Science for Solutions

**NOAA COASTAL OCEAN PROGRAM**
Decision Analysis Series No. 9

# ATMOSPHERIC NUTRIENT INPUT TO COASTAL AREAS

## *REDUCING THE UNCERTAINTIES*

Richard A. Valigura
Winston T. Luke
Richard S. Artz
Bruce B. Hicks

**NOAA AIR RESOURCES LABORATORY**

**JUNE 1996**

**U.S. DEPARTMENT OF COMMERCE**
**National Oceanic and Atmospheric Administration**
Coastal Ocean Office

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*Cover photo: Convective coastal storms are an efficient mechanism for the transfer of atmospheric nitrogen to a given water body. Soluble nitrogen compounds in the atmosphere are dissolved into precipitation during storm formation as well as by falling rain. (Photo by Glenn Rolph, NOAA Air Resources Laboratory, 1992)*

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**Michael Kantor, Secretary**
**National Oceanic and Atmospheric Administration**
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Donald Scavia, Director

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# Note to Readers

*Atmospheric Nutrient Input to Coastal Areas--Reducing the Uncertainties* by Richard A. Valigura, Winston T. Luke, Richard S. Artz, and Bruce B. Hicks of NOAA's Air Resources Laboratory is a synthesis of the findings and the management implications of research sponsored by the NOAA Coastal Ocean Program as part of its nutrient enhanced productivity activities. The atmospheric deposition of nutrients to estuaries, particularly along the U.S. East Coast, is being increasingly recognized as a significant contributor to eutrophication with its concomitant adverse impacts on living marine resources. This study by the Air Resources Laboratory is a seminal investigation of the subject particularly relating to the Chesapeake Bay.

The NOAA Coastal Ocean Program (COP) provides a focal point through which the agency, together with other organizations with responsibilities for the coastal environment and its resources, can make significant strides toward finding solutions to critical problems. By working together toward these solutions, we can ensure the sustainability of these coastal resources and allow for compatible economic development that will enhance the well-being of the Nation now and in future generations. The goals of the program parallel those of the NOAA Strategic Plan.

A specific objective of COP is to provide the highest quality scientific information to coastal managers in time for critical decision making and in a format useful for these decisions. To help achieve this, COP inaugurated a program of developing documents that would synthesize information on issues that were of high priority to coastal managers. A three-step process was used to develop such documents: 1) to compile a list of critical topics in the coastal ocean through a survey of coastal resource managers and to prioritize and select those suitable for the document series through the use of a panel of multidisciplinary technical experts; 2) to solicit proposals to do research on these topics and select principal investigators through a rigorous peer-review process; and 3) to develop peer-reviewed documents based on the winning proposals. Seven topics were selected in the initial round, and COP is planning a second round. Additionally, the series is being expanded to include the synthesis of findings from other COP-funded research. A list of titles in print appears on the inside back cover.

As with all of its products, COP is very interested in ascertaining the utility of the Decision Analysis Series particularly in regard to its application to the management decision process. Therefore, we encourage you to write, fax, call, or E-mail us with your comments. Please be assured that we will appreciate these comments, either positive or negative, and that they will help us direct our future efforts. Our address and telephone and fax numbers are on the inside front cover. My Internet address is dscavia@cop.noaa.gov.

Donald Scavia
Director
NOAA Coastal Ocean Program

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# FOREWORD

The overall goal of Atmospheric Nutrient Input to Coastal Areas (ANICA) Program was to develop methods for assessing the importance of atmospheric nutrient input, using the Chesapeake Bay as a first target of contemporary importance (as evidenced by specific mention of atmospheric deposition to the Bay, among other water bodies, in the Clean Air Act Amendments of 1990).

As an atmospheric component of the nutrient research program of NOAA's Coastal Ocean Program, the long-term objectives of the research program were:

- To determine the wet and dry deposition of nitrogen to Chesapeake Bay and other East Coast estuarine areas selected for intensive study
- To develop a strategy for assessing the dry and wet deposition affecting other coastal watersheds in the Northeastern United States and Maritime Canada
- To apply the models that are developed or modified in this program to describe and predict present and future atmospheric deposition scenarios for catchment areas impacted by nitrogen deposition
- To link the findings from ANICA with the ecological components of NOAA's Coastal Ocean Program and the Clean Air Act's Great Waters Program objectives

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# LIST OF TERMS AND ACRONYMS

| | | | |
|---|---|---|---|
| CO | Carbon monoxide | $D_H$ | Heat transfer coefficient |
| $F_d$ | Dry deposition Flux | Gg | 1 Gigagram = $10^9$ g |
| HCL | Hydrochloric acid | $HNO_3$ | Nitric acid |
| Mg | 1 Megagram = $10^6$ g | $N_2$ | Diatomic nitrogen |
| $N_{org}$ | Organic nitrogen | $N_T$ | Total nitrogen |
| $N_2O$ | Nitrous oxide | $NH_3$ | Ammonia |
| $NH_4^+$ | Ammonium | $(NH_4)_2SO_4$ | Ammonium sulfate |
| NO | Nitrogen oxide | $NO_2$ | Nitrogen dioxide |
| $NO_X$ | Sum of NO and $NO_2$ | $NO_Y$ | Total reactive nitrogen |
| $NO_3^-$ | Nitrate | $NO_3NH_4$ | Ammonium nitrate |
| p-$NO_3^-$ | Particulate nitrate | PAN | Peroxyacetyl nitrate |
| $O_3$ | Ozone | $R_a$ | Aerodynamic resistance |
| $R_b$ | Quasi laminar resistance | $R_c$ | Canopy resistance |
| $R_T$ | Total air-surface resistance | SLM | Standard liters per minute |
| $SO_2$ | Sulfur dioxide | $u_z$ | Windspeed at height z |
| $V_d$ | Deposition velocity | $V_g$ | Gravitational settling velocity |
| z/L | Monin-Obukhov coefficient | | |

| | |
|---|---|
| AEOLOS | Atmospheric Exchange Over Lakes and Oceans Study |
| AEROCE | Air/Ocean Chemistry Experiment |
| AIRMoN | Atmospheric Integrated Research Monitoring Network |
| CAAA | Clean Air Act Amendments of 1990 |
| CAD | Citric Acid Denuder |
| CBOS | Chesapeake Bay Observing System |
| CL | Ozone Chemiluminecence technique for measuring NO |
| DDIM | Dry Deposition Inferential Method |
| HY-SPLIT | Hybrid Single Particle Lagrangian Integrated Trajectory Model |
| GFC | Gas Filter Correlation |
| GPCP | Global Precipitation Chemistry Project |
| IC | Ion Chromatography Analysis |
| NADP | National Atmospheric Deposition Program |
| NAPAP | National Acid Precipitation Assessment Program |
| NCDC | National Climatic Data Center |
| NCEP | National Centers for Environmental Prediciton |
| NDIR | Non-Dispersive Infrared Adsorption |
| PMT | Photomultiplier Tube |
| RADM | Regional Acid Deposition Model |
| RAMS | Regional Atmospheric Modeling System |
| UV | Ultraviolet |
| WATOX | Western Atlantic Ocean Experiment |

# EXECUTIVE SUMMARY

A significant fraction of the total nitrogen entering coastal and estuarine ecosystems along the eastern U.S. coast arises from atmospheric deposition; however, the exact role of atmospherically derived nitrogen in the decline of the health of coastal, estuarine, and inland waters is still uncertain. From the perspective of coastal ecosystem eutrophication, nitrogen compounds from the air, along with nitrogen from sewage, industrial effluent, and fertilizers, become a source of nutrients to the receiving ecosystem. Eutrophication, however, is only one of the detrimental impacts of the emission of nitrogen containing compounds to the atmosphere. Other adverse effects include the production of tropospheric ozone, acid deposition, and decreased visibility (photochemical smog).

Assessments of the coastal eutrophication problem indicate that the atmospheric deposition loading is most important in the region extending from Albemarle/Pamlico Sounds to the Gulf of Maine; however, these assessments are based on model outputs supported by a meager amount of actual data. The data shortage is severe. The National Research Council specifically mentions the atmospheric role in its recent publication for the Committee on Environmental and Natural Resources, *Priorities for Coastal Ecosystem Science* (1994). It states that, "Problems associated with changes in the quantity and quality of inputs to coastal environments from runoff and atmospheric deposition are particularly important [to coastal ecosystem integrity]. These include nutrient loading from agriculture and fossil fuel combustion, habitat losses from eutrophication, widespread contamination by toxic materials, changes in riverborne sediment, and alteration of coastal hydrodynamics."

Much of the initial understanding of the atmospheric deposition problem derived from work of NOAA's Air Resources Laboratory (ARL). During the 1980s, under the auspices of the National Acid Precipitation Assessment Program (NAPAP), ARL conducted a major study (the Western Atlantic Ocean Experiment - WATOX) of the fate of air pollutants carried by the wind beyond the east coast of the continental U.S. This study revealed that almost all of these pollutants are deposited to the ocean, with greatest deposition rates occurring in the nearshore region. About 30% of the total U.S. air emissions of nitrogen are deposited to the Atlantic, again with heaviest deposition to the near-shore region. Further impetus was added to the atmospheric transport issue by the passage of 1990 Clean Air Amendments which require that:

> *The Administrator [of the Environmental Protection Agency], in cooperation with the Under Secretary of Commerce for Oceans and Atmospheres, shall conduct a program to identify and assess the extent of atmospheric deposition of hazardous air pollutants (and in the discretion of the Administrator, other air pollutants) to the Great Lakes, the Chesapeake Bay, Lake Champlain and coastal waters.*

To address the need for an objective methodology to assess the importance of the atmospheric input to coastal regions, the ARL/Atmospheric Nutrient Input To Coastal Areas (ANICA) program was developed through the NOAA Coastal Ocean Program. During the four-year

lifetime of ANICA, methods for assessing the role of atmospheric nitrogen loadings to coastal areas were developed, and other stakeholders were alerted to the importance of the atmospheric deposition issue.

Much of the progress under the ANICA program was made by cooperative effort with the Chesapeake Bay Program through alliance with the NOAA Chesapeake Bay Office. Through this alliance, ARL researchers were invited to assume the chairmanship of the multi-agency Air Quality Coordination Group (AQCG) of the Chesapeake Bay Program. Subsequently, the AQCG hosted two major atmospheric loadings workshops. The first was a scientific workshop at Baltimore, Md., in 1994 (the "Mt. Washington Workshop") which succeeded in defining and prioritizing immediate research needs to reduce existing uncertainty surrounding the atmospheric loadings issue. Six research areas were identified which refelected the need to:

1) conduct integrated (intensive and coordinated) monitoring at specified locations
2) work to improve atmospheric models
3) work to improve biogeochemical watershed models
4) improve emissions inventories
5) conduct process-oriented measurements to extend spatial representativeness
6) develop an extensive network of less intensive measurements.

Through its leadership role in the AQCG, the success of the Mt. Washington Workshop strategically positioned ARL at the head of coastal nutrient/atmospheric loadings research and assessment in the U.S. This position was strengthened in areas to the north and south of the Chesapeake Bay through a the second workshop of local, state, and federal policy makers conducted near Warrenton, Va., in 1995 (the "Airlie Workshop"). The Airlie Workshop concluded that there is need for:

1) a better understanding of how all atmospheric nitrogen species affect coastal ecosystems and the related policy options
2) a cross-media approach to the atmospheric deposition and loadings problem
3) a coalition of interested parties extending from the north to the south of the potentially affected eastern coast of the continental U.S., including both terrestrial and biological interests as equals.

Participants of the Airlie Workshop noted that the work needed is essentially multimedia, requiring attention by a consortium of workers rather than separate attention by specialists operating independently

The ANICA program was designed as a targeted research program designed specifically to answer two particular questions: To what extent is the perceived problem due to deposition from the atmosphere and how can this understanding be extrapolated to other circumstances? After several years of work on the Chesapeake Bay, there is now a strong recognition of the importance of the atmosphere among the scientific community which deal with Atlantic coastal

ecosystems. This is widely seen as an area of NOAA leadership, providing crucial guidance to EPA and the states to assure that regulatory controls on industry, agriculture, and waste treatment are considered in proper context with air quality controls. ANICA scientists have been exporting the lessons that have been learned. In fact, ANICA has been slowly expanding its horizons, with recent activity in all of the Great Lakes, Pamlico-Albemarle Sounds, the Gulf of Maine, and Tampa Bay.

There have been approximately 35 studies around the world which addressed at least one aspect of atmospheric loadings, the majority of which were published since 1990. However, the measurement and modeling techniques used varies considerably between individual studies, making intercomparisons difficult. Though published estimates of the relative contribution from the atmosphere fall in an apparently constrained range (10-45%), the actual amount of atmospheric loadings vary widely depending, primarily, on the size of the waterbody and its watershed (as elucidated in this report). The uncertainties of the studies to date make it imperative that a better understanding be obtained of the processes that transport and deposit nitrogen to estuaries and coastal zones, and that the scope of this understanding be extended to areas along both the East Coast and the Gulf of Mexico which remain to be investigated. The most recent estimate of a 27% contribution of atmospheric deposition to total nitrogen loadings to the Chesapeake Bay (Chesapeake Bay Program, 1996), falls within the range reported for other estuaries (10-45%). Projections for the coming decades estimate that the atmosphere will become a more significant source of nitrogen loadings to coastal areas with anticipated increases in population and land development resulting in more mobile and new power plant emissions.

The results and recommendations of the two Workshops listed above, and the underlying science behind atmospheric nutrient loadings to coastal areas are substantiated in the documentation that follows. This report will: a) review the underlying framework needed for understanding atmospheric loadings issues, b) present the specific research conducted by ARL and associated scientists under the ANICA background/measurement/modeling framework, c) summarize the current state of the science, and d) suggest the remaining research and management needs.

# Chapter 1
# INTRODUCTION

## *Nitrogen in the Environment*

Though the availability of nitrogen normally limits biological productivity in coastal waters, overabundance of nitrogen is of concern in areas which have developed nutrient enrichment problems (i.e., eutrophication). In addition to increasing productivity, nutrient enrichment generally alters the normal ratios of nitrogen to phosphorus and to other elements such as silicon. This alteration may induce changes in phytoplankton community structure. Species which normally occur in low abundances may be favored, and, in some cases, toxic and/or noxious algal blooms may result. For the New England coast in particular, the number of red and brown tides and shellfish problems from nuisance and toxic plankton blooms have increased over the past two decades. Furthermore, in coastal areas with poor or stratified circulation patterns (e.g., Chesapeake Bay, Long Island Sound) the "overproduction" of algae tends to sink to the bottom and decay, using all (anoxia) or most (hypoxia) of the available oxygen in the process, causing loss of habitat. In extreme cases, the increase in suspended matter due to overproduction decreases light infiltration, in turn causing a loss of submerged aquatic vegetation.

There is some anecdotal evidence that nitrogen loadings have been an issue for longer than is generally appreciated. Paleoecological studies have revealed that there is a threshold up to which ecosystems can tolerate stress without obvious adverse consequences. Once this threshold is passed, however, the system may no longer be able return to its original equilibrium state. What is seen now could be a manifestation of a nitrogen problem that is just starting to be observable. In some cases (i.e., Chesapeake Bay, Long Island Sound), the overall nutrient loads have already tipped the balance and are producing obvious negative effects. The decline has been evident in seagrass and in fisheries productivity. Other estuaries may not have yet reached their balance points. Here, the emphasis will be on the role of atmospheric nitrogen compounds.

> *Note that the following discussion uses a standardized distinction of the terms "deposition" and "loadings." Deposition is the flux of nitrogen from the atmosphere to whatever surface is beneath. Indirect loading is the portion of nitrogen deposited onto the terrestrial watershed which is transmitted to the water body itself, defined in terms of flow to the tidal waters. Deposition to the water surface itself constitutes a direct loading.*

## *Atmospheric Nitrogen*

The exact role of deposition of atmospheric nitrogen compounds as contributors to the decline of the health of coastal, estuarine, and inland waters is still uncertain. From the perspective of coastal ecosystem eutrophication, nitrogen compounds from the air, along with nitrogen from sewage, industrial effluent, and fertilizers, become a source of nutrients to the receiving ecosystem (Figure 1.1). Eutrophication, however, is only one of the detrimental impacts of the emission of nitrogen containing compounds to the atmosphere. These compounds are also

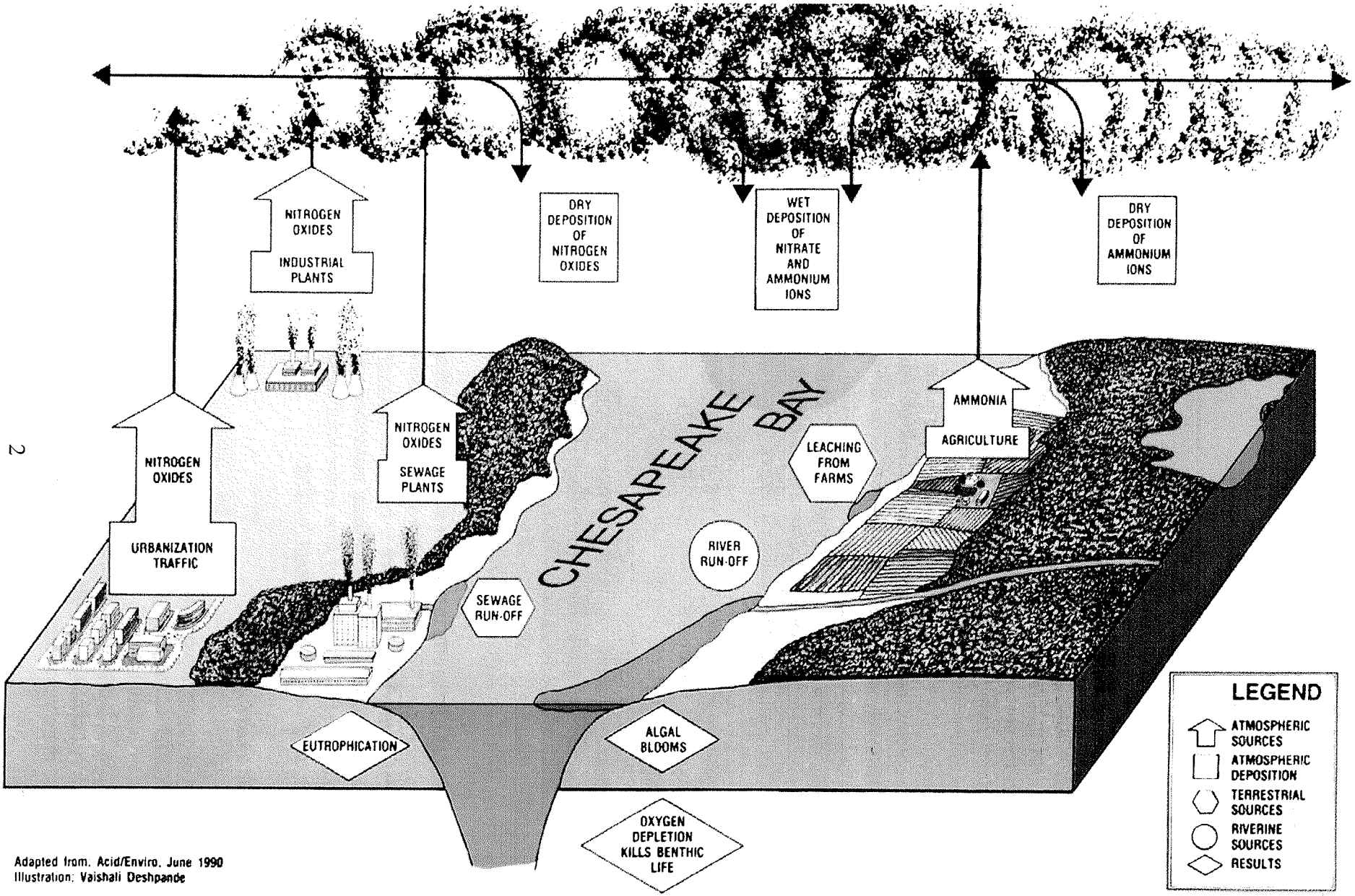


Figure 1.1 Atmospheric input of nitrogen to coastal areas

significant contributors to decreased visibility (photochemical smog), acid deposition, and the production of tropospheric ozone.

