed that observed with N alone, making atmospheric deposition a particularly potent stimulant of marine primary production (Paerl et al. 1999). This finding combined with the fact that atmospheric-deposition of N, Fe and other nutrients is a significant source of "new" nutrients extending seaward beyond estuarine nutrient stripping zones creates a basis for suspecting this source to play key roles in coastal eutrophication and harmful algal bloom dynamics (Zhang 1994; Paerl 1997).

<u>What do we need to know from research and management perspectives?</u>

AD-N warrants close scrutiny and management from water quality, habitability and fisheries resource perspectives. Furthermore, management of N emissions, transport and deposition must be incorporated in air/watershed and larger-scale nutrient

management schemes. The scale of AD-N management to be considered in combination with watershed management is geographically quite encompassing. This is suggested by the overlap of the oxidized-N airsheds of widely-spaced estuaries shown in Figures 3 and 4 and the broad spatial coverage of the reduced-N airsheds shown in Figure 5. In the case of oxidized airsheds for the mid-Atlantic region there is overlap with at least six contiguous watersheds (Fig. 11). A super airshed is defined as the outer envelope of the oxidized-N airshed of the first 11 watersheds in Table 1 (New England and Mid-Atlantic region). The percent of oxidized-N deposition explained by this super airshed is greater than 80% for a majority of the 11 watersheds. This super region for the East Coast covers 20 States of the Eastern U.S. and overlaps part of the eastern Mississippi drainage area. A similar enhancement of the percent oxidized-N deposition explained occurs for the Gulf Coast estuaries with the construction of a super airshed based on the Gulf Coast and Southeast airsheds. It would appear very difficult for a watershed or state to have a major effect on AD-N if acting alone. Thus, efforts to address coastal AD-N management need to be as large as the multi-state regional (and national) air pollution programs for ozone and fine particulates spawned by the 1990 Clean Air Act Amendments to be efficient and effective.

In the context of the coastal zone, the following research and management questions and needs emerge:

1) Budgetarily, what is the contribution of AD-N relative to other “new” and regenerated N sources in <u>specific</u> N sensitive water bodies? This question should be pursued on regional (overlapping air- and watersheds), national (i.e., regional comparisons) and international (e.g., Atlantic Seaboard) levels.

2) What are the relative biogeochemical and trophic importance and roles of AD-N along the gradient spanning estuarine, coastal and open ocean waters?
3) What are the quantitative and qualitative ramifications of specific AD-N constituents (DIN, DON, PON) in terms of biogeochemical and trophic responses along this gradient?
4) There is a need to temporally and spatially couple sources (emission), routes of transport, deposition and biological response of atmospheric N. Development of appropriately-scaled process-level models capable of coupling sources to transport and fate is needed.
5) Utilizing a combined experimental and modeling approach, evaluate acute vs. chronic AD-N biogeochemical and trophic impacts on estuarine, coastal and oceanic waters.
6) Determine possible spatio-temporal linkages between AD-N and other atmospheric nutrient inputs (Fe, P, trace elements) and harmful algal bloom dynamics
7) Incorporate information from 1-6 into regional and global assessments of the roles and impacts of AD-N on marine productivity, trophic structure and function and nutrient (N, C, P, etc.) cycling. In addition, AD-N impacts on air-sea exchange of N, C and other trace gases should be evaluated and factored into global budgets.

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Table 1: The physical-chemical characteristics of major US Atlantic and Gulf Coast Airsheds.

Characteristics of Oxidized-Nitrogen Airsheds					
Watershed	Size (km^2)	Size Factor Over Watershed Area	% Ox-N Deposition Explained	Airshed NOx Emissions as % of E. North American	Efficiency of Deposition %Dep. per %Emiss.
Casco Bay	624,000	244	47	10	4.7
Great Bay	547,200	214	60	13	4.6
Narragansett Bay	595,200	138	73	18	4.1
Long Island Sound	905,600	22	70	23	3.0
Hudson/Raritan Bay	912,000	22	62	25	2.5
Barnegat Bay	505,600	361	67	16	4.2
Delaware Bay	729,600	22	75	26	2.9
Delaware Inland Bays	326,400	584	52	12	4.3
Chesapeake Bay	1,081,600	6.5	76	34	2.2
Pamlico Sound	665,600	25	63	18	3.5
Winyah Bay	886,400	19	69	24	2.9
Charleston Harbor	806,400	20	56	18	3.1
St. Helena Sound	588,800	48	59	11	5.4
Altamaha	678,400	18	68	13	5.2
Tampa Bay	256,000	45	76	5	15.2
Apalachee Bay	441,600	31	50	9	5.6
Apalachicola Bay	812,800	16	69	17	4.1
Mobile Bay	992,000	8.7	68	17	4.0
Lake Pontchartrain	659,200	17	63	11	5.7
Barataria-Terrebonne	409,600	55	63	8	7.9

Table 2. Summarized Characteristics of Principal Airsheds for Oxidized-Nitrogen Deposition.

Percentiles	Principal Ox-N Airshed Area (km^2)	Size Factor Over Watershed Area	% Ox-N Deposition Explained by Airshed Emissions	Airshed NO_X Emissions as % of E. North American Emissions
Maximum	1,081,600 Chesapeake Bay	584 Delaware Inland Bays	76 Chesapeake Bay Tampa Bay	34 Chesapeake Bay
80th	896,000 Long Island Sound Winyah Bay	176 Great Bay Narragansett Bay	71.5 Narragansett Bay Long Island Sound	23.5 Winyah Bay Long Island Sound
50th	662,000 Pamlico Sound Lake Pontchartrain	23.5 Pamlico Sound Long Island Sound	65 Barnegat Bay Pamlico Sound	16.5 Apalachicola Bay Barnegat Bay
20th	474,000 Barnegat Bay Apalachee Bay	17.5 Altamaha Lake Pontchartrain	57.5 St. Helena Sound Charleston Harbor	10.5 St. Helena Sound Casco Bay
Minimum	256,000 Tampa Bay	6.5 Chesapeake Bay	47 Casco Bay	5 Tampa Bay
$80^{th}/20^{th}$	1.9	10.1		
? (80th-20th) Spread as % of 50th	±32%	na	± 11%	± 39%

Table 3. Characteristics of Principal Airsheds for Reduced-Nitrogen Deposition.

Watershed	Principal Red-N Airshed Area (km^2)	Red-N Area as % of Ox-N Area	% Red-N Deposition Explained by Airshed Emissions	Airshed NH_3 Emissions as % of E. North American Emissions
Chesapeake Bay	688,000	64%	55%	11%
Pamlico Sound	406,400	61%	60%	6.8%
Apalachee Bay	313,600	71%	49%	4.3%

Table 4: Estimated contributions of atmospheric deposition of N (AD-N) to "new" N inputs in diverse estuarine, coastal and open ocean waters. When identified, the sources (wet;W and/or dry deposition;D) and chemical forms (inorganic;I and/or organic;O) of AD-N are indicated. Informational sources and references are provided.