Atmospheric nitrogen compounds are ubiquitous. Diatomic nitrogen ($N_2$) is the dominant component of the atmosphere, and is comparatively unreactive. However, nitrogen is also present in the atmosphere in other chemical forms, some of which are relatively reactive. These fate of these nitrogenous compounds are the central topic for the present report.

Most atmospheric nitrogen compounds (other than $N_2$ and nitrous oxide [$N_20$]) fall into two categories: reactive nitrogen (composed primarily of nitrogen oxides), and reduced nitrogen (typically dominated by ammonia [$NH_3$]). There are also organic nitrogen species that are typically referred to as a subset of reactive nitrogen. These chemical species arise in the atmosphere from the interaction between nitrogen oxides and biogenic or anthropogenic hydrocarbons. Though available evidence suggests that organic nitrogen originates from both anthropogenic and natural sources, speciation of organic nitrogen in the atmosphere is very poorly understood.

The dominant source of the reactive oxides of nitrogen present in air over North America is high-temperature combustion (industry, power plants, automobiles, etc.). Nitric oxide (NO) generated by combustion (some also derives from natural biological processes) reacts quickly in the lower atmosphere generating nitrogen dioxide ($NO_2$), which is then the dominant nitrogen oxide in the lower atmosphere in polluted regions. $NO_2$ slowly deposits to the underlying surface, but a large proportion of it remains in the atmosphere where it is subjected to further chemical reactions. One of these reactions generates nitric acid vapor ($HNO_3$) which is easily and quickly deposited. Other reactions generate ozone; the ozone issue is therefore intimately related to the $NO_x$ (defined as $NO + NO_2$) question.

The different atmospheric nitrogen compounds deposit differently, and once deposited they vary greatly in their ability to move through a watershed to affect the water body it contains. Specific influencing factors, in addition to the chemical form in which the nitrogen compound is deposited - reactive, reduced, or organic nitrogen species - vary widely based on proximity to sources, receiving waters, transformations in the atmosphere as well as on the land surface and transfer through the watershed via surface runoff (Paerl, 1996). Current estimates are that nitrogen oxides are the largest contributor to atmospheric nitrogen loads to coastal waters of eastern North America (40-60%), with ammonia (20-40%) and organic nitrogen (about 20%) also contributing significant amounts on an annual basis.

## *Defining the Problem*

The initial impetus to investigate the importance of the atmosphere as a transport mechanism for nitrogen to estuarine areas was the 1988 Environmental Defense Fund (EDF) report (Fisher et al., 1988). Based on one year of measurements (1984), and assuming relationships between wet and dry deposition that are likely to be conservative, the authors estimated that one-third of the inorganic nitrogen entering the Chesapeake Bay comes from the atmosphere. There have been several subsequent efforts to quantify the atmospheric nitrogen loadings to the Bay. However, the assumptions used in these studies overshadow the results; the error associated with these estimates is typically quoted as being a factor of two or sometimes as much as a factor of about three. Further impetus was added to the atmospheric transport issue by the passage of 1990 Clean Air Amendments that require:

> *The Administrator [of the Environmental Protection Agency], in cooperation with the Under Secretary of Commerce for Oceans and Atmosphere, shall conduct a program to identify and assess the extent of atmospheric deposition of hazardous air pollutants (and in the discretion of the Administrator, other air pollutants) to the Great Lakes, the Chesapeake Bay, Lake Champlain and coastal waters.*

In FY 1991 the NOAA Coastal Ocean Program initiated the Atmospheric Nutrient Input to Coastal Areas (ANICA) program. The ANICA program was proposed and managed through the NOAA Air Resources Laboratory (ARL). Through participation in the multiagency National Acid Precipitation Assessment Program, ARL scientists gained experience in creating data bases, techniques, and models useful for evaluating the atmospheric sources of nitrogen to coastal waters. The long-term goal of ANICA was to:

> *Develop methods for assessing the importance of this atmospheric input, using the Chesapeake Bay as a first target of contemporary importance.*

ANICA was first proposed as a program to address scientific uncertainties involved in assessments of the kind put forward by the initial EDF report. When ANICA commenced, only a minimal data base existed with which to test computer models, and little experimental capability to obtain additional data. However, there was already a large, multi-state and federal organizational research effort addressing the Chesapeake Bay problem, the Chesapeake Bay Program. Most of attention was being directed at monitoring the flow of nutrients into the Bay via streams and rivers, monitoring changes in the Bay water quality and in its biology, and developing models to describe the interaction between such nutrient inputs and the recycling of nutrients within the Chesapeake Bay ecosystem. The ANICA program was designed to provide precisely the information that has previously been missing – direct experimental quantifications of areal deposition rates of atmospheric nutrients – and to introduce this new information into the models being developed.

> *ANICA was a targeted research program designed specifically to answer two particular*

*questions: To what extent is the perceived problem due to deposition from the atmosphere and how can this understanding be extrapolated to other circumstances?*

After several years of work on the Chesapeake Bay, there is now a strong recognition of the importance of the atmosphere among the scientific community which deal with Atlantic coastal ecosystems. The specialization of ARL is widely recognized as being crucial to this science. This is all widely seen as an area of NOAA leadership, providing crucial guidance to EPA and the states to assure that regulatory controls on industry, agriculture, and waste treatment are considered in proper context with air quality controls. ANICA scientists have been exporting the lessons that have been learned. In fact, ANICA has been slowly expanding its horizons, with recent activity in all of the Great Lakes, Pamlico-Albemarle Sounds, the Gulf of Maine, and Tampa Bay.

In FY 1991 ANICA was implemented as a series of 23 specific tasks (listed in Appendix A). These tasks were divided into three general areas of research: background development, measurement, and model and data evaluation. At the end of FY 1995, nine (primarily background oriented) tasks were completed or implemented and six of the measurement and modeling phase tasks were initiated. Much of this progress was made through cooperative efforts with the Chesapeake Bay Program through the NOAA Chesapeake Bay Office. This report will: a) review the underlying framework needed for understanding atmospheric loadings issues, b) present the specific research conducted by ARL and associated scientists under the ANICA background/measurement/modeling framework, c) summarize the current state of the science, and d) suggest the remaining research and management needs.

# Chapter 2
# SCIENTIFIC FRAMEWORK

## *Mass Balance Paradigm*

Biogeochemical cycling of nitrogen and contaminants on local, regional, and global scales is a complex system of emissions, transformations, dispersion, and deposition. This system is most complex in coastal environments, such as Chesapeake Bay, where landscape processes affect coastal processes and vice versa. Figure 2.1 is a simplified schematic that shows an idealized picture of a coastal ecosystem divided into four basic compartments or reservoirs, and the transfers among these compartments. This view provides a convenient basis for the current mass balance paradigm that attempts to quantify the transfers (loadings) between designated system components. To date, most emphasis has been placed on quantifying and identifying direct, well-defined emissions to each compartment (i.e., emissions from smokestacks, outfalls). However, the terrestrial watershed and the riverine and estuarine processes affect the transport of these emissions to the Bay both directly and indirectly.

Atmospheric deposition includes wet deposition (through rain and snow) and dry deposition (as gases and aerosols). In each case, it also is necessary to consider whether the deposition is deposition to the water surface (i.e., direct deposition) or deposition to the watershed, with subsequent transport to the receiving stream (i.e., indirect deposition). Determining the magnitude of deposition is necessary but not always sufficient for addressing management issues. To deal efficiently with such issues requires an understanding of both the sources of atmospheric nitrogen (e.g., long-range versus short-range transport, emission source type, and associated meteorological conditions) and the relative magnitude of the atmospheric depositional loadings compared to that of all other sources of nitrogen surface waters.

## *Sources and Emissions*

Most atmospheric nitrogen compounds (excluding $N_2$ and $N_2O$, which are relatively inert in the lower atmosphere) fall into two categories: reactive nitrogen, sometimes referred to as oxides of nitrogen or odd nitrogen, and reduced nitrogen (typically dominated by ammonia [$NH_3$]). Some organic nitrogen species arise in the atmosphere from the interaction between nitrogen oxides and biogenic or anthropogenic hydrocarbons, and are thus typically referred to as a subset of reactive nitrogen. The relative portions of the different forms nitrogen can take--i.e., nitrate, nitrite, ammonia, dissolved organic nitrogen--vary widely based on proximity of sources to receptors, receiving waters, and atmospheric transformations as well as on the land surface and transfer through the watershed via surface runoff (Paerl, 1996). Current estimates are that reactive nitrogen is the largest contributor to atmospheric nitrogen loads to coastal waters (40-60%), with ammonia (20-40%) and organic nitrogen (0-20%) also contributing significant amounts.

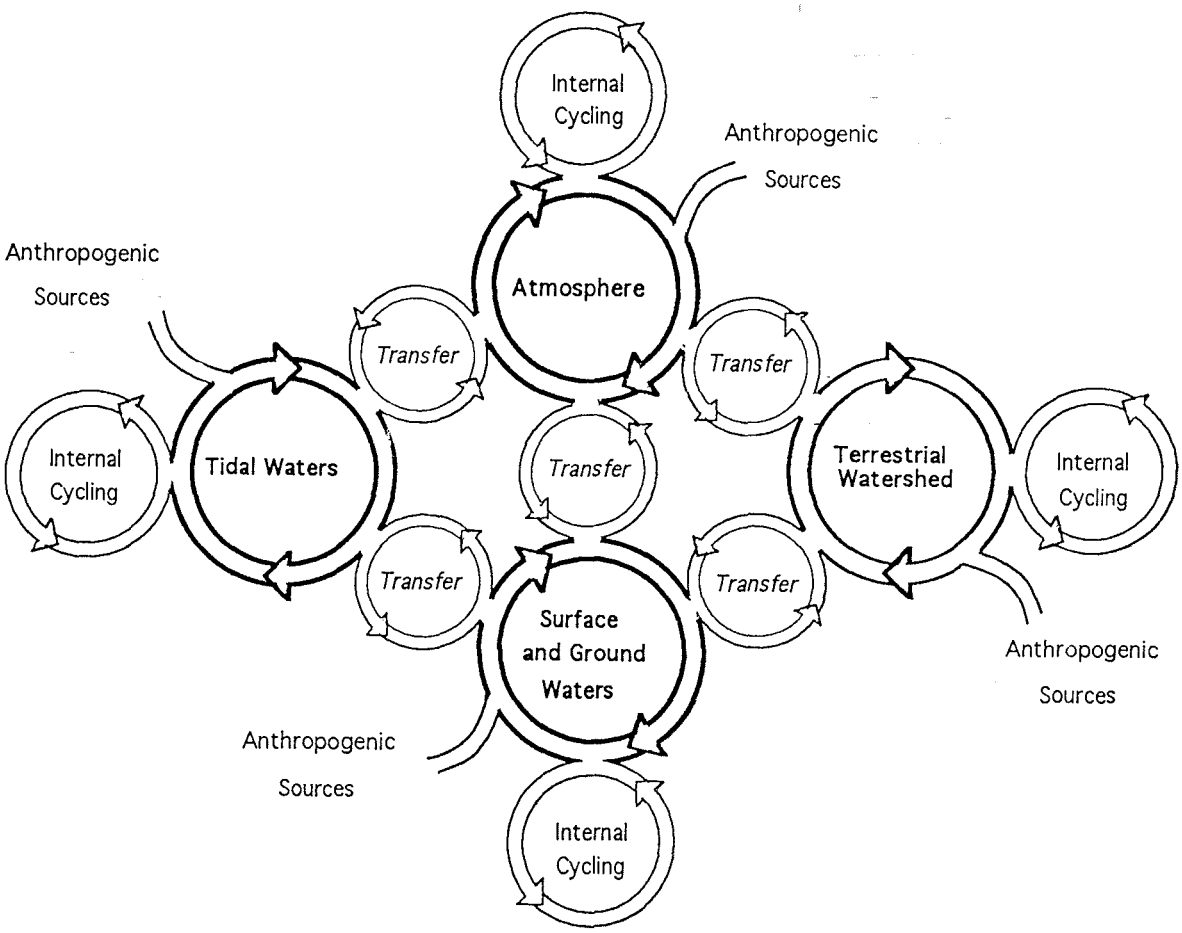


Figure 2.1. A simplified schematic of the coastal nitrogen cyle.

**Reactive Nitrogen: Nitrogen Oxides**

Reactive nitrogen compounds (primarily oxides of nitrogen) are emitted to the atmosphere through both natural and anthropogenic pathways, overwhelmingly (95%) as nitric oxide, or NO. Natural sources of NO include emission from soils and generation by lightning; dominant anthropogenic sources include emission from automobiles, power plants, and biomass burning. On a global basis, anthropogenic and natural sources of reactive nitrogen are approximately equal in strength (Table 2.1). In North America, and especially in northeastern North America, the overwhelming majority of nitrogen oxides is of anthropogenic origin.

**Table 2.1. Budget of global $NO_x$ emissions by source (Teragrams [1 Tg = $10^{12}$ g] N $yr^{-1}$).** Adapted from Watson et al., 1992.

| Sources of $NO_x = NO + NO_2$ | Tg N $yr^{-1}$ |
|---|---|
| Fossil fuel combustion | 14-28 |
| Lightning | 2-20 |
| Microbial activity in soils | 5-20 |
| Biomass burning | 3-13 |
| Oxidation of ammonia | 0-10 |
| Oceans | < 1 |
| Stratospheric input | <1 |

Once in the atmosphere, NO is transformed via a multitude of secondary reactions to form higher oxides of nitrogen. Of the reactive nitrogen components, $HNO_3$ and particulate nitrate ($p\text{-}NO_3^-$) are believed to dominate nitrogen deposition (Huebert and Robert, 1985; Huebert et al., 1988; Meyers et al., 1989). However, deposition of $NO_2$ also may be significant in near-urban environments where concentrations are high; its spatial and temporal extent is an important question being addressed. Peroxy acetyl nitrate (PAN) is a compound which arises from the reaction of $NO_2$ with the photo-oxidation products of both natural and anthropogenic hydrocarbons. PAN is efficiently produced in polluted urban air due to the reactive nature of many anthropogenic hydrocarbons. Few studies of PAN deposition have been conducted. Smullen et al. (1982) views PAN deposition as insignificant; however, Singh (1987) states that it may be important near polluted urban and semi-rural locations.

**Reduced Nitrogen: Ammonia and Ammonium**

Ammonia is emitted into the atmosphere through both natural and anthropogenic pathways. Natural sources of $NH_3$ include microbial decomposition of organic nitrogen compounds in soils and ocean waters and volatilization from animal and human wastes. Anthropogenic sources

include the manufacture and release of commercial and organic fertilizers during and after application and fossil fuel combustion. Human activities such as manure management and biomass burning exacerbate emissions from otherwise natural processes. Two estimates of the global emission budget are presented in Table 2.2. The uncertainties apparent in these estimates are related to the intrinsically local nature of ammonia emissions, which make regional estimates highly difficult to construct.

Ammonia is a highly reactive compound and has a short residence time in the atmosphere. It is primarily emitted at ground level and quickly deposits to the area near its source unless it reacts with other gaseous chemicals (e.g., $SO_2$, $HNO_3$) and converted to ammonium ($NH_4^+$) aerosol (Langland, 1992; Asman, 1994). Ammonium can be transferred regionally as an ammonium salt (e.g., ammonium nitrate [$NO_3NH_4$]) and is the primary contributor to ammonium concentrations measured in precipitation.

**Table 2.2. Budget of global $NH_3$ emissions by source (Tg N $yr^{-1}$).** Adapted from Schlesinger and Hartley, 1992 (numbers in parenthesis indicate range); Dentener and Crutzen, 1994.

| Source | Schlesinger and Hartley, 1992 | Dentener and Crutzen, 1994 |
|---|---|---|
| Domestic animals | 32.0 (24-40) | 22.0 |
| Sea surface | 13.0 (8-18) | 7.0 |
| Undisturbed soils | 10.0 (6-45) | |
| Wild animals | | 2.5 |
| Vegetation | | 5.1 |
| Fertilizers | 9.0 (5-10) | 6.4 |
| Biomass burning | 5.0 (1-9) | 2.0 |
| Human | 4.0 | |
| Coal combustion | 2.0 | |
| Automobiles | 0.2 | |
| Total | 75.2 (50-128) | 45.0 |

**Organic Nitrogen**

To date, studies of atmospheric nitrogen deposition have almost exclusively addressed dissolved inorganic nitrogen (reactive and reduced nitrogen). Because of the paucity of reliable measurements, the historical variability in analytical techniques and results, and the current lack of suitable and uniform analytical measurement techniques, only limited work has been reported

on the deposition of organic nitrogen. In fact, only wet deposition of organic nitrogen has been addressed.

This dearth of information is becoming widely recognized by the scientific community and is receiving increased attention. Recent reports (Gorzelska et al., 1992; Milne and Zika, 1993; Cornell et al., 1995; Scudlark et al., 1995) suggest that organic nitrogen is a significant fraction of the total nitrogen measured in precipitation. Various estimates for the relative flux of organic versus total N via wet deposition range from <10% to >60%. These recent data suggest that the contribution of the unresolved organic fraction may significantly augment the atmospheric deposition of nitrogen to coastal waters. However, in addition to the lack of dry deposition data, there remain many conceptual questions related to source identification and bioavailability of deposition organic nitrogen.

Current analytical techniques are unable to speciate specific organic N compounds measured in precipitation. Therefore, it is difficult to determine relative contributions of biogenic versus anthropogenic sources. Cornell et al. (1995) speculated from their open ocean studies that the higher concentrations in continental rains, the need for a relatively large sea-surface fractionation to sustain a marine source, and the isotope results all suggest that a continental source is more likely. They also suggest that industrial combustion sources could contribute to dissolved organic nitrogen formation via reactions of soot with $NO_x$ and $NH_3$.

## *Deposition Flux Estimates*

The process by which atmospheric nitrogen is transferred to terrestrial and water surfaces is generally termed atmospheric deposition. Deposition is divided into two categories: wet and dry. Wet deposition involves the incorporation of gaseous or particulate nitrogen into cloud/rain formations (including fog), and the subsequent deposition of this water onto an underlying surface. Dry deposition involves the exchange of gaseous and particulate nitrogen between the atmosphere and a surface either through settling or by impact deposition.

### Wet Deposition

With the exception of organic nitrogen compounds, the analytical techniques for major nitrogen species in precipitation are well established and can be considered fairly routine. Most of the current debate over the appropriate approach for measurement of wet nitrogen deposition is centered around field sampling protocols (i.e., the process by which the sample is collected and transported to the analytical laboratory). The question of precipitation sample collection frequency remains a topic of active debate. Many precipitation sampling networks have adopted a one-week sampling protocol as a reasonable compromise between high data quality and reasonable operational costs. Shorter collection intervals are generally not required to quantify trends in the wet deposition of stable chemical compounds; ecosystems do not usually respond rapidly to changes in deposition. On the other hand, longer-term sampling (e.g., monthly) is usually avoided because of difficulty in maintaining adequate quality control over precipitation

samples which remain in the field for long periods of time. Overall, weekly sampling provides data which are quite adequate for long-term trend detection and ecosystem input assessment, but which are of limited use in coupling with meteorological models, and are often useless for process-oriented studies. In addition, while many ions in precipitation are relatively stable for periods of weeks or months, nitrogen compounds are more chemically labile and so require more frequent sample collection and analysis intervals to ensure sample stability and, by extension, a proper assessment of their environmental impacts. Thus, as the questions posed to the research community become more difficult, the demand for daily sampling is increasing.

Wet deposition is chaotic in nature, which makes estimating short-term patterns difficult. However, review of nitrogen deposition data shows that deposition at one site is much the same as at a neighboring site when long-term averages are evaluated. This fact allows meaningful areal (isopleth) maps of wet deposition and nitrogen chemistry to be constructed using long-term data.

**Dry Deposition**

When considering total atmospheric deposition of nitrogen to a given watershed, the largest uncertainties are associated with the ability to estimate the spatial distribution of dry deposition. Enough is known about the processes that control dry deposition to permit deposition to be estimated on a point-by-point basis. However, in contrast to wet deposition, long-term averaging does not reduce differences between sites; it clarifies the differences. This fact makes understanding large-scale dry deposition patterns difficult. Thus, it is not possible to extract meaningful site-specific dry deposition data from large-area, time-averaged data without detailed consideration of the site in question.

The mechanisms that control dry deposition are tied to biological and land surface features that are highly variable from one specific location to another. The problems with estimating dry deposition are further complicated by the fact that the capability for long-term, continuous monitoring is limited by both scientific and economic factors. In an effort to circumvent these problems, investigators have used mathematical models to estimate the distribution of dry deposition. However, even detailed, site-specific models used to estimate dry deposition from field measurements at a site under investigation are limited in their ability. Comparative measurement and modeling studies have shown that site-specific models - at good sites and in selected conditions - perform well a little over half the time. The reasons for the inadequacies are known to be associated with hard-to-quantify surface characteristics (e.g., leaf wetness, moisture conditions). These issues are not new, and they have been the subject of considerable debate. Efforts to resolve these problems have been made and continue to be made, but a universally acceptable spatial dry deposition model is still far distant.

The primary assumption made by published loading studies is that dry deposition is equal to wet deposition. This assumption is necessary because there is no independent measurement basis for estimating areal dry deposition rates. This same lack of data also means that there is no existing

evidence that this estimate is grossly misleading. It would seem obvious, considering the vastly dissimilar atmospheric and surface mechanisms that cause dry and wet deposition, that equality between them would be an extremely unlikely and quite fortuitous finding, in practice.

## *Loadings to Chesapeake Bay*

### Direct Loadings

Studies have explored the idea that atmospheric deposition may contribute a significant proportion of phytoplankton nitrogen demands in coastal areas (Paerl, 1985; Paerl, 1988; Paerl et al., 1990). Fogel and Paerl (1991), for example, have estimated that 20-50% of annual new nitrogen demands for Pamlico-Albemarle Sound may be supplied by direct atmospheric deposition to the water surface (wet and dry). Furthermore, there have been two recent, and opposing, papers published on the effects of wet-deposited nitrogen effects on phytoplankton off Bermuda (Owens et al., 1992; Michaels et al., 1993). It is not currently known if the over-land measurements are representative of over-water deposition, but it is suspected that this is not the case. To investigate this question, a daily precipitation chemistry site was established on Smith Island, Md., in late 1995. This site will provide the first time series measurements of over-water wet deposition along the East Coast. Estimates of wet deposition to the Chesapeake Bay surface range from 3.45 to 4.2 Gg $NO_3$-N $yr^{-1}$ (1 Gigagram = $1*10^9$g) (Fisher and Oppenhiemer, 1991; Hinga et al., 1991; Tyler, 1988).

Although the air/surface exchange of nitrogen has been estimated for most nitrogen species over open ocean (Galloway, 1985; Duce et al., 1991), these rates may not apply to coastal situations in that coastal areas involve different meteorological processes (NRC, 1992).
Through the use of instrumented Chesapeake Bay Observing System (CBOS) buoys, owned by the University of Maryland, estimates of nitrogen ($HNO_3$, $NO_2$, $NH_4$) dry deposition rates to the Bay surface have been developed (Valigura, 1995). These estimates corroborate those given by other investigators to some extent, but still cover a wide range of values, from 745 Mg $y^{-1}$ (1 Megagram = $1*10^6$g) to 2.24 Gg $y^{-1}$. From this data set, calculations were performed to determine the effect of atmospheric dry deposition on phytoplankton dynamics. This analysis demonstrated that dry-deposited nitrogen may provide 10% of the annual "new nitrogen" demands in Chesapeake Bay, and that individual events could supply up to 75% of the new demands for periods of several days (Malone, 1992; Owens et al., 1992).

### Indirect Loadings

The greatest uncertainty in the quantification of loadings to coastal areas such as Chesapeake Bay is how much is transferred through the terrestrial watershed to the surface waters, and how much is subsequently transported downstream to the Bay. Nitrogen activity within a given watershed depends on the amount of soil nitrogen, historical acidic deposition, physical characteristics of the soil, site rainfall and temperature characteristics, the elevation and slope of the land, and the type and age of the vegetative cover (see Figure 2.2). These characteristics vary at all scales,

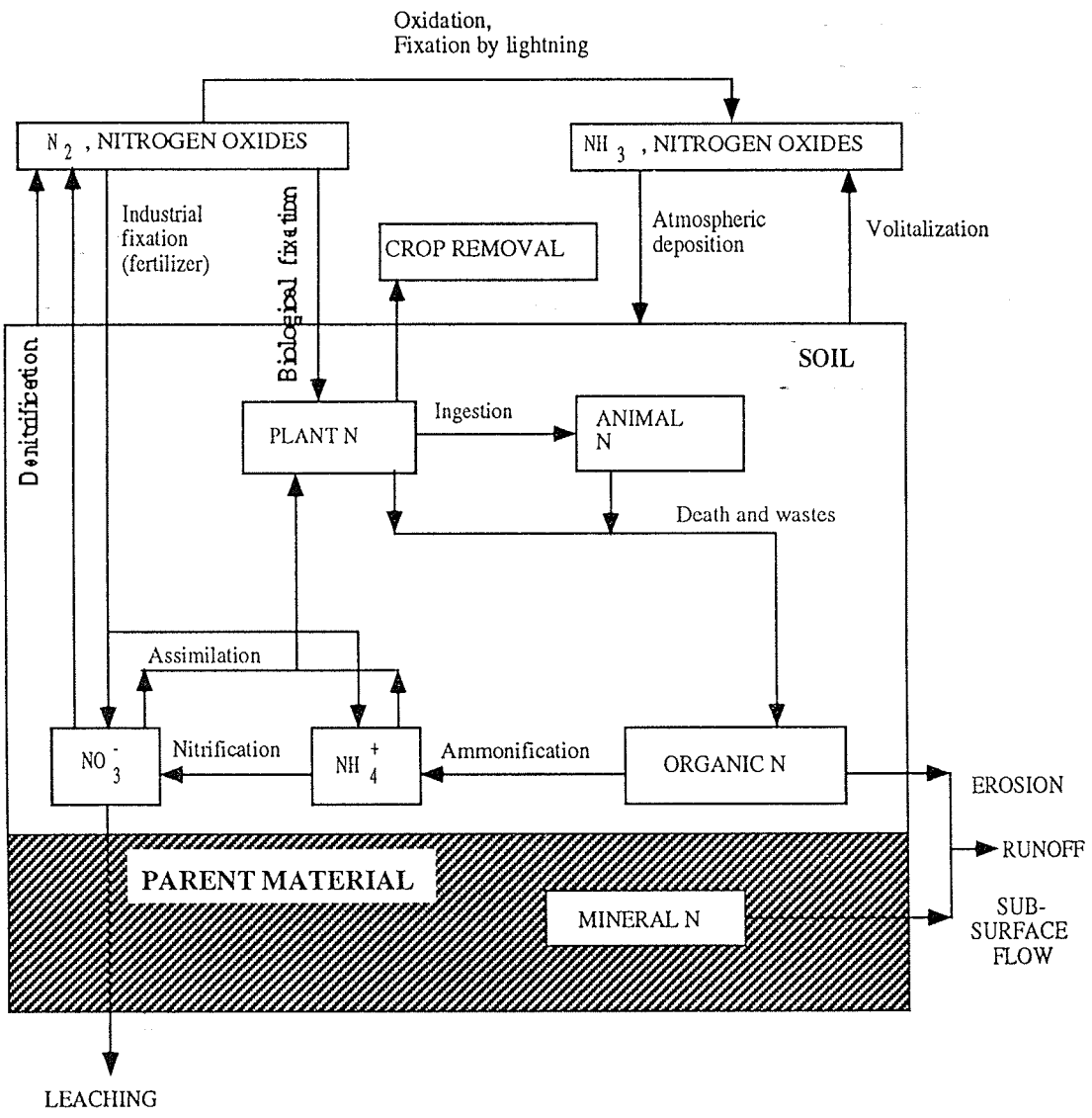


Figure 2.2. A simplified schematic of the terrestrial nitrogen cycle.

making it difficult to determine the general fate of atmospherically deposited nitrogen over any area of significant size. However, using these criteria, a classification scheme for forested sites has been developed to evaluate a site's potential to retain/leach nitrogen (Melillo et al., 1989; Johnson and Lindberg, 1992). For example, sites in the Chesapeake Bay watershed generally fall into the zero-to-low leaching classifications (Hunsaker et al., 1994).

A central difficulty in all discussion of watershed retention relates to the use of average values in assessments. Watershed retention assumptions used in the Chesapeake Bay studies (see above) are presented in Table 2.3. These estimates vary over several orders of magnitude, primarily because of the lack of adequate evaluation data. Assembling an adequate understanding of long-term behavior when the processes involved are fundamentally episodic is one of the major challenges, and represents an area in which contemporary

**Table 2.3. Watershed retention values (in % of nitrogen loading) used in Bay loading studies to date** (numbers in parenthesis indicate range tested).

| Land Use | Tyler, 1988 | Fisher and Oppenheimer, 1991 | Hinga et al., 1991 |
|---|---|---|---|
| Forest | 95.2-100.0 | 80.0 (51.0-100.0) | 80.0 (25.0-95.0) |
| Pasture | 93.7-99.96 | 70.0 (51.0-90.0) | 80.0 (25.0-95.0) |
| Cropland | 76.0-99.97 | 70.0 | 60.0 (45.0-75.0) |
| Residential | 62.0-95.3 | 35.0 (0.0-70.0) | 25.0 (10.0-50.0) |

models are sorely deficient. It is apparent from measurements that the majority of the atmospheric wet deposition occurs during a few episodes (Dana and Slinn, 1988; Fowler and Cape, 1984), such that the wet-deposited nitrogen (as well as previously dry-deposited nitrogen) is deposited directly to or can flow quickly into the surface waters without intermediate reduction in concentration.

### Total Loading Estimates

The role of atmospheric transport in providing an important path for nitrogen to estuarine areas was publicized in the EDF report (Fisher et al., 1988). Based on one year of measurements (1984), and assuming relationships between wet and dry deposition that are likely to be conservative, the authors estimated that one-third of the inorganic nitrogen entering the Chesapeake Bay comes from the atmosphere. There have been several subsequent efforts to quantify the atmospheric nitrogen loadings to Chesapeake Bay (Fisher and Oppenhiemer, 1991; Hinga *et al.*, 1991; Tyler, 1988). The approach taken in these studies can be divided into two components: estimating wet and dry deposition and estimating watershed retention. However, the assumptions used in these studies overshadow the results; the error associated with these estimates is typically quoted as being a factor of 2 or sometimes as much as a factor of about three. The most recent and best estimate of atmospheric nitrogen loads (i.e., 27% of the annual

load) to the Bay were developed through the Chesapeake Bay Program (CBP; Chesapeake Bay Program, 1996). This estimate falls within the range reported for other estuaries (10-45%), see below. To estimate wet deposition, the CBP combines output from a regression model developed from NADP weekly and daily precipitation chemistry measurements with data from the high density NOAA rainfall network. This approach yields daily estimates of rainfall to 74 sub-basins of the Chesapeake Bay watershed. Dry deposition is assumed to be equal to wet deposition for over-land areas and 44% of wet for over-water areas. Indirect atmospheric loadings from the terrestrial watershed are estimated with the CBP Watershed Model, a bulk-parameter model. In the coming decades, it is predicted that the atmosphere will become a more significant source of nitrogen loadings to the Chesapeake Bay with anticipated increases in population and land development resulting in more mobile and new power plant emissions (Fisher et al., 1988; Pechan, 1991).

## *Loadings Intercomparison Between Coastal Waters*

There have been approximately 40 studies around the world which addressed at least one aspect of atmospheric loadings, the majority of which were published since 1990. However, the measurement and modeling techniques used vary considerably between individual studies, making intercomparisons difficult. Table 2.4 presents a summary of selected studies performed along the U.S. East Coast which are comparable in broad terms. There were two criteria for selection based not on scientific merit but on the approach and information content. These criteria required that the results were either:

- published in a credible peer reviewed journal
- advocated by a major management organization (e.g., an EPA National Estuary Program)

These studies can be divided into two groups: those which considered both direct and indirect nitrogen loads and those which considered only direct loads. Table 2.4 confirms the common belief that the amount of atmospheric nitrogen input is related to the size of a waterbody and its watershed.

It is interesting to note that although the percentages listed in Table 2.4 have an apparently constrained range (10-45%), the numerical estimates of atmospheric loadings vary widely. This point highlights the danger of using percentages as the basis for large scale management decisions. Many areas along both the East Coast and the Gulf of Mexico remain to be investigated. The uncertainties of the studies to date make it imperative that a better understanding be obtained of the processes that transport and deposit nitrogen to estuaries and coastal zones.

**Table 2.4 Current estimates of nitrogen loading (Millions of Kg) to selected coastal waters attributed to direct and indirect atmospheric input.**

| | Surface area watershed ($km^2$) | Surface area of tidal waters ($km^2$) | Deposition onto the watershed | Deposition onto the tidal waters (i.e., direct load) | Atm. load delivered from the watershed (i.e, indirect load) | Total atm. Load | Total load from all sources (incl. Atm.) | % load from the atm. | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| Narragansett Bay (R.I.) | 4708 | 328 | 4.2 | .3 | .3 | .6 | 5 | 12 | 1 |
| Delaware Bay | 36905 | 1846 | 53 | 3 | 5 | 8 | 54 | 15 | 2 |
| Long Island Sound | 43481 | 4820 | 45 | 5 | 7 | 12 | 60 | 20 | 3 |
| Albemarle-Pamlico Sounds | 59197 | 7754 | ~ 39 | 3.3 | 6.7 | 10 | 23 | 44 | 4 |
| Chesapeake Bay | 165886 | 11400 | 175 | 16 | 29 | 45 | 170 | 27 | 5 |
| New York Bight | 50107 | 38900 | 69 | 54 | 8 | 62 | 164 | 38 | 1 |
| Rhode River (Md.) | 33 | 4.9 | - | .005 | - | .005 | .012 | 40 | 6 |
| Waquiot Bay (Ma.) | ~ 70 | ~ 8 | .062 | - | .0065 | .0065 | .022 | 29 | 7 |
| Flanders Bay (N.Y.) | 83 | 39 | - | .027 | - | .027 | .36 | 7 | 8 |
| Delaware Inland Bays | 800 | 83 | - | .28 | - | .28 | 1.3 | 21 | 9 |
| Sarasota Bay (Fl.) | 524 | 135 | - | .16 | - | .16 | .6 | 26 | 10 |
| Patuxent River (Md.) | 2393 | 137 | - | .22 | - | .22 | 12.6 | 13 | 11 |
| Newport River Coastal Waters (N.C.) | 340 | 225 -1600 | - | .095-.68 | - | .095-.68 | .27-.85 | 35-80 | 4 |
| Narragansett Bay (R.I.) | 4708 | 328 | - | .4 | - | .4 | 9 | 4 | 12 |
| Choptank River (Md.) | 1779 | 361 | - | .57 | - | .57 | 1.54 | 37 | 11 |
| Guadalupe Estuary (Tx.) | - | 551 | - | .31 | - | .31 | 4.2-15.9 | 2-8 | 13 |
| Potomac River (Md.) | 29940 | 1210 | - | 1.9 | - | 1.9 | 35.5 | 5 | 11 |
| Tampa Bay (Fl.) | 6216 | 1031 | - | 1.1 | - | 1.1 | 3.8 | 28 | 14 |
| Massachusetts Bays | - | 3700 | - | 1.6-6 | - | 1.6-6 | 22-30 | 5-27 | 15 |

1. Hinga et al., 1991; 2. Scudlark and Church, 1992; 3. Long Island Sound Study, 1996; 4.Paerl and Fogel, 1994; 5. Chesapeake Bay Program, 1996; 6. Correll and Ford, 1982; 7. Valiela et al., 1996; 8. Peconic Bay NEP; 9. Delaware Inland Bays NEP; 10. Sarasota Bay NEP; 11. Boynton et al., 1995; 12. Nixon et al., 1995; 13. Brock et al., 1995; 14. Tampa Bay NEP; 15. Massachusetts Bays NEP.

# Chapter 3
# REMAINING ISSUES

As the ANICA Program progressed it became clear that there is a large need for information dissemination regarding atmospheric nitrogen issues. ANICA scientist were directly involved in three such informational projects. In early 1994, a literature synthesis entitled, "Atmospheric Deposition of Nitrogen and Contaminants to the Chesapeake Bay and Its Watershed" (Valigura et al., 1995) was completed for and published by the Chesapeake Bay Program Scientific and Technical Advisory Committee. The second effort was a scientific workshop (referred to as the Mt. Washington Workshop) entitled, "Atmospheric Loadings to Coastal Areas - Resolving Existing Uncertainties," and was held in June 1994 in Baltimore, Maryland. The third effort was a policy-oriented workshop (referred to as the Airlie House Workshop) entitled, "Airsheds and Watersheds - The Role of Atmospheric Nitrogen Deposition," and was held in October 1995 in Warrenton, Virginia.

## *The Literature Synthesis*

The literature synthesis concluded with the following recommendations for steps to reduce uncertainties associated with prediction of atmospheric loadings. Depending on chemical species, the current uncertainties in estimates of atmospheric loading of nitrogen and contaminants to Chesapeake Bay and its watershed range from ± 20% to orders of magnitude. However, if ways are to be found to reduce such atmospheric deposition, it is essential that the processes be better understood and that the quality and reliability of the estimates be improved. Accordingly, it is recommended that the following steps be initiated. These steps are not comprehensive or specific suggestions, but one list of key areas of uncertainty which will serve as discussion points in future deliberations. They are:

- Conduct monitoring and research experiments focused on improving measurements and modeling techniques to further understand and quantify the emission cycles of the key chemical species

- Develop and perform nitrogen speciation experiments including on organic nitrogen and ammonia compounds; subsequently, conduct intensive studies of the dry deposition rate of nitrogen compounds from air crossing the watershed zone of the Chesapeake Bay region

- Investigate the effect of localized contaminant deposition in both urban and near-urban environments; specifically, develop estimates of surface-water loadings attributable to urban runoff and investigate the temporal and spatial distribution of $NO_y$ deposition

- Establish integrated monitoring sites of atmospheric emission and deposition; initial focus should be on the concurrent measurement of the chemistry, intensity, and duration of precipitation and streamflow events

- Establish over-water precipitation chemistry sites and compare the results with those from land-based precipitation chemistry sites

- Establish common data bases to process and store data that can be used as input to models and/or to test specific predictions of the models; this effort should include emission inventories (anthropogenic and natural), wet and dry deposition rates at specific locations to be covered by the model, spatial distributions of soil and atmospheric moisture, chemical concentration distributions, and relevant meteorological supporting data

- Clarify the role of urban areas as a source of atmospheric contaminants to surface waters; conduct research on sampling methods for small particle deposition and source attribution for organic contaminants

- Investigate the bioavailability of materials deposited from the atmosphere; conduct exposure studies to learn how chemical speciation influences exposure

## *The Mt. Washington Workshop: Developing Science Priorities*

To focus attention on the problem, and to take a first step towards ordering scientific programs to reduce existing uncertainties in the quickest manner, a meeting of active scientists from different contributing disciplines was conducted at Mt. Washington, Maryland, on June 29-30, 1994. The workshop was sponsored by the Scientific and Technical Advisory Committee and the Air Quality Coordination Group of the Chesapeake Bay Program (CBP). The gathering included representation from the Great Lakes research community and federal and state agencies.

The challenge given to the workshop was simple -- to construct a prioritized listing of practical studies that would make the greatest impact on reducing the current uncertainty in estimates of the contribution of atmospheric deposition to declining aquatic ecosystem health. The workshop was constructed to produce such an ordering through meetings of interacting working groups and concluding with extensive plenary discussion of the working group conclusions.