Receiving Waters	% of "new" N as AD-N	References
Baltic Sea (Proper)	~ 30 W+D, I	Elmgren 1989, Ambio 1990
Kiel Bight (Baltic)	40% W, I	Prado-Fiedler 1990
North Sea (Coastal)	20-40% W+D, I	GESAMP 1989
Western Mediterranean Sea	10-60% W, I	Martin et al. 1989
Waquoit Bay, MA, USA	29% W, I+O	Valiela et al. 1992
Narragansett Bay, USA	12% W, I+O	Nixon 1995
Long Island Sound, USA	20% W, I+O	Long Island Sound Study 1996
New York Bight, USA	38% W, I+O	Valigura et al. 1996
Barnegat Bay, USA	40% W, I+O	Moser 1997
Chesapeake Bay, USA	27% W, I+O	Chesapeake Bay Program 1994
Rhode River, MD, USA	40% W, I+O	Correll and Ford 1982
Neuse River Estuary, NC, USA	34% W, I+O	Whitall 2000
Pamlico Sound, NC, USA	~ 40% W+D, I	Paerl and Fogel 1994
Sarasota/Tampa Bay, FL, USA	30% W+D, I	Sarasota Bay NEP 1996
Mississippi River Plume, USA	2-5%, W+D, I+O	Goolsby et al. 2000

Table 5: Nitrogen retention model based on GIS land cover data for the Neuse River Watershed (USGS). N retention values are from Tyler et al. (1988), Hinga et al. (1991), Fisher and Oppenheimer (1991) and Valigura et al. (1996). The Best Estimate value is bounded by the Highest and Median reported retention values (lowest reported values produced unrealistically high AD-N fluxes to estuary).

Model	**Percent N retained by land**	**Percent N retained by land**	**Percent N retained by land**	**Percent N retained by land**	**Percent N retained by land**
	Forest	Crop	Pasture	Urban	Other
Highest	100	99.97	99.96	95.3	75
Median	90	80	85	60	60
Best Estimate	99	96	97	70	75

Table 6: In-stream degradation model. Model assumes that the degree to which an N parcel is degraded due to denitrification and settling is directly proportional to travel distance in stream. Model developed by the North Carolina Department of Environment and Natural Resources, Division of Water Quality. Refer to figure 6 for the locations of zones 1 through 4.

Region	**Percent N reaching estuary**
Zone 1 (Above Falls Lake Dam)	10
Zone 2 (Falls Lake Dam to Contentnea Creek)	50
Zone 3 (Contentnea Creek to Streets Ferry)	70
Zone 4 (Below Streets Ferry)	100

Table 7: The contribution of AD-N to the total "new" nitrogen flux to the Neuse River Estuary. Columns 1, 5 and 6 are measured values and columns 3 and 7 are derived from model outputs (refer to Tables A and C). Total "new" flux to the estuary (column 6) is equal to the riverine flux measured at the head of the estuary (which inherently includes indirect AD-N), plus point and non-point sources below the head of the estuary and plus direct AD-N to the estuary.

Indirect Wet AD-N Deposition (Mg/yr)	**Model Used**	**Indirect AD-N Exported to Rivers (Mg/yr)**	**Indirect AD-N Reaching Estuary (Mg/yr)**	**Direct AD-N to Estuary (Mg/yr)**	**Total "new" N Flux to Estuary (Mg/yr)**	**AD-N as % of total "new" N flux**
15,026	Highest	863	718	385	7.408	15
15,026	Median	2,722	1,953	385	7.408	32
15,026	Best Estimate	1,861	1,412	385	7.408	24

FIGURE CAPTIONS

Figure 1. Schematic diagram showing the interactions of airshed N emissions and deposition with estuarine physical, chemical, and biological processes.

Figure 2. Estimated annual wet deposition of nitrate and ammonium for the mainland USA during the intervals 1985-89 and 1995-99. Annual N deposition is given as millimoles per square meter. Data are from the National Acid Deposition Program (NADP) network of collection sites. Figure courtesy of the NADP (2000).

Figure 3. Oxidized-Nitrogen Principal Airsheds for the U.S. East Coast: Narragansett Bay, Hudson R./Raritan Bay, Chesapeake Bay, Pamlico Sound, Altamaha Sound.

Figure 4. Oxidized-Nitrogen Principal Airsheds for the U.S. Gulf Coast: Tampa Bay, Apalachee Bay, Mobile Bay, either Lake Pontchartrain or Barataria-Terrebone.

Figure 5. Reduced-Nitrogen Principal Airsheds for Chesapeake Bay, Pamlico Sound, Apalachee Bay.

Figure 6. Location of the Neuse River Estuary and Pamlico Sound, Eastern North Carolina. The watershed boundaries for both systems are shown, as are the atmospheric deposition collection sites located in watershed zones used to estimate annual atmospheric N deposition inputs to the Neuse R. Estuary (values given in table 6). Neuse River watershed zones for the in-stream degradation model (Table 6) are also shown.

Figure 7. Conceptual diagram illustrating the role of atmospheric deposition of nitrogen in estuarine N cycling.

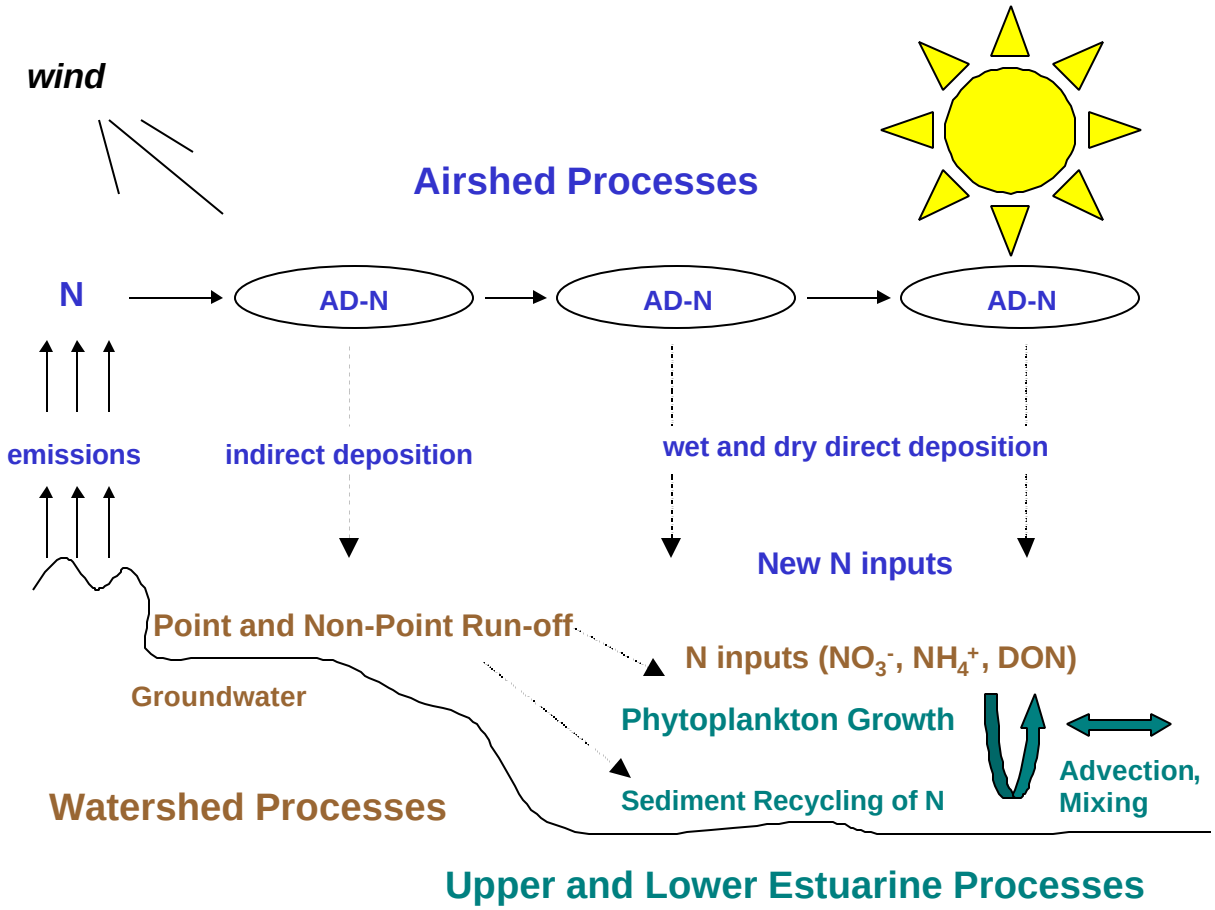
Figure 8. Conceptual diagram illustrating the impacts of changes in phytoplankton composition on estuarine carbon flux, sediment oxygen demand and nutrient cycling in response to eutrophication. If an increase in externally-supplied or "new" nutrient inputs lead to selective stimulation of phytoplankton that are not readily grazed and transeferred up the food web (e.g., nuisance cyanobacteria and dinoflagellates), these phytoplankton will proportionately increase the sediment oxygen demand (SOD) and hypoxia and anoxia burden of the estuary. By contrast, if readily-consumed phytoplankton are favored, sediment oxygen demand will be reduced.

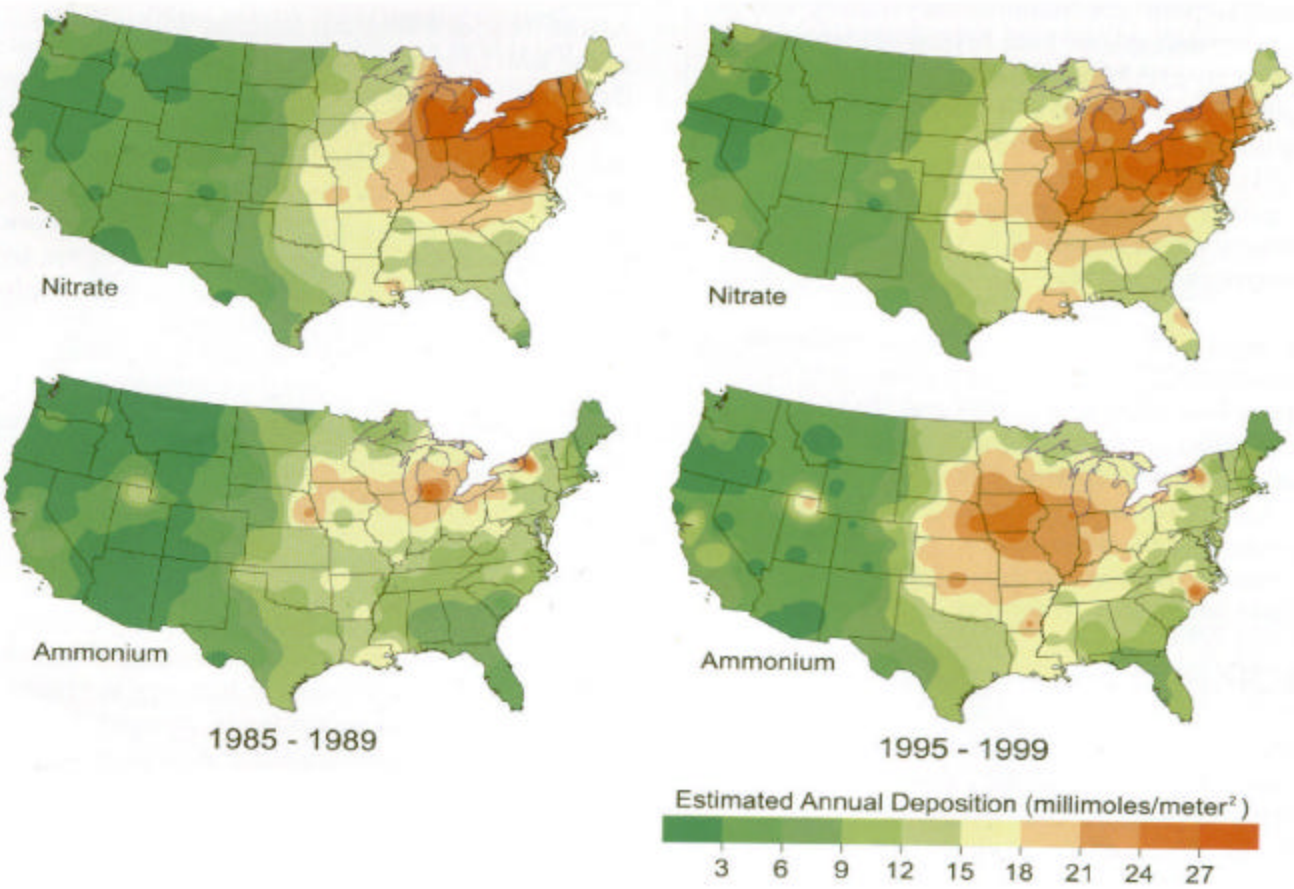
Figure 9. A 20 year record (1978-1998) of NH_4^+ and the ratio of NH_4^+ to NO_x in wet deposition at NADP site NC 35, Sampson County, NC

Figure 10. Phytoplankton community composition in bioassays performed in April/May 1998. N additions were equimolar, and identical sets of samples were incubated at 100% and 10% of ambient irradiance under natural irradiance and temperature conditions. The pie represents the total amount of chlorophyll a, which is partitioned among the major algal groups (Adapted from Harrington 1999).

Figure 11. Oxidized-Nitrogen Airsheds that Significantly Overlap and Whose Outer Boundary Comprises a Northeast Super-region: Hudson/Raritan Bay, Barnegat Bay, Delaware Bay, Delaware Inland Bays, Chesapeake Bay, Pamlico Sound, Winyah Bay.