The listing that resulted is summarized below and substantiated in the documentation that follows. It was concluded, however, that scientific investigations that are already under way are making considerable progress; in essence, any new efforts should be arranged to build on existing programs rather than risk new starts that compete with older ones. It was also concluded that there is a general need for improvement in the scientific programs already ongoing for all measurement methods, models, and evaluation of pollution reduction strategies.
The emphasis of the workshop discussion was on all nitrogen species, toxic chemicals, trace metals, precipitation chemistry, airborne aerosols, and supporting meteorological investigation. In every one of these cases the general call for a new focus applies, although with different weights according to the particular emphasis. The workshop put priorities in the following order:

Priority 1 -- **Conduct intensive, coordinated integrated monitoring at special locations within the watershed, with wet deposition, dry deposition, and local catchment area characterizations.** It was concluded that the single most limiting factor in assessing the adequacy of current models is the lack of quality data on actual deposition within the target watershed. Until an integrated monitoring station is operational, there will be no comprehensive data set for evaluating model performance.

Priority 2 -- **Work to improve existing atmospheric models.** In brief, there are many limitations of current models, especially including their limited grid size (smaller grid cells are desired) and their inability to handle orographic and chemical factors that are likely to be of critical importance.

*The above top priorities reflect the workshop's recognition that current models are likely to be misleading, but that the extent of any errors cannot be judged because the key observations of deposition are not yet made.*

Priority 3 -- **Improve biogeochemical watershed models.** The workshop recognized the important role of watershed chemical retention and emphasized the need for close linkages with the appropriate expert scientific community.

Priority 4 -- **Improve emissions inventories and projections.** It was noted that assessments of atmospheric deposition are necessarily at the mercy of emissions estimates and that such estimates are currently highly imperfect both in the adequacy of reporting requirements and the spatial resolution used to report the emission values.

Priority 5 -- **Conduct process-oriented measurements to extend vertical and spatial meteorological and chemical concentration coverage and to quantify representativeness.** The models that are now needed for assessment purposes need more advanced input data than do the simpler models used in early assessments. As time progresses and as these models evolve further, input data requirements will increase. It was concluded that measurement programs to provide the data required by the models should be established.

Priority 6 -- **Establish an extensive array of less intensive measurements.** This item follows from Priority 1. In essence, a nested network is envisioned with a small number of Priority 1 intensive stations supporting a denser array of simple stations designed to provide improved spatial resolution for some selected variables.

The workshop considered the needs for uncertainty reduction in two distinct contexts:

- to build confidence by separate attention to individual parts of the source-emission-dispersion-deposition-delivery-effects process

- to test the accuracy of overall understanding and model predictions

In addition, it was pointed out that a quality assurance program to consolidate the existing network of wet and dry deposition (for nitrogen) sites is currently not in place. Therefore, deposition must be monitored, keeping ecological considerations in mind.

The meeting noted that current assessments are almost entirely based on large-grid model outputs without the benefit of actual deposition observations to the coastal areas that are thought to be affected. Consequently, the top research priority was associated with the need for one (or preferably several) Integrated Research Sites where actual deposition measurements could be made at locations where supporting ecological data are collected. Other priorities reflected the current state of science and the relative importance of different areas of uncertainty. In general, each participant was encouraged to think in terms of the science at the highest possible level leaving personal agendas and agency perspectives behind.

> *In general, it was concluded that work should continue on the development of atmospheric models which produce output of finer-grid resolution for the airshed affecting the Chesapeake Bay. Ancillary work should focus on studying the influence of key urban areas on the atmospheric loading to the watershed and tidal waters and to develop spatially-detailed wetfall and dryfall atmospheric-deposition input data for the watershed, tributaries, and coastal waters off the Bay mouth. Coordination of this activity appears to be an appropriate role for the CBP Air Quality Coordination Group.*

Finally, it was noted that no part of the workshop deliberations should be considered relevant only to the Chesapeake Bay. It was specifically concluded that the ordering listed above would be equally appropriate for other affected coastal areas.

## *The Airlie House Workshop: Identifying Implications for Management*

A workshop was conducted at Airlie House Conference Center, Warrenton, Virginia, in October 1995, where leading scientists and key policy and regulatory officials assembled to explore mechanisms by which air and water pollution control programs can work together to help protect coastal ecosystems. The focus of the workshop was on atmospheric nitrogen compounds, but many of the conclusions would apply equally well to other pollutants occurring in the air, such as toxic chemicals, trace metals, and persistent organic compounds. In all such instances, the atmosphere constitutes a resource that is shared among many different coastal jurisdictions and between the air and water regulatory communities.

Scientific uncertainty has historically been an obstacle to proactive management response. The Airlie House Workshop reported here benefitted from the ability to draw upon scientific conclusions and recommendations about the coastal atmospheric deposition problem that were developed following the Mt. Washington Workshop. Given this information, participants concluded that scientific uncertainty has been reduced to the extent that some new or modified

regulations and controls can be justifiably implemented.

Atmospheric deposition of nitrogen species is recognized by all East Coast estuarine programs as either a significant contributor to estuarine eutrophication or a mechanism of possible concern. The region from which the atmospheric nitrogen pollution arises is much larger than the water surface that is potentially affected, and even much larger than the watershed that drains into it. The extent of "airsheds" are now starting to be recognized. The Chesapeake Bay airshed, depending on the definition used, is up to 600,000 square miles ($10^6$ $km^2$) in area, extending upwind of and bordering the water body itself. Emissions from an airshed of this magnitude affect more than a single estuary. For example, the emissions from the Chesapeake Bay airshed may affect the entire coastline such as from the Carolinas to New York. Thus, airsheds constitute an important "shared resource" that must be recognized. Reductions in emissions in airsheds benefit many downwind ecosystems, and assessments of the benefit of such reductions must take all benefitting water bodies into account, not just one single ecosystem that is especially favored.

It was noted that some reductions in nitrogen emissions have already been made as a result of the controls mandated by the Clean Air Act Amendments (CAAA) of 1990. However, participants expressed concern that political pressures may not permit the full emissions reductions proposed by the CAAA to be realized. Water quality scenarios need to be weighed carefully, since some assume full implementation of the CAAA controls whereas others disregard them. Current assessments of projected water quality (and of ecosystem viability) do not take the additional controls proposed by the Ozone Transport Commission into account. It should be noted that the CAAA, and therefore the present document, concentrates on the deposition of the products of emissions of nitric oxide (NO) into the atmosphere - essentially nitrates ($NO_3^-$). Very little is said about the role of products of ammonia emission - essentially ammonium compounds - which are of considerable importance but about which relatively little is known. The role of organic nitrogen species is also not emphasized; these are poorly understood but are known to be strongly influenced by biological sources that cannot be regulated.

The following five recommendations summarize the conclusions drawn by the participants of the Shared Resources Workshop.

- Efforts to resolve scientific uncertainties associated with the quantification of atmospheric deposition and the resulting loadings should be continued. The priorities identified at the 1994 Mt. Washington workshop serve as a useful reference for planning future work. Future research should also focus on quantifying atmospheric nitrogen fluxes to the coastal ocean and characterizing the biochemical cycle of organic nitrogen through the Chesapeake Bay watershed.

- Although there is uncertainty in many areas, enough is known to determine a general direction for action. Managers and regulators should move forward and not wait for all of the uncertainties to be resolved. Accuracy is possibly most needed when weighing costs of controls *versus* benefits.

- A set of basic information for use in explaining the cause for concern about atmospheric deposition and waterbody effects to the public, politicians, regulators, etc., should be generated. It was considered likely that a single set of basic material could be used as the core of issue-related material addressing current understanding about emissions, atmospheric deposition loadings by watershed and water body, areas of greatest uncertainty, etc. This would promote cooperation and coordination across the organizations involved and avoid sending mixed messages.

- A cross-media approach to quantifying atmospheric deposition and resulting loadings needs to be developed. Greater cooperation across issues, estuaries and bays, scientific disciplines, and governmental units is essential. Barriers to greater cooperation should be identified and eliminated.

- In order to assure that such coordination continues, a future meeting of the present kind (but with representation from an enlarged group of organizations) should be held in about a year's time.

The workshop concluded that there is need for: a) a better understanding of how all atmospheric nitrogen species affect coastal ecosystems and of the related policy options, b) a cross-media approach to the atmospheric deposition and loadings problem, and c) a coalition of interested parties extending from the north to the south of the potentially affected East Coast of the continental U.S., including both terrestrial and biological aspects as equals. The work that is needed is essentially multi-media, requiring attention by a consortium of workers rather than separate attention by specialists operating independently.

> *The workshop resulted in a clear and loud call for more cooperation across different issues, estuaries and bays, scientific disciplines, and state and federal agencies. Outreach to state and federal agencies, non-government organizations, industry, and the public at large, is critically needed.*

Even in these days of calls for cooperation and integration, the close association required in the present context calls for attention by teams of workers that has classically been difficult to arrange and maintain. In the present case, there seems to be no option; the importance of the issue and its environmental sphere of influence combine to make it more important than ever before to build a working alliance of researchers and regulators addressing the atmospheric deposition issue. The role of atmospheric deposition is known to be important in many areas of concern, the atmosphere does indeed constitute a genuine **shared resource**, and a coordinated attack on the problem is recognized as an essential element rather than a desired goal. **The Airlie House workshop was a start along a road to more extensive cooperation specifically intended to lead to more accurate assessments of atmospheric deposition to all East Coast estuaries and to arrange for the results to be presented in an optimal format for assimilation by policy and regulatory processes.**

## Appendix A
# LIST OF ANICA TASKS

TASK 3.1.1: Bring together data from various wet deposition networks, examine quality assurance, and assemble appropriate information into a single data set for further analysis.

TASK 3.1.2: Assess deposition of organic nitrate using specially-equipped monitors at a single site, and later using a number of sites as determined on the basis of the initial exploration.

TASK 3.1.3: Sort deposition data according to event precipitation rates and amounts, and reported in a probabilistic manner as well as in terms of long-term average deposition rates.

TASK 3.1.4: Set up new sampling sites. Sites will be sought that provide precipitation data representative of the central portions of the Chesapeake Bay, and precipitation records will be compared against values interpolated from terrestrial isopleths. If no existing sites that are suitable can be located, then special sites will be set up.

TASK 3.1.5: Central-bay sites will be sought for data on wet deposition on an event basis. If no existing sites can be located, then special sites will be set up to test the hypothesis that wet deposition to the water surface of the Chesapeake Bay can be estimated adequately by interpolating terrestrial wet deposition isopleth maps.

TASK 3.2.1: Measure $HNO_3$ concentrations routinely at the Wye River site.

TASK 3.2.2: Conduct intensive intercomparisons against annular denuder methodologies to evaluate the quality of $HNO_3$ data reported by the NOAA filterpack techniques.

TASK 3.2.3: Conduct intensive air chemistry investigations of other airborne nitrogen compounds, especially $NO_2$.

TASK 3.2.4: Assess the spatial variability of air chemistry across the Chesapeake Bay watershed by use of Regional Acid Deposition Model or some better modeling capability benchmarked against the Wye River data.

TASK 3.2.5: Initiate Dry Deposition Inferential Method operation at the Wye River site and commence archiving deposition velocities for $HNO_3$ and $NO_2$.

TASK 3.2.6: Obtain satellite imagery and derive land-use categorized depiction of the Chesapeake Bay catchment area.

TASK 3.2.7: Produce modeled wind fields and related meteorological data for the Chesapeake Bay catchment area.

TASK 3.2.8: Produce areal representations of deposition velocities for the entire catchment area.

TASK 3.2.9: Benchmark the DDIM predictions for the Wye River sites for both $NO_2$ and $HNO_3$.

TASK 3.2.10: Instrument water buoys to monitor the stability regime over the water surface. Use the data obtained to compute deposition velocities for $NO_2$ and $HNO_3$ appropriate for the water surface itself.

TASK 3.2.11: Derive probabilistic representations of deposition velocity regimes in order to express water surface deposition of $NO_2$ and $HNO_3$ (primarily) as a function of month and season.

TASK 3.2.12: Combine terrestrial deposition velocity fields (from Task 3.2.8) with air concentration fields (Task 3.2.4) to provide monthly and seasonal quantifications of the dry deposition of nitrogen species to the terrestrial watershed.

TASK 3.2.13: Combine aquatic deposition velocity fields (from Task 3.2.11) with air concentration fields (Task 3.2.4) to provide monthly and seasonal quantifications of the dry deposition of nitrogen species to the water surface of the Bay.

TASK 3.2.14: Conduct intensive field studies as required to evaluate the accuracy and adequacy of these quantifications.

TASK 3.3.1: Assemble a data base giving weekly, monthly, and seasonal values representing: a) dry deposition to the water body, b) wet deposition to the water body, c) dry deposition to the surrounding watershed, d) wet deposition to the surrounding watershed, e) precipitation quantity, f) riverine nutrient input, and g) representative Bay water concentrations of related nutrients.

TASK 3.3.2: Conduct multiple lag correlation analyses of the assembled data so as to deduce statistical relationships among the variables as a function of season.

TASK 3.4.1: Conduct aircraft assessments of the horizontal fluxes of nitrogen species in air flowing across the Chesapeake Bay watershed as a function of altitude and season.

TASK 3.4.2: Utilize the ANICA data set to improve regional deposition models for future use in assessing atmospheric nutrient deposition to vulnerable ecosystems.

# Appendix B
# ESTIMATING DEPOSITION: SPECIFIC STUDIES

*A Regression Approach for Estimating Precipitation Chemistry*

## Background

The modeling subcommittee of the Chesapeake Bay Program was interested in an immediate improvement to the input of atmospheric nitrogen from $NO_3^-$ and $NH_4^+$ into the Bay Watershed model via precipitation (i.e., wet deposition). Data from 15 National Atmospheric Deposition Program (NADP) sites within and around the Chesapeake Bay watershed were used to investigate statistical relationships between the amount of precipitation and the concentration of nitrogen species in the rainfall. Using these statistical relationships and NOAA precipitation records, improved methods for estimating wet deposition nitrogen loading to the Chesapeake Bay were developed. Although statistical methods are not complete solutions to the problem both are an improvement over older approaches used by the Bay Program.

## Method

Two datasets were used to develop the proposed methods; one from the NADP and another from the MAP3S precipitation chemistry network. The primary network collecting precipitation chemistry data is coordinated by the NADP. The NADP was initiated in 1978 and is still in operation, consisting of some 193 sites funded on a site-to-site basis by a variety of organizations. These sites have identical siting and sampling criteria, and all data are analyzed in the same laboratory and using the same methodology. Precipitation samples are collected for one week with wet-only samplers and then sent to the Illinois State Water Survey for analysis. The proposed methods were either developed from or directly use the dataset collected by the NADP during 1984-1992 from the 15 NADP sites in and nearest to the Bay watershed.

The MAP3S network was begun in 1976 and collected data until 1990 from nine sites along the Northeast United States. The MAP3S sites, like the NADP sites, had coordinated siting, sampling, and analytical criteria to allow intercomparisons between sites. However, precipitation samples were collected on a event basis using wet-only samplers. The regression method was tested using datasets collected from 1978-1986 by three MAP3S sites located within the watershed.

The regression method is based on the basic logarithmic relationship between amount of precipitation (mm $ha^{-1}$) and the $NO_3^-$ and $NH_4^+$ concentrations in the precipitation (mg $mm^{-1}$). A relationship was developed using weekly data collected over an eight year period at the 15 NADP sites. Due to the weekly sampling protocol of NADP, the data were quality controlled by selecting those data where the precipitation event occurred only on the last day of the weekly sample. These data can be interpreted as daily samples, analyzed by the NADP network. Using this criterion, 265 samples were obtained from the approximately 5020 samples collected from the

NADP sites, and these samples were used to develop the regression model. The coefficients of the final regression model are shown in Table B.1. The final model was chosen from a list of variables which included log of precipitation, month, month$^2$, sine of month, cosine of month, latitude, and longitude. This model was then tested (estimated vs. measured) on 8 years of event based data (approximately 1800 samples) collected independently at three MAP3S sites in and around the watershed (Table B.2). Estimates of annual total nitrogen ($NO_3 + NH_4$) deposition were within 20% of that measured. On an individual event basis, estimates generally fell within a factor of two.

**Table B.1. Regression coefficients of the selected models (p values).**

| | Intercept | ln(ppt) | month | month$^2$ | Latitude | $R^2$ |
|---|---|---|---|---|---|---|
| $NO_3$ | -1.289 (.0811) | -.3852 (.0000) | | -.0037 (.0000) | .0744 (.0001) | .41 |
| $NH_4$ | -1.226 (.0000) | -.3549 (.0000) | .3966 (.0000) | -.0337 (.0000) | | .31 |

**Table B.2. Testing statistics for total nitrogen ($NO_3^- + NH_4^+$) deposition estimates (in percent).**

| Site Location & Network | Mean Error in Annual Estimates | Mean Error in Event Estimates | Error Variance in Event Estimates | Maximum/Minimum Event Errors |
|---|---|---|---|---|
| State College, Pa. MAP3S | -19 | 5 | 77 | 998 / -80 |
| Charlottesville, Va. MAP3S | -18 | 21 | 95 | 649 / -94 |
| Lewes, Del. MAP3S | - 2 | 44 | 339 | 973 / -81 |
| 15 Sites NADP | -19 | 17 | 65 | 490 / -80 |

## Implementation

The Watershed Model used by the Chesapeake Bay Program is a bulk parameter model which divides the Chesapeake Bay watershed into 70 segments related to small-and-intermediate-scale watersheds. Each of the watershed segments has an associated hourly precipitation data record. To develop wet deposition estimates for the entire watershed, the regression method was employed using the precipitation data records. The result was a daily wet deposition data set for each segment. Figure B.1 shows the average annual deposition estimates by watershed segment.

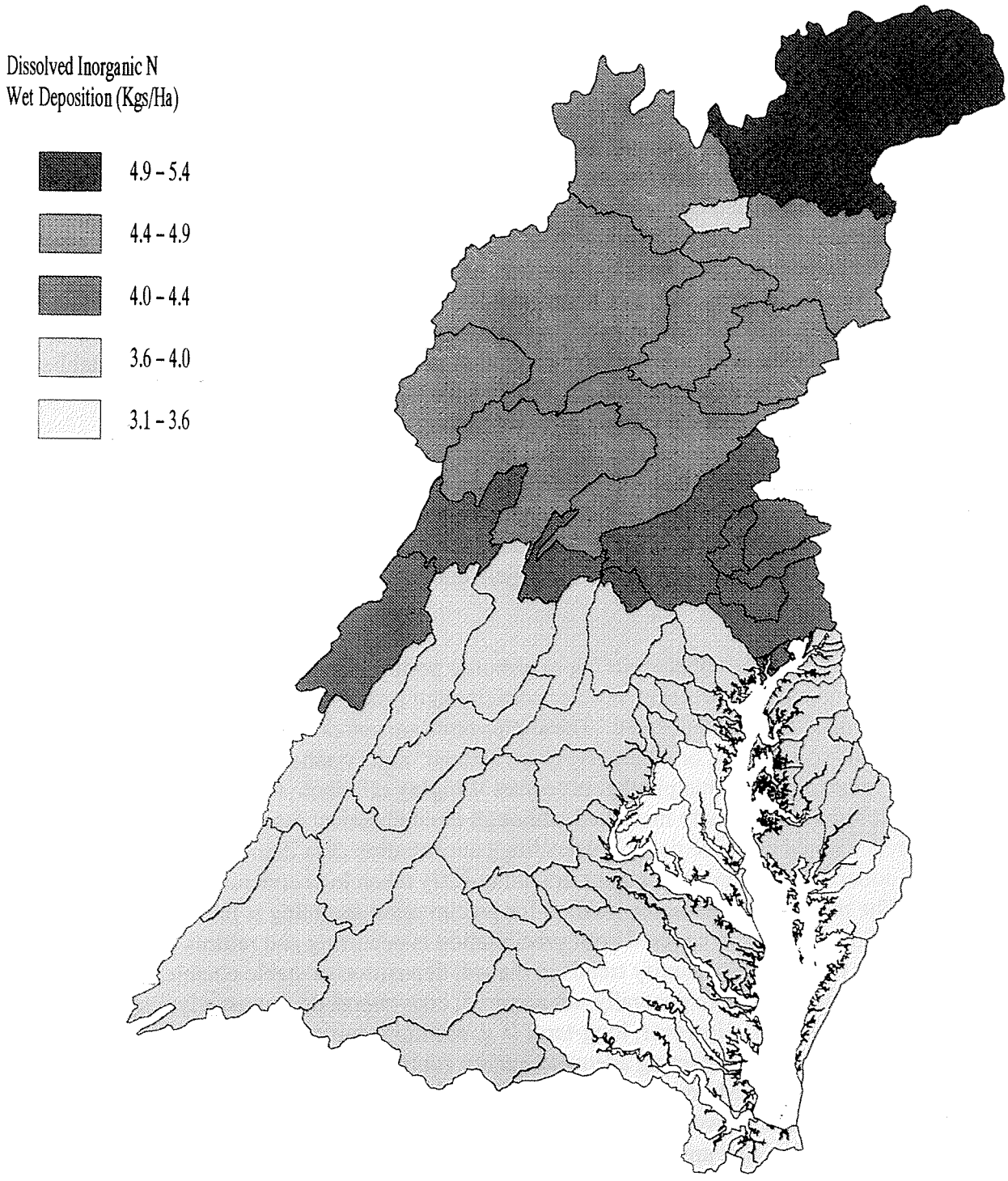


Figure B.1. Spatial distribution of the wet deposition of inorganic nitrogen across the Chesapeake Bay watershed.