1093


wind
Airshed Processes
N
AD-N
AD-N
AD-N
emissions
indirect deposition
wet and dry direct deposition
New N inputs
Point and Non-Point Run-off
N inputs (NO_3^-, NH_4^+, DON)
Groundwater
Phytoplankton Growth
Advection, Mixing
Sediment Recycling of N
Watershed Processes
Upper and Lower Estuarine Processes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Nitrate
Ammonium
Ammonium
1985 - 1989
1995 - 1999
Estimated Annual Deposition (millimoles/meter²)
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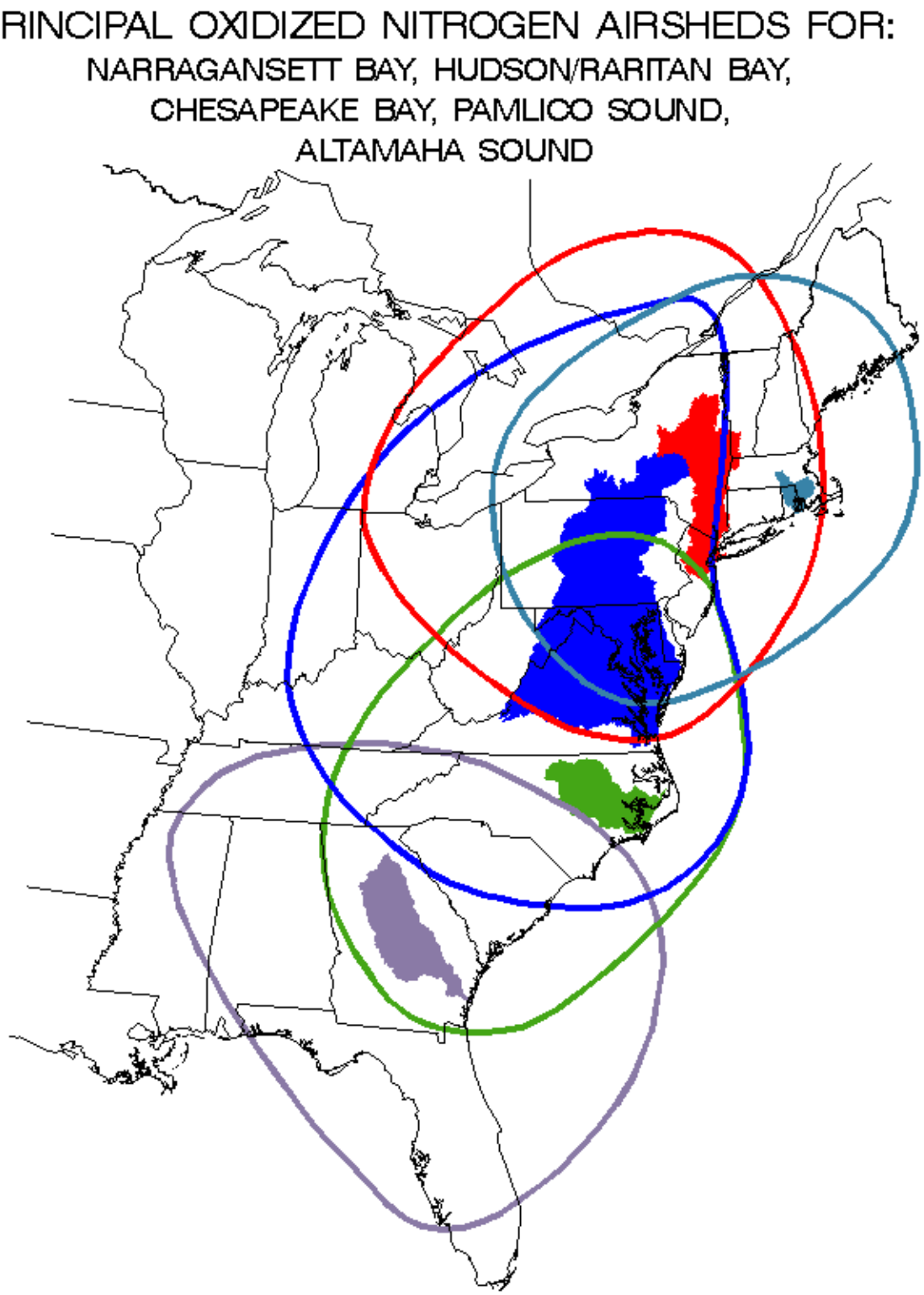
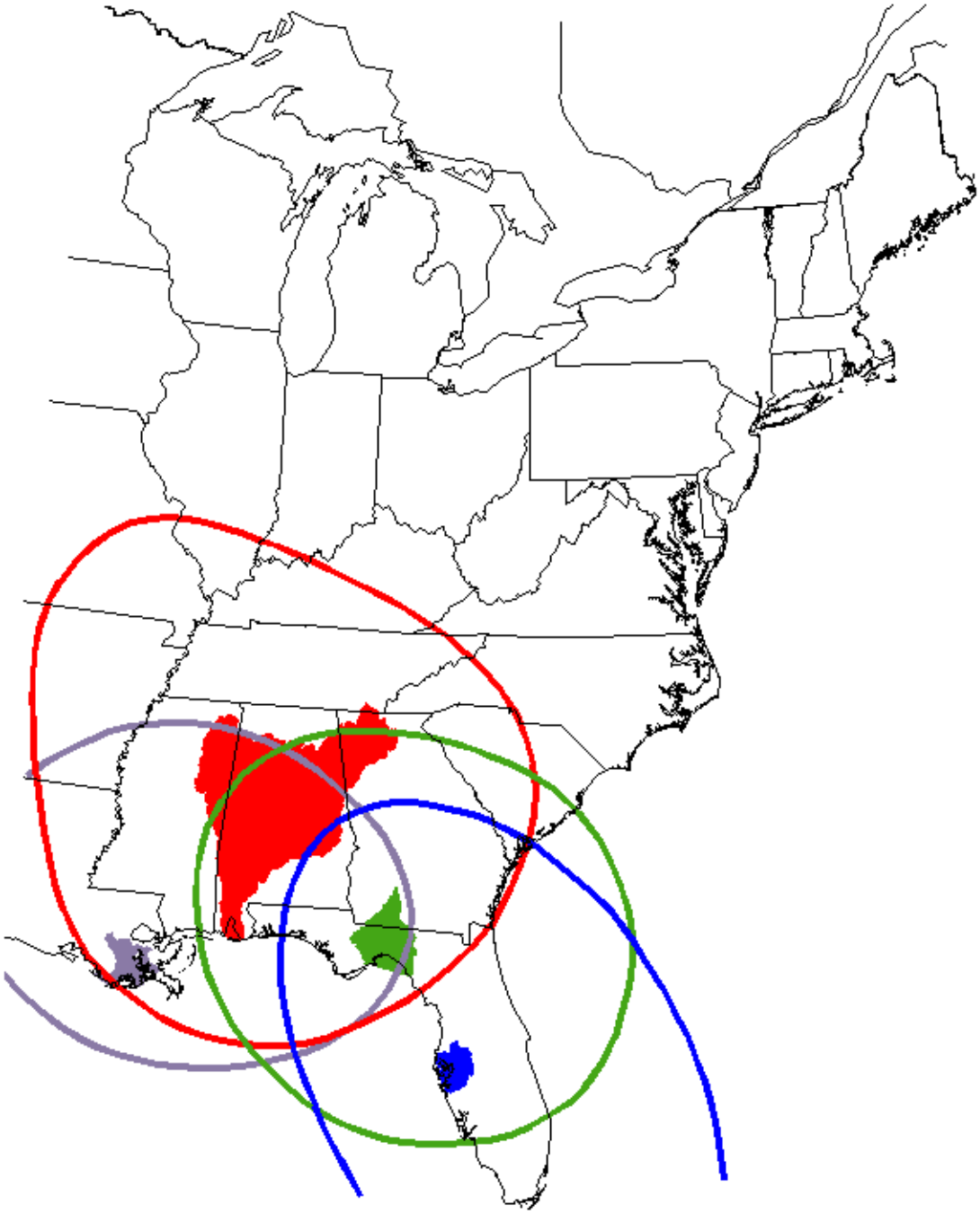