*Wet Deposition Over Chesapeake Bay*

## Background

The Mt. Washington Workshop listed as a top priority the need to provide actual data against which to compare model predictions and assessments. Wet-fall deposition of nitrogen has traditionally been estimated by creating isopleths of deposition between over-land precipitation chemistry sites. It is currently suspected that over-land wet deposition data do not adequately represent direct wet deposition rates to large waterbodies, primarily due to the complex meteorology in coastal areas such as Chesapeake Bay. The dearth of data concerning wet deposition of nitrogen to the Chesapeake Bay surface waters prompted ANICA scientists to propose the establishment of an overwater precipitation chemistry site. The site was established in September 1995. The resulting data set will provide a first opportunity to evaluate the effectiveness of over-land based sampling for estimating over-water deposition to large waterbodies, and to test model outputs against actual data obtained over the target area. The project will provide measurements of wet deposition of nitrogen species to the waters of the Chesapeake Bay using a wet-only collector erected on Smith Island in the lower Bay. Samples will be collected and analyzed using the National Atmospheric Deposition Program's (NADP) Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN) field and laboratory protocols.

Wet deposition is the result of scavenging of airborne particles and trace gases by clouds, fog, condensation, and by the collection of other particles and gases by hydrometeors as they fall from the clouds in which they were formed. These processes are sometimes referred to as "in-cloud" and "sub-cloud" scavenging, or alternatively as "rainout" and "washout" respectively. In general, scavenging of nitrogen by precipitation processes is highly efficient. Concentrations in collected precipitation samples are easily measured, although rapid chemical reactions occurring after samples are collected can give rise to misleading concentration data if analysis is not performed soon after collection, or if adequate steps are not quickly taken to chemically preserve sample integrity. The most widely accepted method for precipitation sampling is the wet-only collector, which is designed to remain covered until precipitation is occurring and returns to covered condition after rainfall. To quantify trends in the wet deposition of stable chemical compounds, short-term deposition data are generally not required; ecosystems do not usually respond rapidly to changes in deposition. However, long-term (e.g. monthly) sampling is usually avoided because of difficulty in maintaining adequate quality control over samples that remain in the field for long periods of time. Many networks have adopted a one-week sampling protocol as a reasonable compromise between high sample quality and reasonable operational costs. Weekly sampling provides data that are quite adequate for long-term trend detection and for assessing ecosystem inputs for stable ions, but are limited in their utility for coupling with meteorological models, and are often useless for process-oriented studies. In addition, while many of the heretofore studied ions are relatively stable for periods of weeks or months, problems such as nitrogen loading to estuaries and other coastal ecosystems require even shorter period collections as well as special handling to adequately ensure sample stability. As the questions posed to the

research community become more difficult, the demand for daily sampling is increasing.

With the exception of organic nitrogen compounds, the analytical techniques for major nitrogen species in precipitation are well established and can be considered fairly routine. Most of the current debate over the appropriate approach for measurement of wet nitrogen deposition is centered around field-sampling protocols (i.e., the process by which the sample is collected and transported to the analytical laboratory).

**Objectives**

Field protocols for the major networks around the world have been developed over 40 years of experimentation and debate. In the United States, the national network is the NADP. As of 1993, NADP consisted of 193 weekly sampling sites, and seven daily sampling sites (affiliated with the NOAA AIRMoN Program). The NADP weekly and AIRMoN sites have identical siting criteria for precipitation chemistry measurements, and all data are analyzed in the same laboratory using similar methodologies. The one major difference is that the weekly NADP samples are filtered at the laboratory to stabilize sample chemistry; AIRMoN samples are stabilized through continuous refrigeration beginning immediately after collection. In general, the site operator will visit the site on a daily basis. By evaluating the collector function record on each visit, the operator will check for precipitation during the previous 24 hours, excessive bucket lid openings other than during precipitation, and if more than one week has passed without a bucket change. If one of these events has occurred the site operator will change the bucket. If a sample has been collected, field chemistry (as appropriate) will be done, and the sample will be prepared and shipped to the central NADP analytical laboratory (the Illinois State Water Survey). The sample will be analyzed using NADP/AIRMoN guidelines. Quality assurance/quality control will be performed before the data is entered into the NADP/AIRMoN electronic database housed at Colorado State University.

*The goal is to produce two years of data on wet deposition of central nitrogen compounds (nitrates, nitrites, and ammonium) to the waters of the Chesapeake Bay, with daily time resolution.*

## *Wet Deposition of Organic Nitrogen*

### Background

Wet-deposition fluxes of inorganic N (primarily $NO_3^-$ and $NH_4^+$) to coastal eastern North America are well characterized and the corresponding dry-deposition fluxes, though substantially less certain, are reasonably constrained. However, the deposition fluxes of organic nitrogen ($N_{org}$) compounds are very uncertain. The lack of reliable measurement techniques and the associated dearth of field data are responsible for the poor state of current understanding. Various estimates for the relative flux of organic versus total N via wet deposition range from <10% to >60%. The four types of methods currently being evaluated for atmospheric investigations of $N_{org}$ are those commonly used to analyze total nitrogen ($N_T$) in seawater. These methods include: persulfate wet chemical oxidation (most widely used), UV photo-oxidation, high-temperature oxidation, and high-temperature catalytic oxidation. In all cases, $N_{org}$ is determined by subtraction from $N_T$ the sum of the ammonium, nitrate, and nitrite concentrations. Recent findings (Suzuki, 1993) suggest that the agreement between methods is reasonably good. The pyro-chemiluminescent method currently shows the most promise due to advantages of rapid and automated analysis, and small sample (100 µl) requirements. Other techniques are labor intensive and require approximately 100 ml of sample -- potentially a very serious constraint when studying small-volume precipitation events. With support from ANICA and the EPA Great Waters Program, the University of Virginia (UVa) has developed a pyro-chemiluminescent technique to reliably measure total N and organic N in dilute aqueous solutions, and is currently investigating sampling artifacts and assessing sample stability.

### Analytical Method

Wet-only precipitation is sampled using an Aerochem Metrics collector. As indicated above, sampling techniques and sample stability assessments are currently under investigation; specific sampling and handling procedures may be refined as a result of these investigations. Preliminary results suggest that organic N in precipitation is very unstable; to generate representative data, it may be necessary to subsample precipitation events in stainless steel containers and to preserve samples immediately against microbial degradation.

Samples are analyzed for $N_T$ using a modified ANTEK model 7000 analyzer. All N compounds are converted to NO via high-temperature combustion, and NO is subsequently quantified via chemiluminescence. Over the past several years, this approach has been used with increasing frequency to analyze atmospheric and marine samples. As described below, however, potentially serious problems may compromise resulting data. Few data generated using this approach have been published in the peer-reviewed literature.

Initial studies by UVa revealed that data generated using a range of "standard" conditions (recommended for application by the manufacturer and by other users) and an off-the-shelf instrument (configured for application by the manufacturer) were subject to large, significant

positive and negative artifacts; all compounds were not recovered with equal efficiency. The direction and magnitude of bias varied as a function of the chemical composition of the test solution and the corresponding method of calibration. "Standard" operating conditions also resulted in poor reproducibility and low precision. Because the organic fraction is calculated by difference, reliable results require highly precise and unbiased analytical data; performance using "standard" configurations and procedures was unacceptable.

UVa subsequently modified the instrument and the analytical procedure and are now able to generate unbiased and highly precise results at expected concentrations for a representative range of test compounds including $NH_4^+$, $NO_3^-$, urea ($CH_4N_2O$), and ethylamine ($C_2H_7N$).

**Proposed Research**

UVa has applied to several funding sources for funds to conduct a subsequent and more comprehensive analysis (i.e., over space and time) of $N_T$, inorganic, and (by difference) $N_{org}$ in wet deposition to eastern North America and to the western North Atlantic Ocean using this new and well-characterized technique. $NH_4^+$ and $NO_3^-$ will be measured by automated colorimetry and ion chromatography, respectively, using standard procedures for the Global Precipitation Chemistry Project (GPCP) and the Air/Ocean Chemistry Experiment (AEROCE); resulting inorganic data are precise to approximately +/-4% and unbiased. The above approach would comprise the most reliable and precise method currently available for measuring the wet-deposition flux of $N_T$ and $N_{org}$.

> *The goal of this investigation will provide the first comprehensive assessment of the atmospheric deposition of $N_{org}$ in eastern North America and the northwestern Atlantic Ocean thereby providing critical information concerning atmospheric N inputs to the Chesapeake Bay and other coastal waters in polluted regions.*

*Dry Deposition Inferential Method (DDIM) Measurements at Wye, Md*

## Background

As of 1992, the NOAA Dry Deposition Inferential Measurement (DDIM) network was composed of 11 dry deposition sites. In December 1992, a DDIM site was established at Wye, Md., constituting the second NOAA/DDIM site in the Chesapeake Bay watershed, the first being at Leading Ridge, Pa. Both Chesapeake Bay sites are collocated with NADP weekly and NADP/AIRMoN stations, thereby allowing estimates of total nitrate nitrogen deposition. The DDIM network was designed to develop methods of deposition estimation at a three core sites, and then expand these methods throughout the DDIM network. Concentrations of sulphur dioxide, particulate sulfate, particulate nitrate, and nitric acid are measured via heated inlet filterpacks. The filterpack samples are exposed for one week with an air flow of three liters per minute. Meteorological variables (e.g., wind speed and direction, standard deviation in wind direction, global radiation, air temperature and humidity, surface wetness, precipitation) are also measured at each site, thereby allowing dry deposition to be estimated via the inferential technique. These techniques were developed over several years of intensive research at the core network prior to network initialization. However, the core sites are not representative of the coastal environment, and it was not clear, *a priori*, if the DDIM method would work in a coastal areas.

## The DDIM Method

This method estimates dry deposition using air concentration data and calculating deposition rate based on measurement of atmospheric and surface factors or by consideration of land-use type (i.e., forest, cropland, etc.). For nitrogen compounds, this method is applicable only to those species that can be considered to be depositing at all times -- primarily $HNO_3$, but also particulate nitrate ($p\text{-}NO_3^-$; Meyers et al., 1989). These chemicals allow surface deposition fluxes to be treated as essentially uni-directional (toward the surface), and thereby inferred from atmospheric concentration data, provided that the characteristics of the situation in question can be formulated in terms of properties that can be measured. In this technique, the transfer coefficient is termed a deposition velocity ($V_d$). The value of $V_d$ is computed from field observations and used to estimate the dry deposition rate ($F_d$) from air concentration measurements C:

$$F_d = \rho V_d C.$$

Estimation of $V_d$ involves a balanced consideration of atmospheric and particle physics, chemistry, and biology (see Figure B.2). The deposition velocity is normally considered as an overall "conductance" of the pollutant to the surface and, consequently, the inverse of $V_d$ is described as the total resistance to pollutant transfer, $R_T$. This basic "resistance analogy" commonly specifies four major resistances:

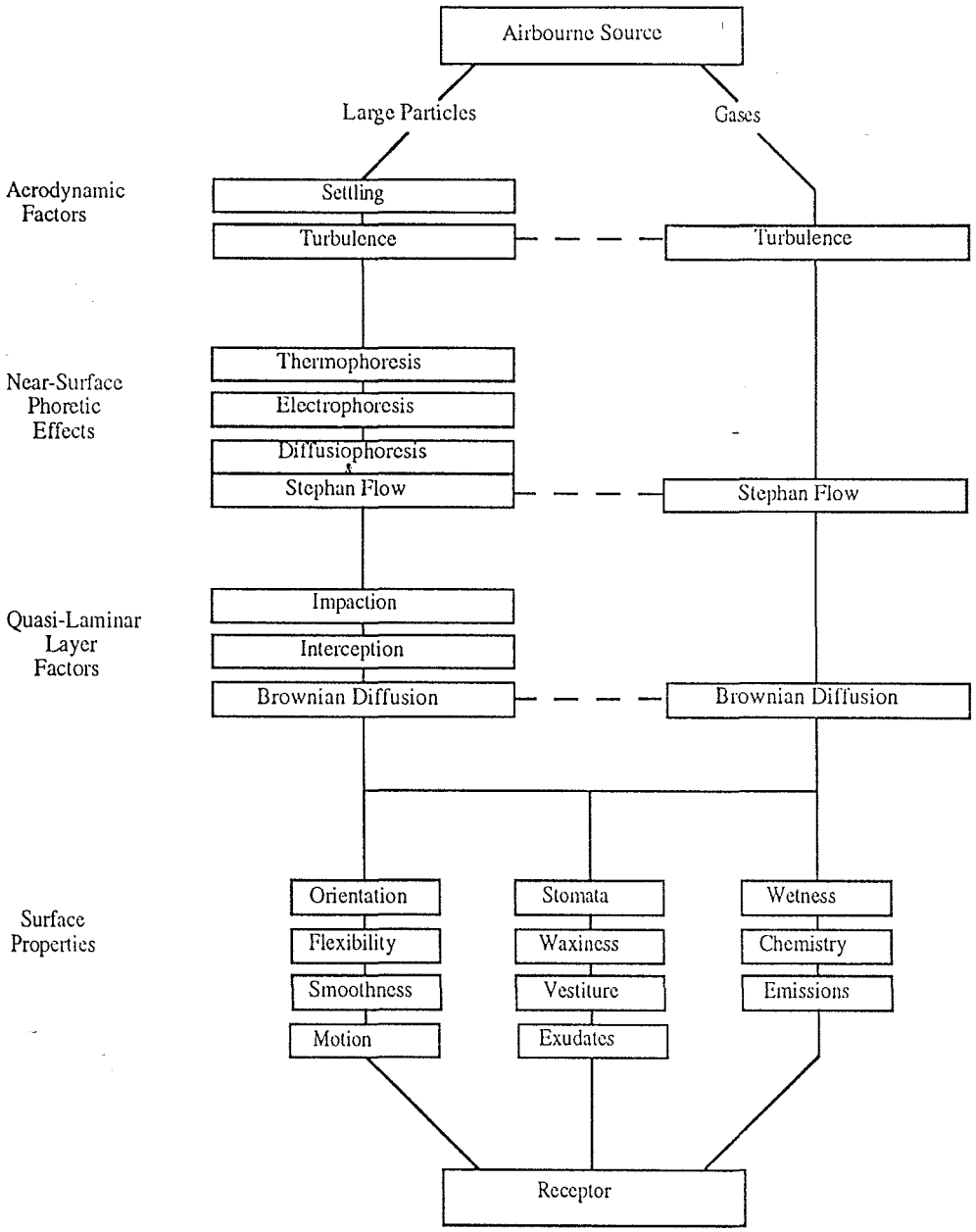


Figure B.2. A representation of the sequence of mechanisms influencing the deposition from the atmosphere of trace gases (right side) and diffusing particles (left). Not all processes are identified. (adapted from Hicks, 1986).

- an aerodynamic resistance, $R_a$, that is a function only of atmospheric properties, such as atmospheric turbulence and stratification;
- a near surface "quasi-laminar" resistance, $R_b$, that relates to the diffusion of pollutants across the near-surface layers where molecular and Brownian properties are important;
- a surface canopy, or residual, resistance, $R_c$, that expresses the consequences of the chemical, morphological, and biological processes influencing pollution adsorption or "capture" by the surface itself;
- gravitational settling, $V_g$, as modified by particle growth due to humidity interactions, is used to incorporate particle dynamics into $R_a$ and $R_b$ (note that $V_g$ is zero for gases).

It is important to note that these resistances are conceptually independent so that they may be considered in series, thereby allowing the calculation of $V_d$:

$$V_d = [(R_a + R_b + R_c + R_a R_b V_g)^{-1} + V_g].$$

There are three major areas of concern with this approach: i) the accuracy of the concentration data, ii) the accuracy of the deposition velocity, and iii) the applicability of the deposition velocity concept in the experimental circumstance. The first two issues have been and are currently being addressed by a variety of air chemistry and research programs; current estimates of the error associated with them is about ± 25%. The third concern points to the conceptual uni-directionality of $V_d$ as a potentially severe limitation, important to both modeling and measuring programs. The $V_d$ concept is derived from relationships developed to describe turbulent transport to surfaces that are effectively horizontal and uniform. When considering non-uniform landscape patterns (i.e., checkerboard forest and croplands), edge effects will be of considerable importance. The mechanisms involved will be largely advective, once again making the problem three dimensional. This is an over-riding problem in that a one-dimensional description is used by almost all existing deposition models. It is especially a problem in the coastal zone where the majority of the landscape is broken and varied.

**Results**

Data from the Wye site have been collected, archived and analyzed from December 1992 through December 1994. These analyses revealed deposition rates which were similar to those reported from other DDIM stations in the region, and that dry deposition of nitrate ($HNO_3$/p-$NO_3$) was approximately 46% of total nitrate deposition. However, further analysis indicated that the filter pack (chemical concentration) data may be suspect due to artifacts associated with high ammonia and sea salt concentrations over Maryland's Eastern Shore. Additional studies are planned to quantify errors associated with filterpack measurements in coastal areas.

## *Atmospheric Nitrogen Speciation Measurements*

### Background

Reactive nitrogen compounds are emitted to the atmosphere through both natural and anthropogenic pathways, overwhelmingly (95%) as NO. Nitrogen oxide is highly reactive in the atmosphere and is transformed into a variety of higher oxides of nitrogen. Understanding these transformations and their by-products is crucial to the understanding of tropospheric ozone production, air quality, and atmospheric nitrogen effects on coastal ecosystems. Through ANICA, NOAA/ARL developed the ability to perform research quality measurements of nitrogen oxides and their associated chemicals (i.e., $O_3$ and CO). Furthermore, several speciation experiments were performed, two of which are relevant to Chesapeake Bay. The first was a cooperative effort with the University of Maryland's Meteorology Department in September 1993. The second experiment, in August 1995, consisted of shipbourne nitrogen speciation investigations as part of the Atmospheric Exchange Over Lakes and Oceans (AEOLOS) Experiment in Chesapeake Bay. The University of Maryland performed a experiment investigation into $NO_x/NO_y$ speciation from September 2-28, 1993 at Wye, Md., making simultaneous measurements of NO, $NO_x$, $NO_y$, $O_3$. Concurrently, NOAA/ARL's Hybrid Single Particle Langrangian Integrated Trajectory (HY-SPLIT) model was used to run 24 hour "back trajectories in an attempt to determine the geographic history of the air-mass being sampled.