PRINCIPAL OXIDIZED NITROGEN AIRSHEDS FOR:
NARRAGANSETT BAY, HUDSON/RARITAN BAY,
CHESAPEAKE BAY, PAMLICO SOUND,
ALTAMAHA SOUND

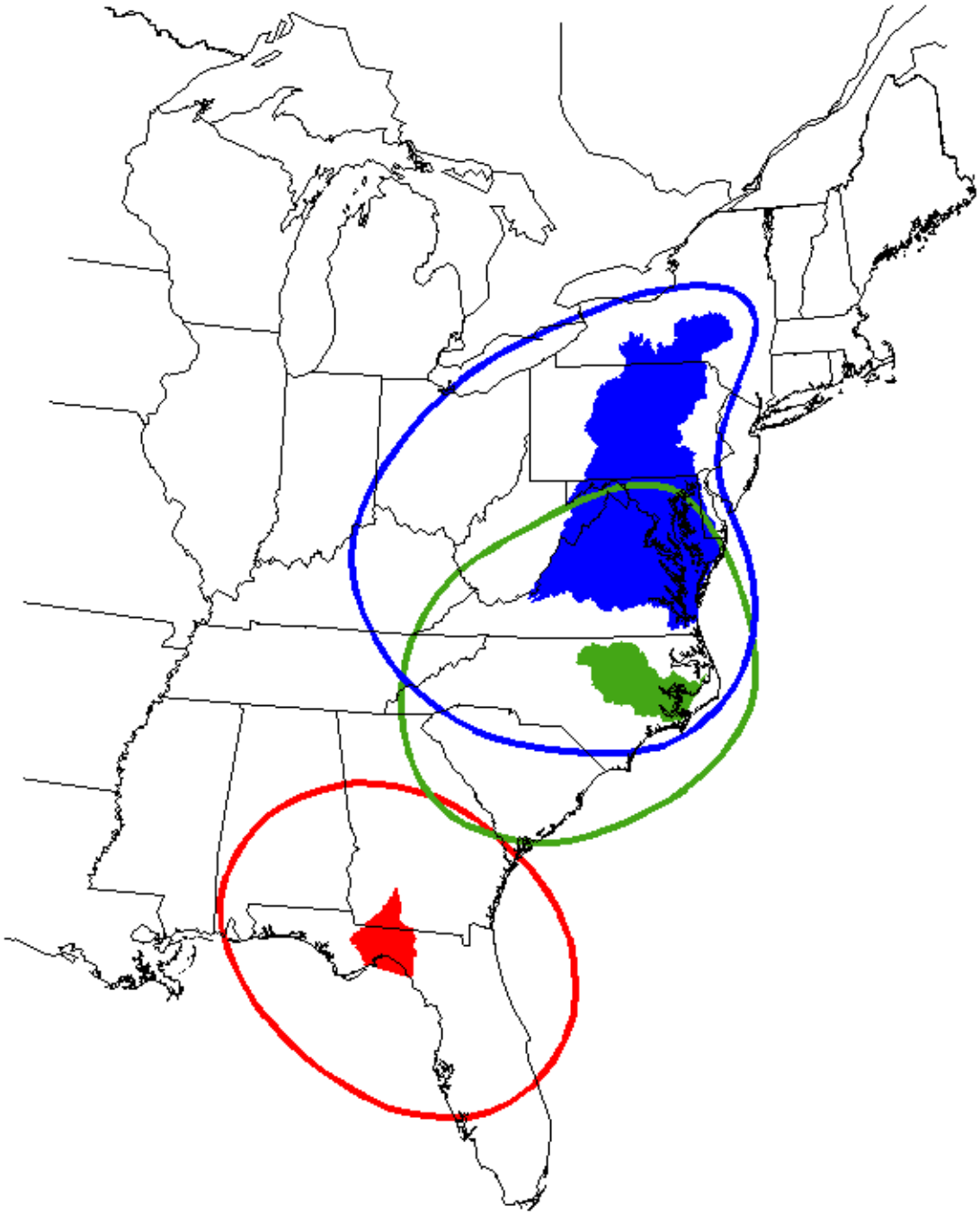
1098

PRINCIPAL OXIDIZED NITROGEN AIRSHEDS FOR:
TAMPA BAY, APALACHEE BAY,
MOBILE BAY, BARATARIA—TERREBONNE BAY



1099

PRINCIPAL REDUCED NITROGEN AIRSHEDS FOR:
CHESAPEAKE BAY, PAMLICO SOUND,
APALACHEE BAY



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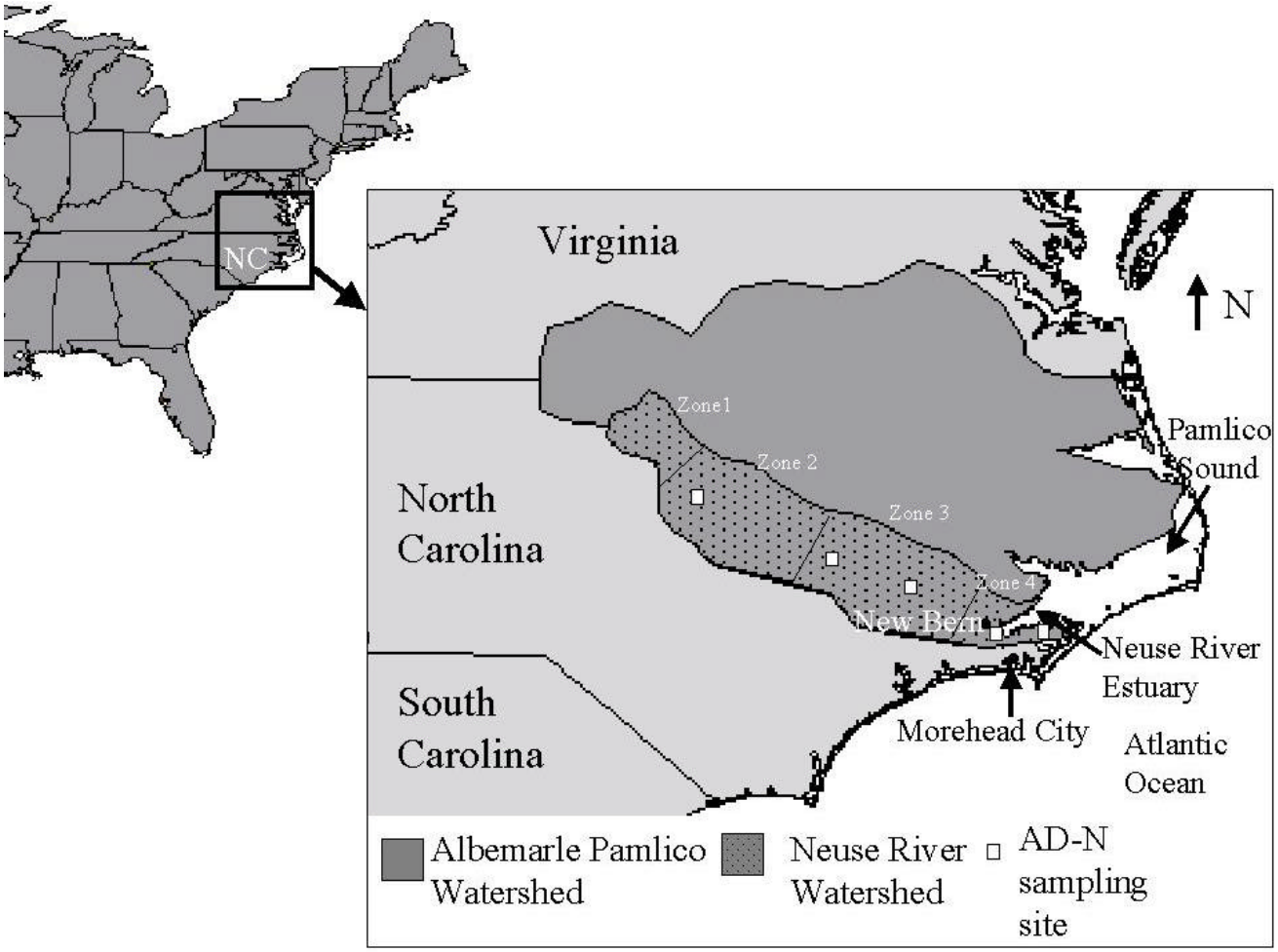
NC
Virginia
N
Zone1
Zone 2
Zone 3
Zone 4
Pamlico Sound
North Carolina
New Bern