### Analytical Method

The accurate determination of $NO_y$ speciation is an intricate and complex undertaking which necessitates the use of several experimental techniques. NO, $NO_x$, and $NO_y$ may all be measured with a single instrument, a standard ozone chemiluminescence NO detector (Luke and Valigura, 1996). The ozone chemiluminescence (CL) technique is, for all practical purposes, the only widely used method of measuring atmospheric levels of nitric oxide. The technique is a continuous measurement method based upon the detection of photons released through the reaction of ozone ($O_3$) with NO. Ambient air is drawn into a reaction vessel at a controlled flow rate by a mechanical vacuum pump and mass flow controller. Ozone is generated within the instrument as a reagent by passing a flow of pure, dry oxygen through a high-voltage electrode; it is then directed into the reaction vessel where it reacts with NO in the sample flow to form $NO_2$. Approximately 10% of the $NO_2$ is formed in an electronically excited state ($NO_2$*) (e.g., Fontijn et al., 1970), a fraction of which relaxes back to the ground state by emitting a photon. The broadband emission spectrum ranges in wavelength from about 600-3000 nm, and the photons are detected by a red-sensitive photomultiplier tube (PMT). Because thermal emission and amplification of electrons by the PMT can overwhelm detection of the low-energy photons, it is necessary to cool the PMT with dry ice or thermoelectric junctions to minimize background noise. As long as ozone is in great excess in the reaction chamber, the amount of light detected at the PMT is proportional to the mixing ratio of NO in the sample air stream and the instrument pumping speed. $NO_x$ ($NO_x = NO + NO_2$) is measured by first passing the air through a photolytic conversion cell, where a fraction of the ambient $NO_2$ is photolyzed to NO and subsequently

detected. $NO_y$ is measured by first passing the ambient sample air through either a gold or molybdenum catalyst which efficiently reduces all $NO_y$ species to NO. The detector provides real-time, continuous output of NO, $NO_x$, and $NO_y$ concentrations.

Given the strong photochemical links between $NO_y$ and $O_3$, ozone concentration was measured using continuous UV photometric technique. Carbon monoxide was also be measured using a continuous technique, gas filter correlation (GFC), non-dispersive infrared (NDIR) absorption. Carbon monoxide is one of several compounds which participate in the photochemical oxidation of $NO_x$ and production of ozone. It is also an excellent tracer of incomplete combustion and can provide information on the severity of pollution events.

**The HY-SPLIT Model**

Grouping of trajectories into common spatial clusters is a method to classify different meteorological situations associated with pollutant transport from different source regions. These regimes can then be identified with specific periods of time, such as those associated with an air sample or deposition measurement.

As with many models using gridded meteorological data fields, the trajectory calculations (HY-SPLIT model; Draxler, 1992) follow a geometric approach. The trajectories' 3-dimensional motion is computed from the u,v, and $\omega$ (dp/dt) component winds output and archived every two hours from NOAA's National Centers for Environmental Prediction's Nested Grid Model (NGM). The time series consists of twice-daily consecutive model forecast fields from +2 h after initialization to +12 h. Archives of the 2-hour fields are available since 1991 from the National Climatic Data Center (NCDC; reference TD-6140). The fields are given on a 180 km polar sterographic grid at 10 model sigma levels from 0.982 to 0.434. There are about 4 levels within the boundary layer.

**Results**

The fraction of $NO_y$ which is most reactive is $NO_x$. Air influenced by fresh $NO_x$ emissions will by characterized by high $NO_x/NO_y$ ratio. Table B.3 shows that the mean ratio for the project was about 0.65. During the day this ratio varied from a broad morning maximum of ~0.80 to an afternoon minimum of <0.50. Polluted air arriving at the site mixes downward to the surface when the sun rises and instability occurs, but photochemistry is still weak. Later in the day, photochemistry dominates and $NO_x$ is converted to higher oxides of nitrogen (e.g., $HNO_3$). In the late afternoon to early evening, $HNO_3$ deposition combined with NO emissions from the soil lead to an increased ratio later in the day.

Results from the HY-SPLIT model back trajectories gave some insight into the origin of pollutants arriving to the Wye site. Figures B.3 and B.4 show the outputs from six model runs; three low $NO_x$ ("clean") days and three high $NO_x$ ("dirty") days, respectively. Note that the air highest in $NO_x$ came from Pennsylvania or the Baltimore/Washington region, while low-$NO_x$ air

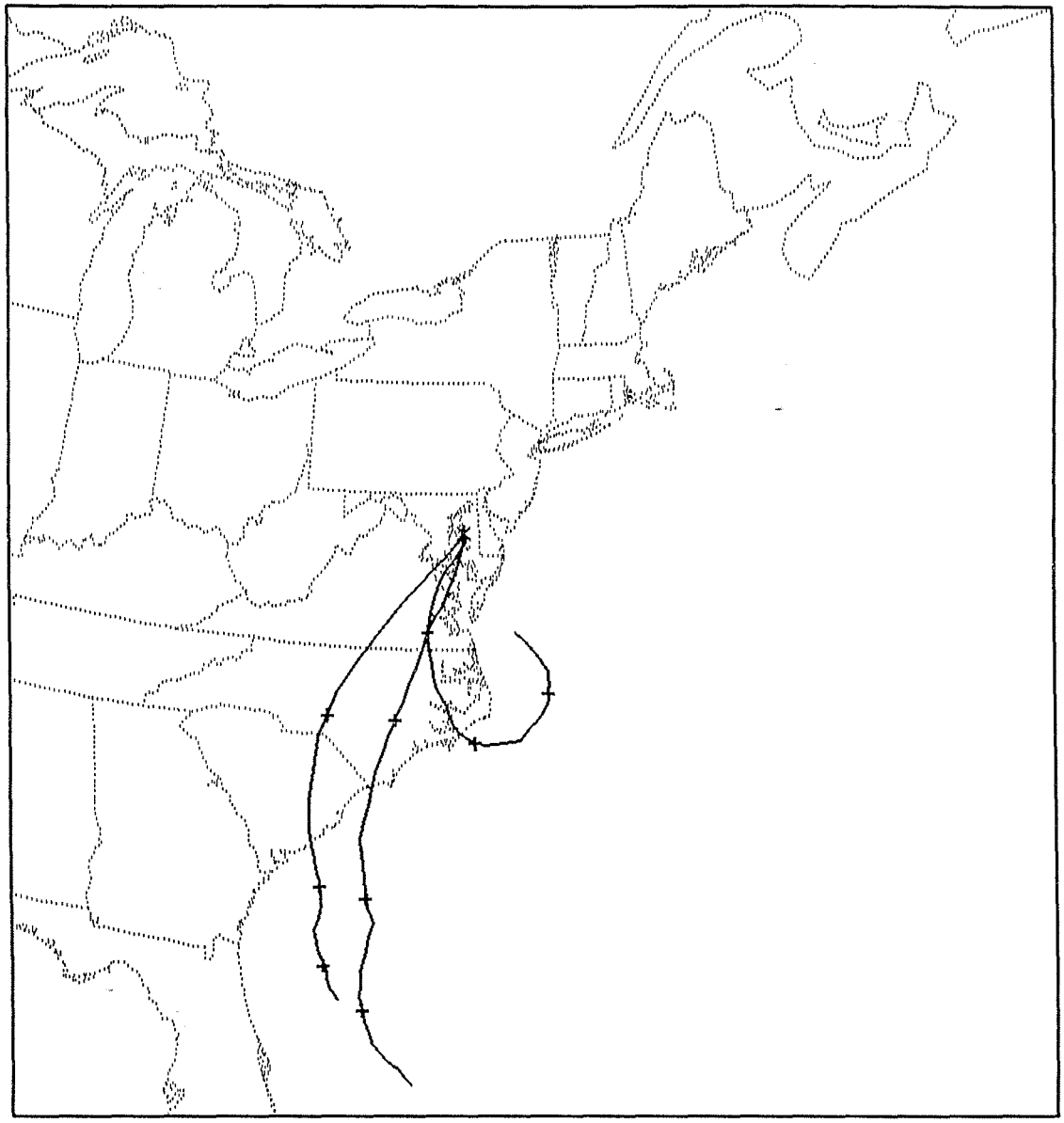

Figure B.3. The 48-hour back trajectories from Wye, Md. corresponding to periods of low measured $NO_x$ concentrations.

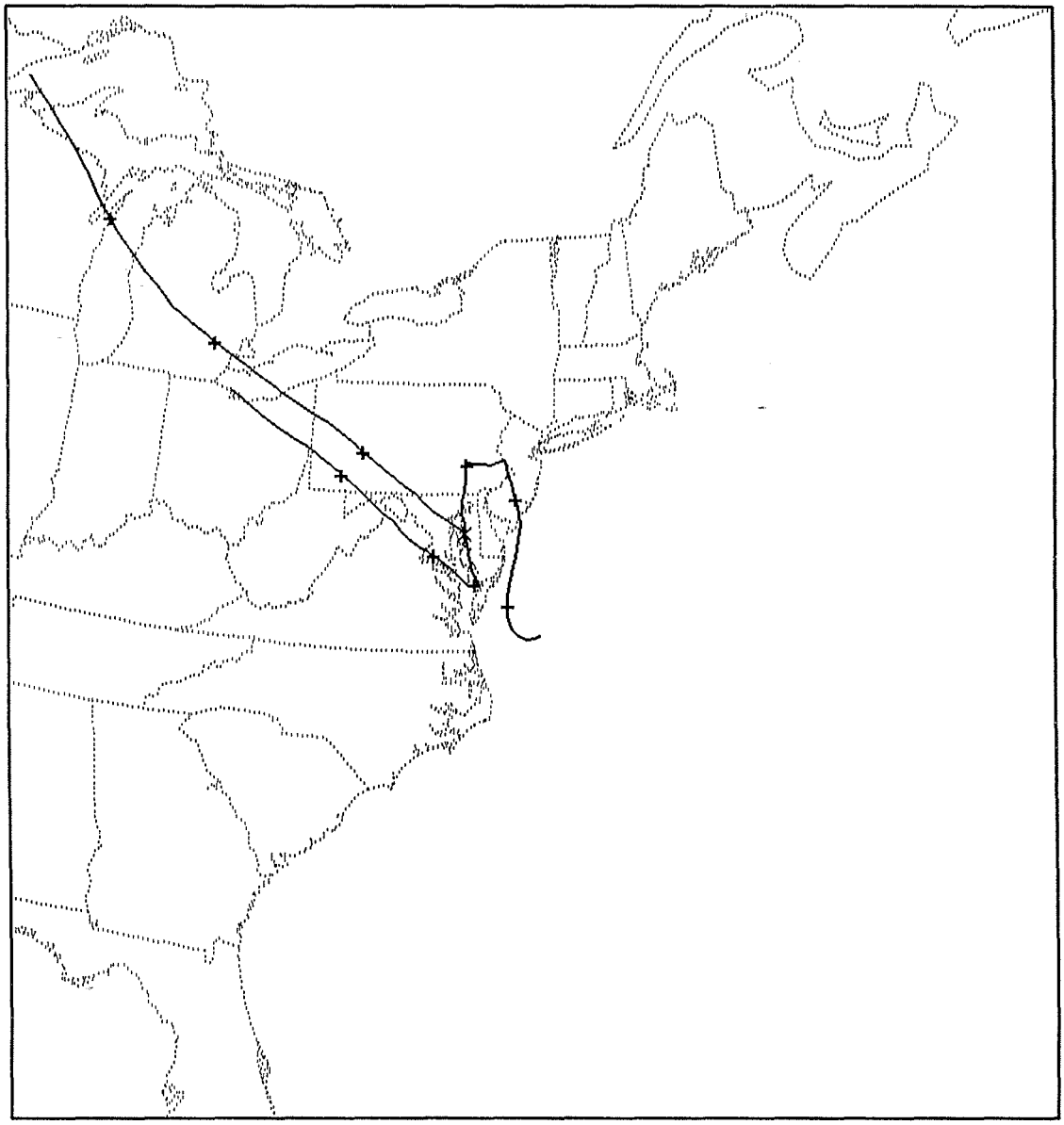

Figure B.4. The 48-hour back trajectories from Wye, Md. corresponding to periods of high measured $NO_x$ concentrations.

originated from the more rural south. Table B.4. contains the mean and observed maximum $NO_x$ mixing ratios during each 24-hour trajectory run.

**Table B.3. Basic $O_3$, CO, daytime NO, $NO_2$, $NO_y$, and $No_x/NO_y$ statistics for data collected at Wye, Md. between September 2-28, 1993.**

| | $O_3$ ppb | CO ppb | $NO_{day}$ ppb | $NO_2$ ppb | $NO_y$ ppb | $NO_x/NO_y$ |
|---|---|---|---|---|---|---|
| Mean | 28 | 211 | 0.56 | 4.20 | 7.67 | 0.65 |
| Median | 26 | 196 | .1 | 3.05 | 5.24 | 0.65 |
| Minimum | 1 | 95 | ~0 | 0.52 | 1.07 | 0.26 |
| Maximum | 76 | 628 | 14.78 | 20.68 | 48.66 | ~1 |
| Mid 67% | 11-45 | 142-274 | 0.03-0.76 | 1.21-7.39 | 2.97-12.14 | 0.40-0.84 |
| Mid 90% | 3-59 | 117-334 | 0.02-2.14 | 0.90-11.78 | 2.01-20.81 | 0.33-0.95 |

During the trajectory for September 11, the lowest $CO/NO_x$ and $CO/NO_y$ ratios were observed. The trajectory came from the industrial midwest. Relatively low CO mixing ratios coupled with high $NO_x$ mixing ratios suggest emissions from coal-burning power plants. Concurrent high $SO_2$ mixing ratios would further suggest that power plant emissions influence this particular trajectory.

**Table B.4. Mean and maximum observed $NO_x$ mixing ratios for "Clean" and "Dirty" days measured at Wye, Md. between September 2-28, 1993.**

| Day | Mean Concentration (ppb) | Maximum Concentration (ppb) |
|---|---|---|
| "*Clean*" Days | | |
| 9/13 | 1.47 | 2.58 |
| 9/26 | 2.01 | 3.69 |
| 9/27 | 2.03 | 3.28 |
| "*Dirty*" Days | | |
| 9/11 | 7.49 | 16.38 |
| 9/12 | 6.03 | 10.55 |
| 9/22 | 7.49 | 20.89 |

*Intercomparison of Filterpack and Denuder Techniques for $HNO_3$ Measurement*

## Background

Despite the importance of $HNO_3$ to overall N deposition, there are remarkably few suitable techniques for its measurement. Real-time instruments typically employ spectroscopic methods of detection, and are often complex, expensive, and power consuming. Integrated, or batch techniques (e.g., filterpacks) have been widely used due to their simplicity and low cost. However, the time resolution of these techniques is limited. Furthermore, artifact formation arising from collection or volatilization of $HNO_3$ from ammonium nitrate aerosols is a perennial worry in filterpack methods, and can pose a problem whenever long sampling times are used. In coastal areas the adsorption of $HNO_3$ on coarse-mode seasalt aerosols can carry the nitrate flux in large particles; therefore, traditional gas-phase filterpack $HNO_3$ measurements may be inadequate in coastal environments.

The perceived need to evaluate the filterpack technique in coastal areas was reinforced by the results from the Wye, Md., Dry Deposition Inferential Measurement (DDIM) station which indicated that it may not be possible to use traditional inferential techniques for estimating dry deposition in the near-coastal environment. The DDIM station pushes the filterpack methodology to its theoretical limit by using low flow rates and a weekly sampling protocol. This is especially true in areas with high $NH_3$ and/or seasalt concentrations (both a problem on Maryland's Eastern Shore). In these areas the chemical equilibrium between $HNO_3/NH_3/NH_4NO_3$ on the initial particle filter can influence the amount of nitrogen trapped by the secondary nylon filter (see below). Through ANICA and the Great Waters Program denuders and support equipment have been acquired for a filterpack/denuder intercomparison.

## Filter Pack

The most widely used method for routine $HNO_3$ concentration and flux measurements is the nylon filterpack (FP) technique (e.g., Goldan et al., 1983). In this method, two filters are typically employed; a Teflon prefilter is typically used to trap particles ($NH_4NO_3$, $(NH_4)_2SO_4$, etc.) and pass $HNO_3$, which is quantitatively scrubbed by reaction with basic $-NH_2$ active sites on the nylon filter. Both filters are extracted after collection and $NO_3^-$ is usually analyzed by ion chromatography. Fast air flow rates and filter pore sizes of 1 μm are typically used, and the open-faced, inlet-less filterpack assembly is faced directly into the wind to avoid surface losses of $HNO_3$. The nylon filter technique showed no interferences in laboratory tests (Goldan et al., 1983) and has been successfully used in a variety of gradient measurements of $HNO_3$ flux (e.g., Huebert and Robert, 1985; Huebert et al., 1988). Side-by-side deployment of the Teflon/nylon filterpacks demonstrated a precision of ca 1%, more than adequate for the successful measurement of $HNO_3$ gradients over Illinois grassland (Huebert et al., 1988). Provided that sample collection intervals are kept short, however, the problem with artifact formation from the collection and volatilization of ammonium nitrate aerosols can be minimized (e.g., Spicer et al., 1982; Huebert et al., 1988).

## Denuders

Denuder measurements of $NH_3$ are based upon the concept of selective scavenging by passing the sample airstream through an acid-coated tube (simple denuder) or concentric tubes (annular denuder). Gas-phase ammonia rapidly diffuses to the walls, is absorbed, and is extracted after sampling for analysis by ion chromatography (IC), colorimetry, or other methods. Ammonium-containing aerosols and vapor phase $HNO_3$ pass unimpeded through the denuder and are collected on Teflon and nylon backup filters (Luke and Valigura, 1996).

The denuder method employed for this study will utilize a citric acid-coated denuder (CAD), followed by a traditional filter pack assembly, with extraction and analysis of ammonia (as $NH_4^+$) by IC. An inverted quartz tube, 60-70 cm long, is suspended vertically from a sampling tower. Air is drawn through the denuder at a flow rate of about 2-10 standard liters per minute (SLM) using a small pump and electronic mass flow controller. Gas-phase ammonia in the sample airstream rapidly diffuses to the walls of the denuder and is absorbed by the citric acid coating. After sampling, a small aliquot of deionized water or 5 mM HCL is used to rinse the walls of the tube and extract the ammonia in the form of an ammonium salt. The backup filter is also extracted. Ammonium concentrations in the tube and filter extracts are quantified by ion chromatography, referenced to independent calibration standards. The concentration in air may be calculated from the measured ($NH_4^+$), air sampling rate, and length of the sampling interval. Although free of readily identifiable interferences, the CAD/IC method may suffer from artifacts under some conditions. Turbulent particle impaction at the inlet and walls of the denuder, as well as particle settling, can artificially increase measured ($NH_3$). These artifacts can be virtually eliminated, however, by maintaining laminar flow through the tube and positioning the denuder vertically (Ferm, 1979). Potentially severe artifacts may arise from the evaporation of ammonium nitrate within the denuder as gas phase $NH_3$ is depleted at the denuder walls. The magnitude of this error will depend strongly upon temperature and residence time of the sample air within the denuder. While this error is difficult to quantify, Langford et al. (1989) estimated its magnitude under conditions of high aerosol loading using the measured $NH_4NO_3$ evaporation rates of Richardson and Hightower (1987). At denuder residence times of 1 s (typical residence times for the research proposed here is less than 0.5 s) and temperatures of 25-35 °C, Langford et al. (1992) estimated that particle evaporation will introduce approximately 6% error in measured ($NH_3$) at high aerosol concentrations ($(NH_4NO_3)/(NH_3) \approx 70$). At the lower aerosol loadings typical of the rural and remote troposphere, artifact formation from aerosol evaporation should be small. Exceptions may occur at locations near strong local $NH_3$ sources (such as agricultural areas) where aerosol loadings may be high.

## Previous Intercomparisons

A multitude of $HNO_3$ intercomparison campaigns have been conducted over the last 10-15 years, and results have not always been consistent. In general, the various chemical techniques have shown substantial agreement at $HNO_3$ concentrations greater than a few ppbv. At lower concentrations the results begin to diverge. In a 1979 study in Claremont, Ca. (Spicer et al.,

1982), a variety of filter pack and denuder methods were compared with the $NO_y$ conversion difference and FTIR techniques (Luke and Valigura, 1996). At $HNO_3$ concentrations of 4-20 ppbv, good agreement was found among most of the methods. Hering et al. (1988) compared the results of $HNO_3$ measurements using several integrated (denuder, thermal denuder, FP) and spectroscopic methods. At $HNO_3$ concentrations of several ppbv agreement was generally good, but scatter increased below 3 ppbv. Overall agreement among all methods was a factor of two. The demonstrated precision of the denuder method was poor, and the denuder method yielded consistently lower results than the spectroscopic methods used. Artifact formation arising from ammonium nitrate volatilization in filterpacks exposed for long periods of time resulted in overprediction of $HNO_3$ by FP techniques. However, for short sampling intervals the FP method agreed well with the spectroscopic techniques. In areas where the majority of nitrate is present as gas-phase nitric acid, intercomparison campaigns suggest that agreement between filterpack and denuder measurements of $HNO_3$ are generally good, owing to the lack of artifact formation from volatilization of ammonium nitrate aerosols (e.g., Benner et al., 1991).

**Measurement Strategies**

The first priority is to deploy the CAD system alongside the DDIM filterpack and conduct calibration, collection efficiency, and artifact formation tests to judge the suitability of the CAD technique for longer term measurements. Collection efficiency of the denuder system will be determined by spiking the ambient airflow with a quantified source of $NH_3$, obtained either from a calibration gas mixture or a permeation tube. Measured efficiencies will be compared to those calculated from the Gormley-Kennedy relationship (e.g., Ferm, 1979; Bollinger et al., 1983). Side-by-side CAD/filterpacks will be deployed in parallel to assess the representativeness of daily integrated samples by comparing results from a single CAD/filter sample collected for 24 hours with those from 8 (6) denuders sampled for 3 (4) hours each. Day/night effects could similarly be studied and may be important considerations when sampling in a humid environment where condensation may be a problem.

The secondary priority is to evaluate the importance of $NH_4NO_3$ artifact formation in high concentration areas such as Chesapeake Bay. Collection efficiency and "breakthrough" tests will be performed by connecting denuders in series and comparing the amounts of $NH_4^+$ collected on front and back tubes. Artifact formation from particle impaction and/or evaporation may be explored by comparing results from parallel samplers, where a Teflon prefilter is placed at the inlet of one denuder and the outlet of the other. In a parallel effort, base-impregnated denuders for $HNO_3$ will be deployed alongside the CAD denuders, and will be used in conjunction with filterpack measurements to assess the importance of aerosol $NH_4NO_3$ formation at the sampling sites and its effects upon long-term filterpack measurements of $HNO_3$ carried out routinely at the Wye Institute. Analytical recovery of the extraction and IC analysis will also be evaluated.

## *Estimating Air-Water Transfer of $HNO_3$*

### Background

When considering the atmosphere as a pathway for nitrogen input, it is necessary to consider whether the nitrogen is transferred directly to the water surface, or indirectly to the watershed, with subsequent transport to the receiving waters. Several ongoing research programs seek to estimate the amount of nitrogen entering the coastal waters via precipitation and indirect deposition; however, rigorous studies of directly deposited nitrogen are few. Air-water exchange has been estimated for most nitrogen species over open ocean (Galloway, 1985; Duce et al., 1991), however, these rates may not apply to coastal situations because coastal areas experience meteorological processes not found over the open ocean (NRC, 1992).

To date, the primary obstacle to estimating coastal air-water nitrogen exchange has been the lack of near-surface, over-water coastal meteorological data. These data are needed to generate improved computer models, which will then be able to simulate existing small-scale coastal conditions. In response to this need, there has been an increased deployment of measurement buoys along the East Coast of the United States. One such network of buoys is the Chesapeake Bay Observing System (CBOS) owned and operated by the University of Maryland's Horn Point Laboratory. Through ANICA, the instrumentation aboard a CBOS buoy was augmented to include relative humidity and water temperature measurements. The results of this project are published in the Journal of Geophysical Research (Valigura, 1995). The two primary objectives were to: i) develop and evaluate an iterative bulk exchange model to estimate air-water exchange of heat, water and momentum from buoy data, and ii) use the model outputs to estimate air-water transfer rates of nitric acid ($HNO_3$).

### The Iterative Bulk Exchange Model

Because of a high affinity for water and relatively high ambient concentrations in coastal areas, $HNO_3$ is considered to be the primary nitrogen species of interest for deposition directly to water surfaces. Given its affinity for water, $HNO_3$ transfer can be considered uni-directional (i.e., downwards). Furthermore, for transfer to water, the quasi-boundary layer resistance ($R_b$) is small (Garratt and Hicks, 1973; Kanemasu et al., 1979) relative to the aerodynamic resistance ($R_{a,HNO3}$) even in very light wind conditions. Consequently, the arguments here will focus on $R_{a,\,HNO3}$ alone, and the resistance form of the general flux ($F_{HNO3}$) equation can be written

$$F_{HNO3} = [HNO_3]_0\text{-}[HNO_3]_z / R_{a,HNO3} = V_d\,[HNO_3]_z$$

where the surface concentration, $[HNO_3]_0$, is taken to be zero and the deposition velocity, $V_d$ (m $s^{-1}$), is the inverse of the aerodynamic resistance $R_{a,HNO3}$ (s $m^{-1}$).

Air-water exchange of sensible heat is similarly regulated by aerodynamic resistance ($R_{a,H}$), allowing for the assumption that $R_{a,HNO3}$ is equivalent to $R_{a,H}$. Using this assumption, it was

therefore possible to use the heat transfer coefficient, estimated with general bulk-transfer equations, to estimate the deposition velocity of $HNO_3$

$$V_d = R_{a,H}^{-1} = D_H u_z \quad (2)$$

where $D_H$ is the dimensionless heat transfer coefficient, see below, and $u_z$ is the measured windspeed (m $s^{-1}$) at height (z).

**Model Evaluation Results**

Three days of eddy correlation measurements of heat, moisture and momentum fluxes were collected on tower, boat, and airplane platforms from June 16-20, 1990 near NOAA's Looe Key National Marine Sanctuary in Florida (Crawford et al., 1993). During the first day, data collection was taken in shallow gulf waters (10 m), 500 m upwind of shore. During the next two days, data collection was performed 13.5 km offshore, 100 m outside the barrier reef in 25 m of water. Mean meteorological variables (wind speed, air temperature, and relative humidity) were recorded from all platforms, with water surface temperature measured by infrared temperature sensor from the boat, for the duration of the experiment. These mean data were incorporated into the bulk exchange model and the resulting output was compared against the eddy correlation data collected from the airplane (Crawford et al., 1993).

Model versus measurement intercomparisons of friction velocity, latent heat flux, and sensible heat flux were quite favorable. Average differences between measured and modeled friction velocities and latent heat fluxes were small, ± 1 cm and ± 10 W $m^{-2}$ respectively. Sensible heat fluxes were very small and intercomparisons were inconclusive. This was due to an apparent disconnect between eddy correlation data measured on the airplane and local water- surface data collected by boat. The disconnect can be attributed to the inherently local nature of the surface temperature measurements and the fact that eddy correlation integrates surface characteristics for some considerable distance upwind. The noise in the water surface temperature measurements was directly translated into noise in the model output, thereby resulting in the measurement versus model differences. Further comparisons are being conducted as data becomes available.

**Experimental Set-Up**

In late March 1992, the CBOS buoy was anchored in the north Chesapeake Bay, off Howell Point, Maryland (39.36°N, 76.1°W) for 3 periods between April 1992 and July 1994 (excluding the winter months) totaling 18 months. The CBOS buoy is owned and operated by the Horn Point Laboratory, Center for Environmental and Estuarine Studies, a member of the University of Maryland system. The buoy is of the wave-follower variety, and allowed data to be telemetered to a central computer system for remote access. The cross-section of the Bay narrows to 4.5 km in the area of the buoy, making the fetch 4.5 km or greater in the geographical window from 210° to 50°, and 1 km or less in the window from 51° to 209°. Water depth is variable across this section of Chesapeake Bay (average depth 5 m), but the buoy is anchored in the deep channel

where the depth of water is 12.5 m.

**Deposition Velocity Estimation Results**

Deposition velocities were calculated for the approximately 25,000 10-minute periods that comprise the CBOS dataset to date. The overall frequency distribution is presented in Figure B.5. When viewed on shorter time scales, the distribution begins to change, as is shown for the first week in December 1993 (Figure B.5). The potential danger of using average/general deposition velocities in short term analysis becomes apparent when the actual time series of $V_d$ is reviewed for the same week in December 1993, Figure B.6. Meyers and Yuen (1987) found that concurrent, high resolution $V_d$ and concentration data improved estimates of $O_3$ deposition, but did not improve estimates of $SO_2$ deposition. The primary reason for the difference between the two chemicals was that the measured variability in $O_3$ concentration was significantly correlated with the corresponding measured variability in $V_d$ (i.e, concentrations were proportional to deposition rates), and concentrations of $SO_2$ were not correlated with corresponding $V_d$ (i.e., concentrations were not proportional to deposition rate). It is unknown if $HNO_3$ concentrations ($[HNO_3]$) over Chesapeake Bay are correlated with $V_d$ ($[HNO_3]$ was not measured during this study). To illustrate the potential errors associated with using average or time series $V_d$, a simple matrix analysis was performed using the December 1993 time series, Table B.5. Deposition was estimated using three different $V_d$ regimes (the actual times series $V_d$, the time series average $V_d$,

**Table B.5. Comparison between deposition (g $HNO_3$ $m^{-2}$) estimates ($V_d$ * $[HNO_3]$) derived using different averaging schemes and the time series average‡ estimate for the first two weeks of December 1993 (% differences are shown in parenthesis).**

| | Low-High 1.2-2.7 ppb | High-Low 2.7-1.2 ppb | Average 1.95 ppb |
|---|---|---|---|
| Time Series $V_d$ | .485 ( 4.5) | .443 (- 4.5) | .464 ( 0.0) |
| Time Series Average $V_d$ (.0049 $ms^{-1}$) | .429 (- 7.5) | .499 ( 7.5) | .464‡ |
| 1993 Annual Average $V_d$ (.0065 $ms^{-1}$) | .567 ( 22.0) | .661 ( 42.0) | .614 ( 32.0) |

and the 1993 average $V_d$), and three different $HNO_3$ concentrations representative of $[HNO_3]$ commonly measured within the Bay region. The concentrations were i) switched from a constant low (1.2 ppb) to a constant high (2.7 ppb) after the front, ii) switched from a constant high to a constant low after the front, and iii) maintained at the average (1.95 ppb). The deposition estimate derived from using the time series average $V_d$ and average $[HNO_3]$ was used as the reference value for intercomparisons, Table B.5. The analysis shows that if $V_d$ and $[HNO_3]$ are

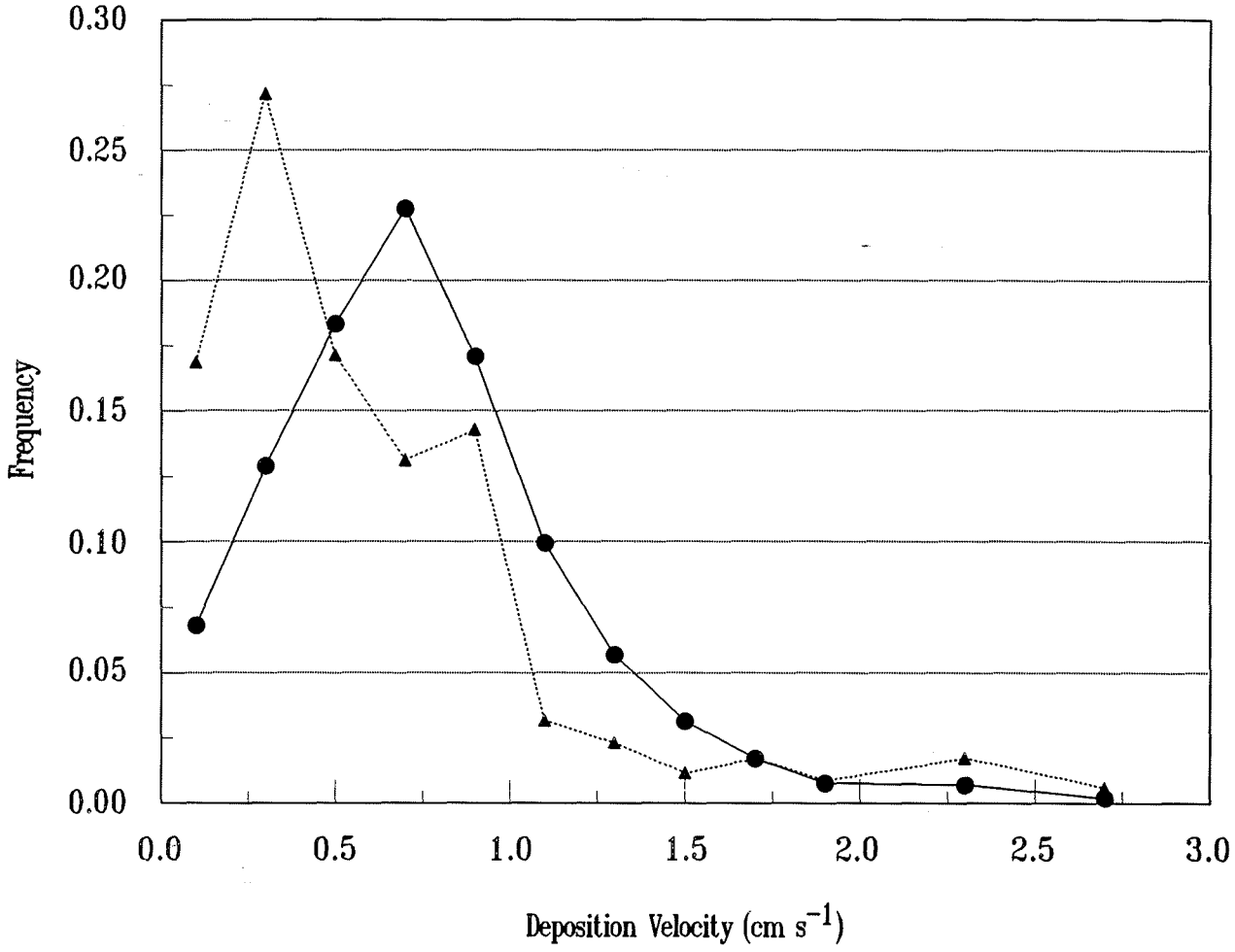


Figure B.5. The frequency distribution for 18 months (excluding winter) of estimated deposition velocities in Chesapeake Bay (solid line) and the distribution for 1 week in December 1993 (dotted line).

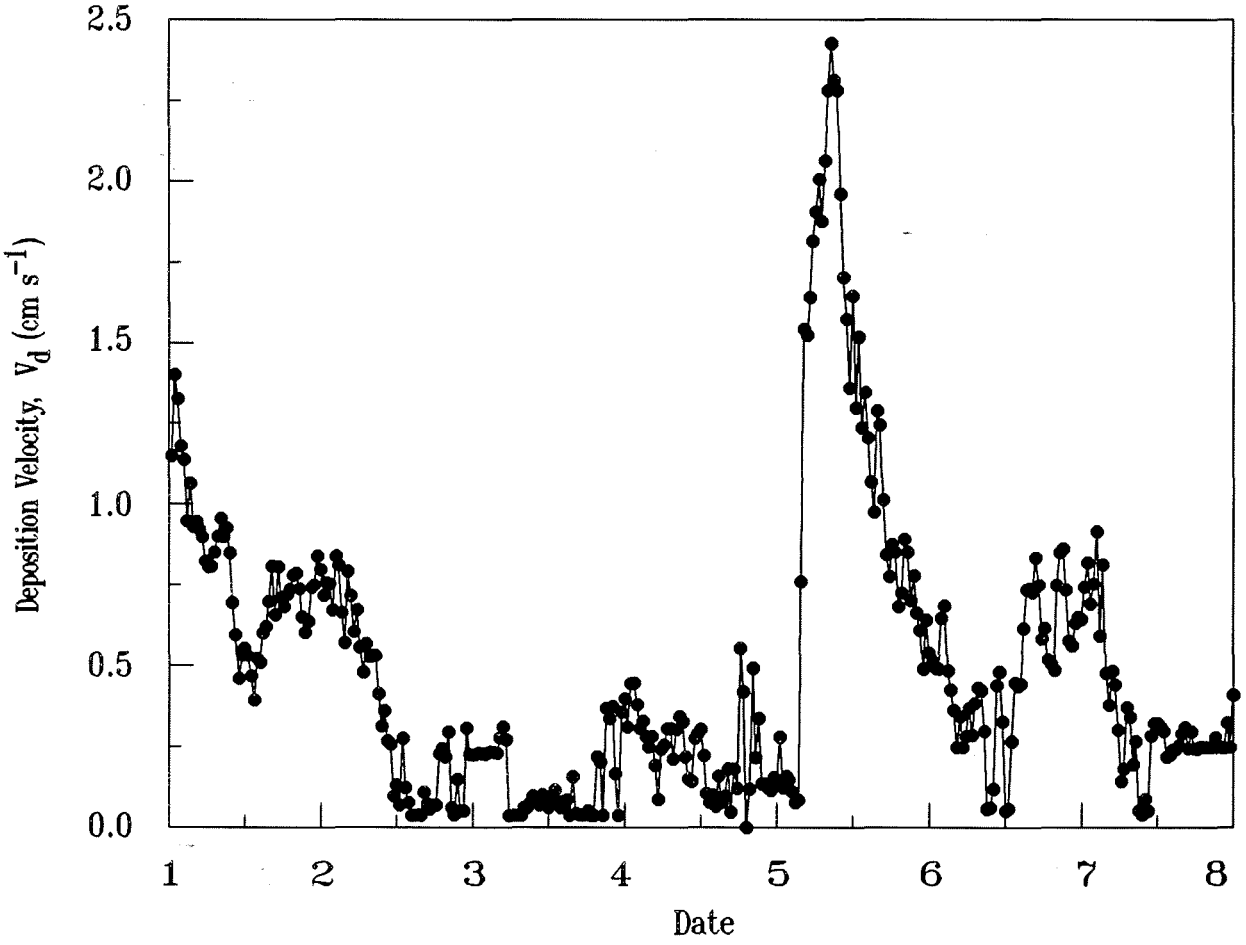


Figure B.6. Ten-minute deposition velocities calculated for December 1-8, 1993.

not correlated, the error in deposition estimates is primarily driven by errors in estimating mean values of $V_d$ and $[HNO_3]$. If they are correlated, determining the source the associated errors is more complex. If $[HNO_3]$ and $V_d$ are correlated, adequate estimation of deposition can only be obtained by concurrent measurements of $[HNO_3]$ and $V_d$. These analyses demonstrate the need to determine if variability in $HNO_3$ concentration is significantly correlated with the corresponding variability in transfer rate to Chesapeake Bay.

The $V_d$ distribution (Figure B.5) is likely to be conservative for two reasons. The first and most important reason is that the winter months are not accounted for because the buoy is removed due to ice. During the winter, air-water temperature differences are likely to be at a maximum (with water being consistently warmer than air), causing transfer rates to be at their peak. Therefore, any distribution that excludes this period is likely to be conservative. Another reason to believe that these estimates are conservative is that assuming equivalent transfer rates for $HNO_3$ and heat does not adequately account for scavenging of $HNO_3$ by aerosol water droplets and particles, which tend to increase deposition rates.