Neuse River Estuary
South Carolina
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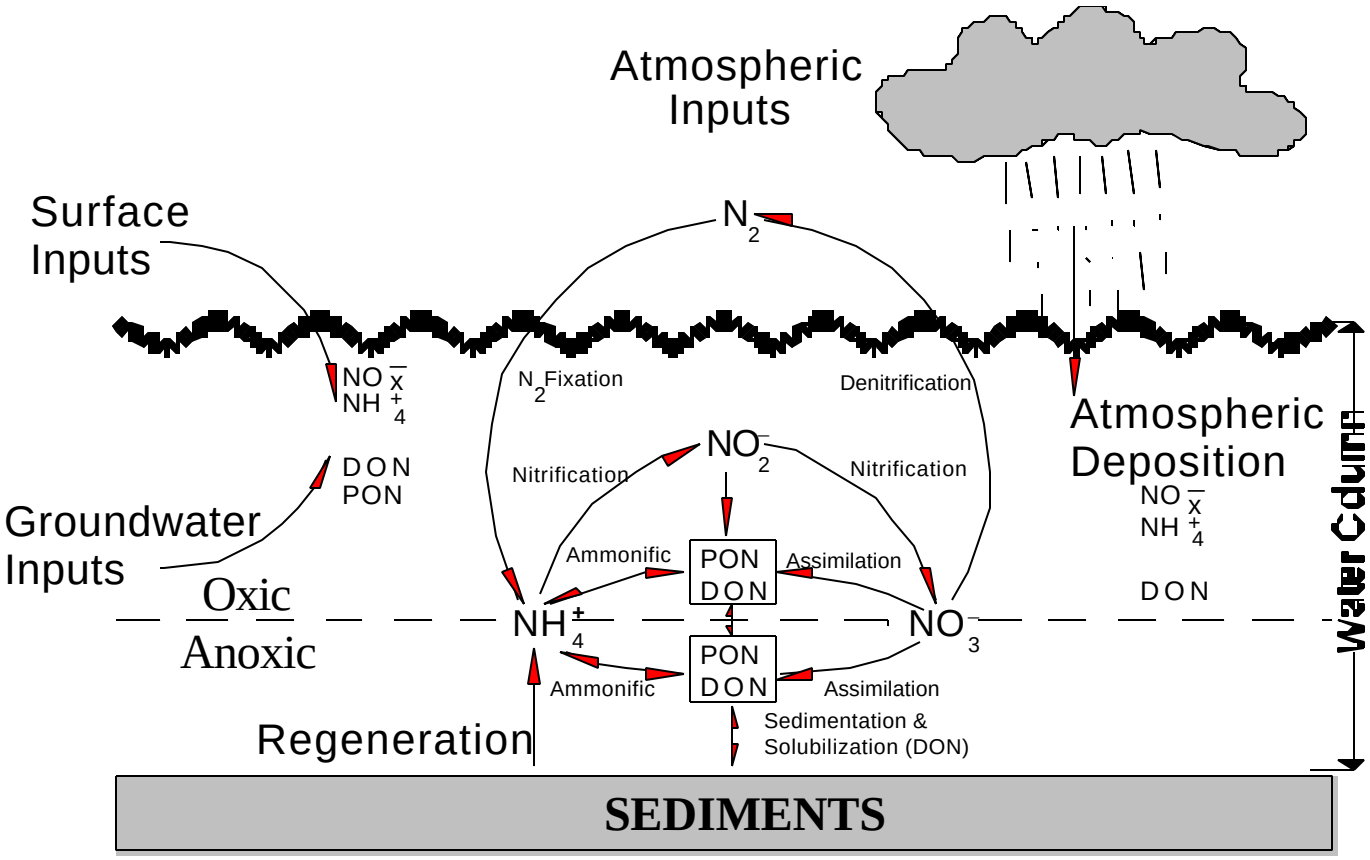
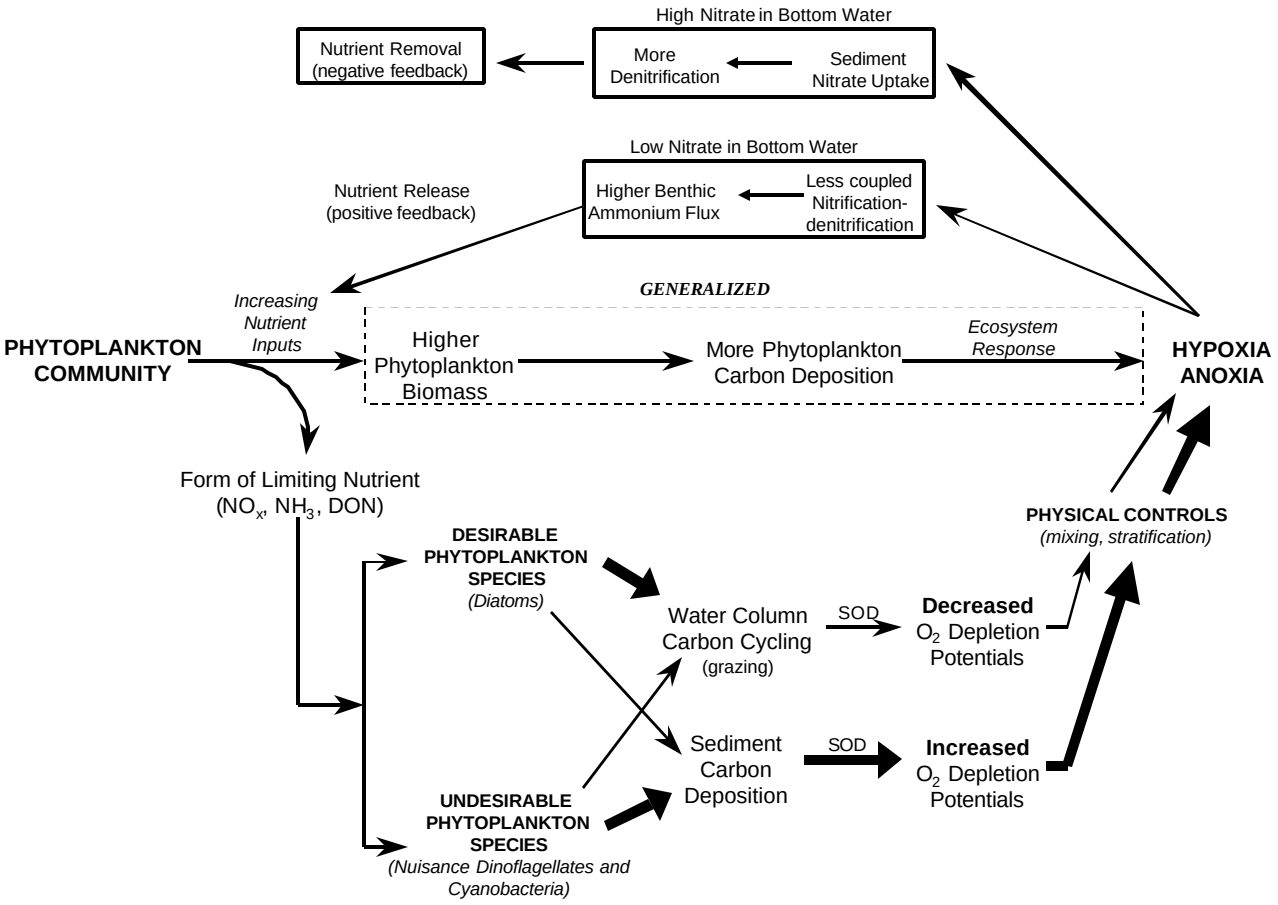
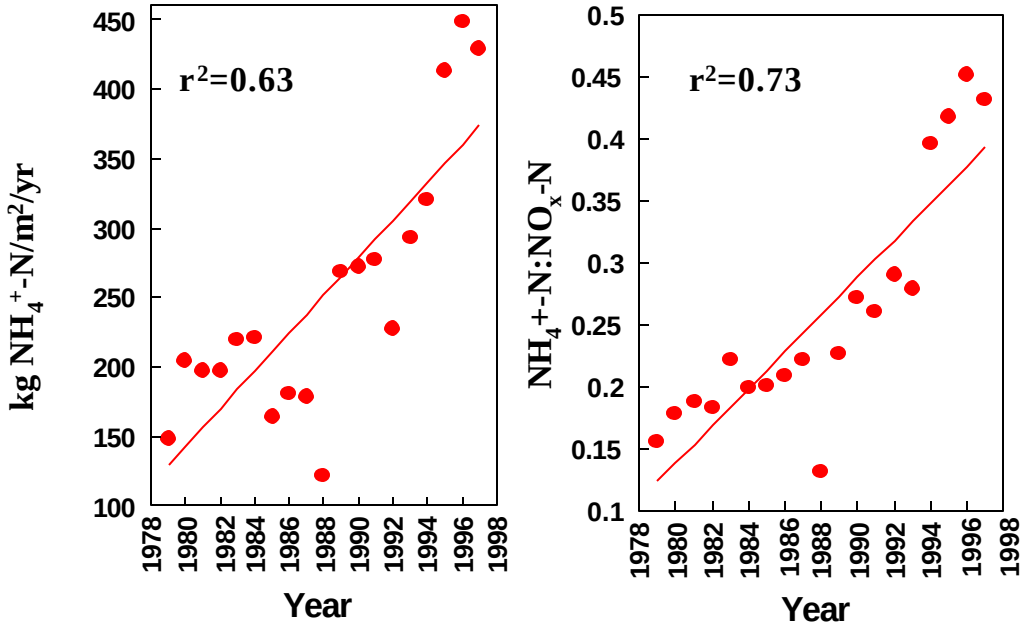
Albemarle Pamlico Watershed
Neuse River Watershed
AD-N sampling site

1103


Atmospheric Inputs
Surface Inputs
N_2
NO_x^-
NH_4^+
N_2 Fixation
Denitrification
Atmospheric Deposition
NO_x^-
NH_4^+
DON
PON
NO_2^-
Nitrification
Nitrification
Groundwater Inputs
Ammonific
PON
DON
Assimilation
DON
Oxic
Anoxic
NH_4^+
NO_3^-
PON
DON
Ammonific
Assimilation
Sedimentation & Solubilization (DON)
Regeneration
Water Column
SEDIMENTS

1104


High Nitrate in Bottom Water
Nutrient Removal (negative feedback)
More Denitrification
Sediment Nitrate Uptake
Low Nitrate in Bottom Water
Nutrient Release (positive feedback)
Higher Benthic Ammonium Flux
Less coupled Nitrification-denitrification
GENERALIZED
Increasing Nutrient Inputs
PHYTOPLANKTON COMMUNITY
Higher Phytoplankton Biomass
More Phytoplankton Carbon Deposition
Ecosystem Response
HYPOXIA ANOXIA
Form of Limiting Nutrient (NO_x, NH_3, DON)
PHYSICAL CONTROLS (mixing, stratification)
DESIRABLE PHYTOPLANKTON SPECIES (Diatoms)
Water Column Carbon Cycling (grazing)
SOD
Decreased O_2 Depletion Potentials
Sediment Carbon Deposition
SOD
Increased O_2 Depletion Potentials
UNDESIRABLE PHYTOPLANKTON SPECIES (Nuisance Dinoflagellates and Cyanobacteria)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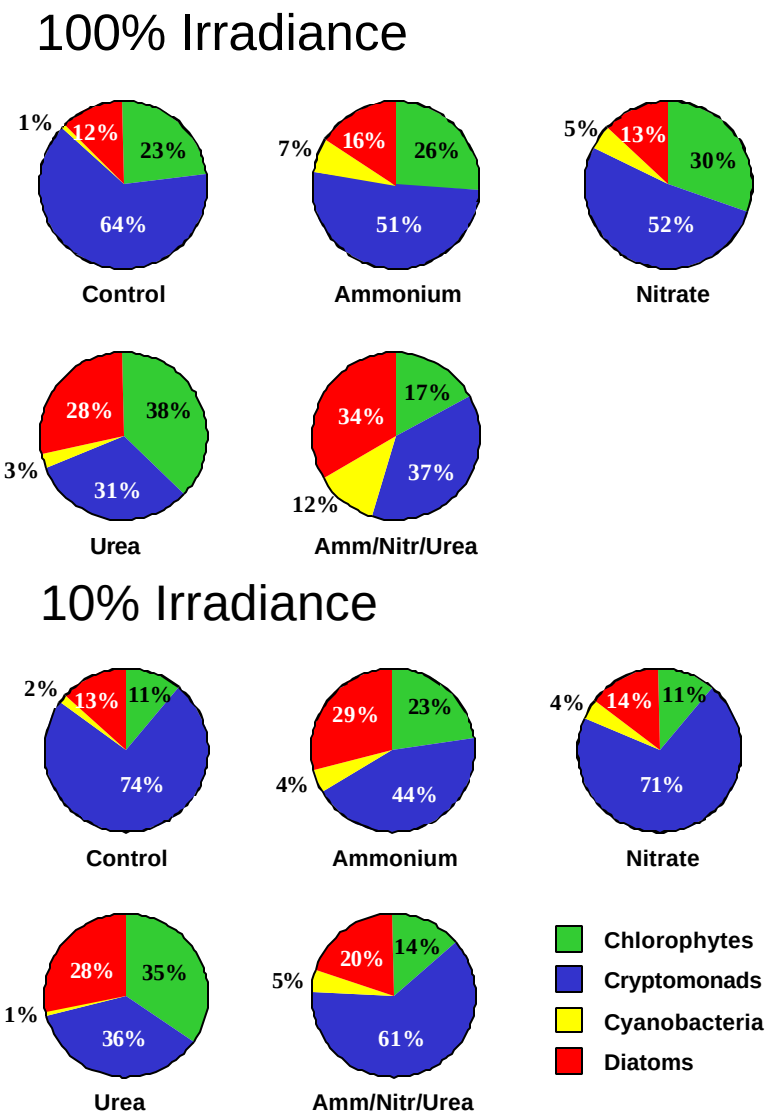
Year
r2=0.73
NH4+-N:NOx-N
Year


100% Irradiance
1%
12%
23%
64%
Control
7%
16%
26%
51%
Ammonium
5%
13%
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52%
Nitrate
28%
38%
3%
31%
Urea
34%
17%
37%
12%
Amm/Nitr/Urea
10% Irradiance
2%
13%
11%
74%
Control
29%
23%
4%
44%
Ammonium
4%
14%
11%
71%
Nitrate
28%
35%
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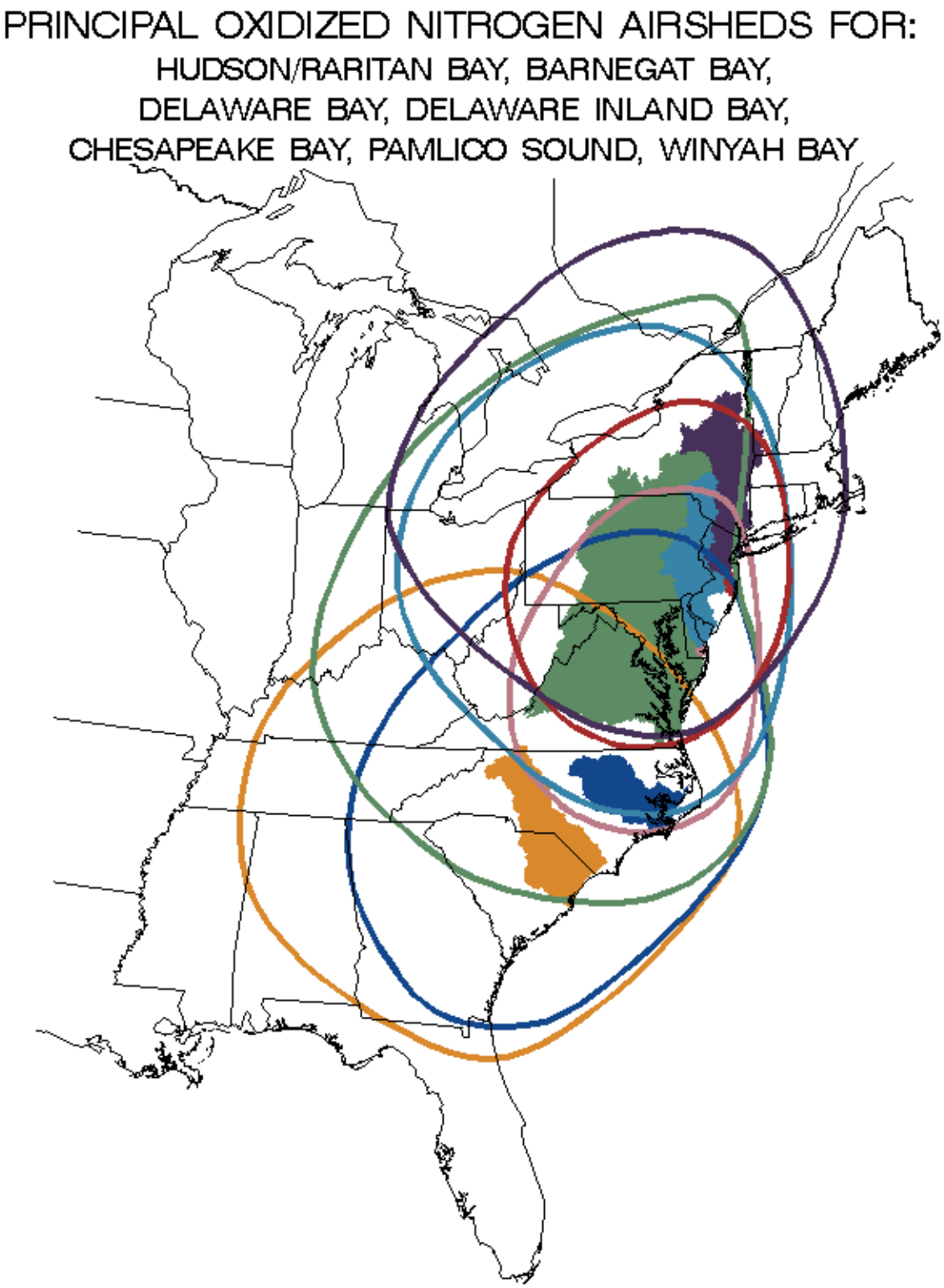
Diatoms


PRINCIPAL OXIDIZED NITROGEN AIRSHEDS FOR:
HUDSON/RARITAN BAY, BARNEGAT BAY,
DELAWARE BAY, DELAWARE INLAND BAY,
CHESAPEAKE BAY, PAMLICO SOUND, WINYAH BAY