There are theoretical limitations with this approach as well: lack of homogeneous conditions in the coastal zone and the inadequacy of similarity theory to describe turbulent conditions measured. Because the northern Chesapeake Bay is narrow, the local landscape tends to affect the meteorology. These effects make fetch assumptions unreasonable, thereby making it difficult to assume that the "local" buoy measurements are representative of any sizeable area. Estimating large-scale deposition patterns will require deployment of buoys at a range of different sites with concurrent mesoscale modeling efforts. The second theoretical consideration concerns the Monin-Obukhov similarity theory upon which the bulk transfer equations are based. This theory has been evaluated, and is considered valid, over a certain range ($-1 \geq z/L \leq 1$) of meteorological conditions. Beyond this range, the atmosphere is either extremely stratified so that the flow is effectively disconnected from the surface or so unstable that it is under free convection conditions. During the two years of data collection, there were periods where model outputs showed that conditions were too stable/unstable to be considered in the "normal" Monin-Obukhov frame. These periods were closely related to low wind speeds, as shown in Figure B.7 for the month of April 1994.

The approach used in this study has been shown to be applicable to $SO_2$ and should be applicable to other hygroscopic chemicals such as ammonia. To improve upon this technique, further eddy correlation projects must be performed to evaluate/modify the bulk transfer equation assumptions under low wind conditions. In future investigations, concurrent evaluation of $HNO_3$ concentrations will allow for the quantification of the actual differences between the time-series and the single-deposition velocity approaches.

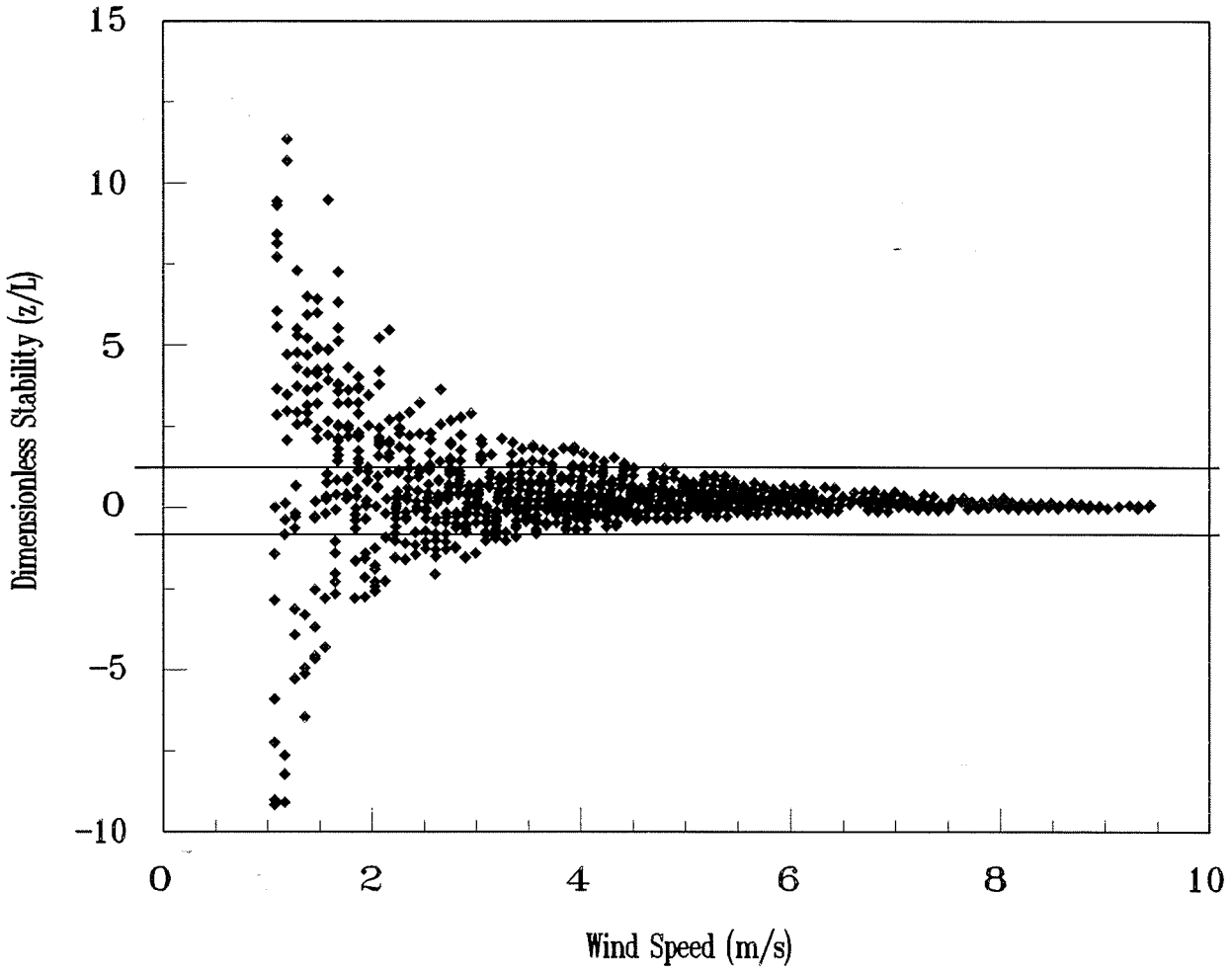


Figure B.7. Ten-minute Monin-Obukhov dimensionless stability estimates versus measured windspeed, calculated from the Chesapeake Bay Observing System data for April 1994. Solid lines denote outer ranges of applicability for Monin-Obukhov similarity theory.

## *Operational RAMS 15 Km Forecasts over Chesapeake Bay*

### Background

The Regional Atmospheric Modelling System (RAMS) version 3a, developed at Colorado State University, has been configured to simulate mesoscale atmospheric circulations on both IBM/6000 workstations at the Air Resources Lab (ARL). The software developed at ARL allows the user to setup and initialize RAMS anywhere in the world using the ARL packed meteorological fields and global land and water surface data sets. The ARL modeling system is described in detail by McQueen et al. (1994, 1995).

### RAMS Description

*Grid Structure*
RAMS utilizes an Arakawa-C grid stagger of the thermodynamic and momentum variables to reduce finite differencing error. An oblique stereographic horizontal grid coordinate can be specified. This varies from the normal polar stereographic coordinates in that the grid is true at the center of the RAMS domain with the "pole" position defined at that center as well. A two-way interactive multiple nested grid scheme exists so that scale interactions can be incorporated. This nested grid approach also allows for a finer mesh to resolve local-scale circulations in the area of interest and a coarser mesh outside this area. Simulations performed over the northern Chesapeake Bay employed the finest nested grid spacings to date ($\Delta X$=2.5 km), Figure B.8. A 15 km finest mesh grid spacing is used to produce operational 24-36 hour forecasts. Grid domains of the finest mesh have ranged from 50 to 600 km depending on the grid spacing. The model can be run in 1, 2 or 3 dimensions.

*Initialization*
The model can be initialized from spatially inhomogeneous meteorological observations and, therefore, simulations are not limited to synoptically undisturbed cases. A program to ingest ARL packed National Centers for Environmental Prediction's (NCEP) model gridded fields into RAMS was developed. More than one input NCEP dataset can be used by combining these fields to create a complete input through the troposphere. Alternatively, NCEP model gridded data and surface and rawinsonde sites can be objectively analyzed to isentropic surfaces before being interpolated to the model grid using the RAMS ISAN package. Objective analysis follows the widely used Barnes approach. Currently, the model defaults to using NCEP model data on a 2.5 degree latitude-longitude horizontal grid and mandatory pressure levels.

The user can choose constant or spatially varying surfaces for RAMS ingest. Spatially varying surface variables such as soil moisture, soil and vegetation type, canopy temperature and water content, terrain height, land roughness, land percentage and water surface temperature can be ingested into RAMS on the model grid. Table B.6 summarizes the available ground surface data sets and their coverage. Over the U.S., surface data exists at a higher (30" latitude-longitude grid or about 1 km resolution) than available globally (10' latitude-longitude grid or about 18 km

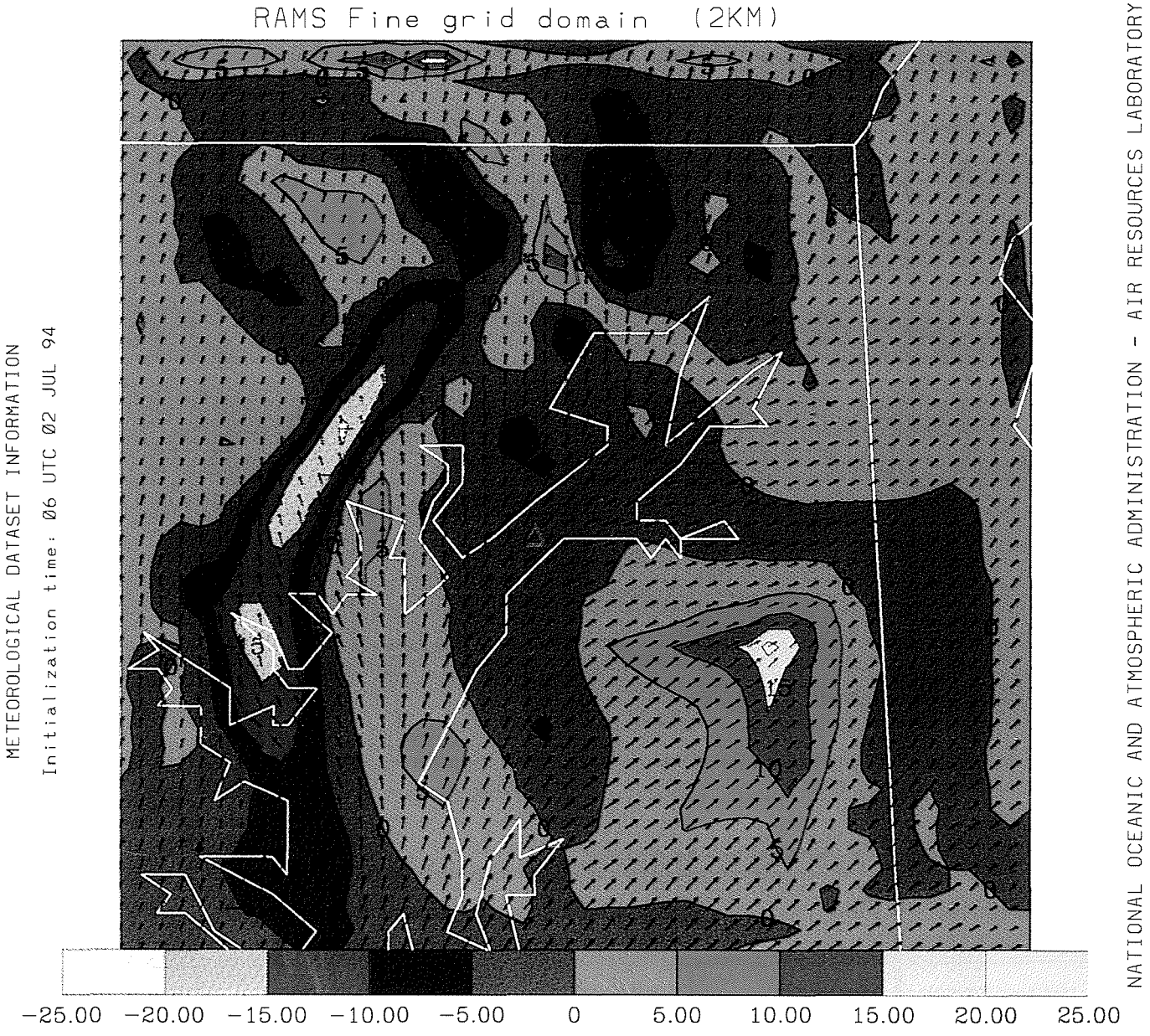


Figure B.8. Horizontal (vectors) and vertical (contours) windspeed simulations performed over the northern Chesapeake Bay employing the finest nested grid spacings ($\Delta X$=2.5 km). Note the high vertical motions on the western shore of the Bay indicating the beginnings of a "Bay Breeze" (Triangle indicates position of CBOS buoy).

resolution). Soil moisture is predicted by first computing an Antecedent Precipitation Index (API) derived from the last few months of observed or model gridded precipitation archived at ARL.

**Table B.6. Summary of surface data available for RAMS.**

| Type | Coverage | Resolution | Range | Update |
|---|---|---|---|---|
| Topography | Global | 10' lat/lon grid | 10 m | |
| " | U.S. | 30" lat/lon grid | 10 m | |
| SST | Global | 1° lat/lon | .1 K | weekly |
| soil type | Global | 1 degree | 14 categories | |
| soil moisture | Global | NMC forecasts | 0-1 | daily |
| " " | U.S. | observed precip | " | daily |
| Land use | global | 1 degree | 167 H-S categories | |
| | U.S. | 1 km | 167 H-S categories | |
| Roughness | global | 1 degree | | |

**Operational Capabilities**

RAMS has been used operationally for air quality dispersion forecasts. At ARL, RAMS is run in both a forecast and hindcast mode. Table B.7 summarizes the current operational configuration.

**Table B.7. RAMS operational configuration.**

| Workstation | Mode | Location | Domain | cpu/wall time | ΔX |
|---|---|---|---|---|---|
| IBM 6000/530 (ARL RISC1) | 12 H hindcast w/ FDDA | Mid Atlantic/ Ches. Bay | 2400 $km^2$ 680 $km^2$ | .33 | 80 km 20 km |
| IBM 6000/560 (ARL RISC2) | 24-36 H forecast | Mid Atlantic/ Ches. Bay | 2400 $km^2$ 680 $km^2$ | .16 | 60 km 15 km |

RAMS is normally run over the Chesapeake Bay and Mid Atlantic region when it is not required for an emergency, exercises, or to support air quality experiments. The RAMS domain can easily be moved through the Real time Emergency Application and Display sYstem (READY; Rolph

et al., 1993; Draxler et al.,1993) by simply specifying the center latitude and longitude of the coarse grid through the READY menu. On RISC2, RAMS is configured to produced 24-36 hour forecasts twice-per-day after the latest ETA model fields are available. On RISC1, RAMS is configured in a hindcast mode while also assimilating four dimensionally surface wind data normally available every hour. An example of operational RAMS predicted winds and temperatures on the fine 15 km domain are shown in Figure B.9. RAMS outputs are available in real-time on a one week rotating archive on the ARL work stations.

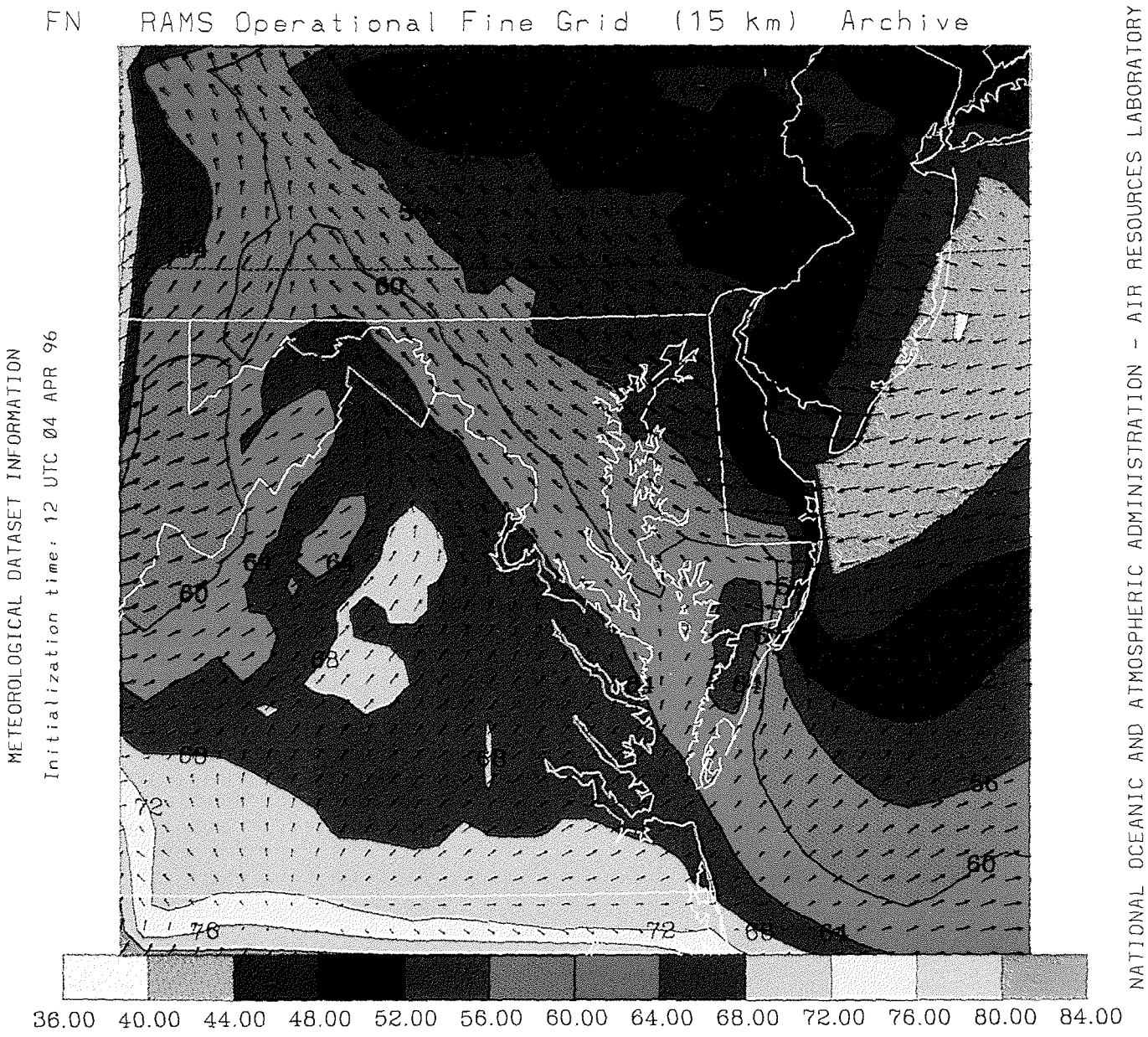


Figure B.9. Operational 15 km RAMS simulations of northern Chesapeake Bay.

## Appendix C
# ANICA ASSOCIATED SCIENTISTS

*University of Delaware*

Thomas Church - College of Marine Studies: Member of the Chesapeake Bay Atmospheric Deposition Study (CBADS) group within the Chesapeake Bay Program. Specializing in wet deposition of nutrients and heavy metals.

Jin Wu - Director, Air-Sea Interaction Laboratory: Investigating physical interactions during low wind speed conditions.

*University of Maryland*

Joel Baker - Chesapeake Biological Laboratory: Head of the CBADS group. Specializing in wet deposition of organic compounds, including nutrients.

William Boicourt - Horn Point Environmental Laboratory: Head of the Chesapeake Bay Observational System (CBOS) buoy project. Specializing in the physical hydrodynamics of the Chesapeake Bay.

Russell Brinsfield - Director, Wye Research Center: Investigating nitrogen cycling through cropped watersheds within the Chesapeake Bay area.

Russell Dickerson - Department of Meteorology: Specialist in the measurement of atmospheric nitrogen species.

John Ondov - Department of Chemistry, College Park: Member of the CBADS group within the Chesapeake Bay Program. Specializing in particle chemistry and transfer.

*University of Virginia*

James Galloway - Professor, Department of Environmental Sciences: Investigating wet deposition of organic nitrogen to the coastal ocean.

William Keene - Department of Environmental Sciences: Investigating wet deposition of organic nitrogen to the coastal ocean. Specializing in atmospheric chemistry.

*University of North Carolina*

Hans Paerl - Professor, Institute of Marine Sciences: Specializing in nitrogen-production interactions in coastal waters.

*Smithsonian Environmental Research Center*

Dave Correll - Director: Specialist in forest watershed nutrient dynamics.

Jess Parker - Forest Ecologist: Specialist in forest canopy Structure dynamics.

Donald Weller - Forest Ecologist: Specialist in forest watershed dynamics modeling.

## Appendix D
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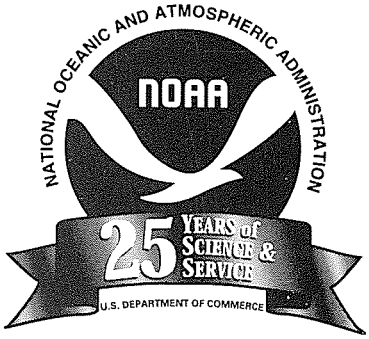
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