NOAA Technical Memorandum ERL ARL-204

SULFUR AND NITROGEN CYCLING IN THE NORTH ATLANTIC OCEAN'S ATMOSPHERE SYNTHESIS OF FIELD AND MODELING RESULTS

J. N. Galloway, J. M. Prospero, H. Rodhe, R. S. Artz, C. S. Atherton,
Y. J. Balkanski, H. G. Bingemer, R. A. Brost, S. Burgermeister,
G. R. Carmichael, J. S. Chang, R. J. Charlson, S. Cober, W. G. Ellis, Jr.,
C. J. Fischer, J. M. Hales, D. R. Hastie, T. Iversen, D. J. Jacob, K. John,
J. E. Johnson, P. S. Kasibhatla, J. Langner, J. Lelieveld, H. Levy, II,
F. Lipschultz, J. T. Merrill, A. F. Michaels, J. M. Miller, J. L. Moody,
J. E. Penner, J. Pinto, A. A. P. Pszenny, P. A. Spiro, L. Tarrason,
S. M. Turner, and D. M. Whelpdale

Air Resources Laboratory
Silver Spring, Maryland
November 1993

UNITED STATES
DEPARTMENT OF COMMERCE

Ronald H. Brown
Secretary

NATIONAL OCEANIC AND
ATMOSPHERIC ADMINISTRATION

D. James Baker
Under Secretary for Oceans
and Atmosphere/Administrator

Environmental Research
Laboratories

Alan R. Thomas
Director

NOTICE

For sale by the National Technical Information Service, 5285 Port Royal Road
Springfield, VA 22161

CONTENTS

Page

FIGURES

TABLES

SULFUR AND NITROGEN CYCLING IN THE NORTH ATLANTIC OCEAN'S ATMOSPHERE SYNTHESIS OF FIELD AND MODELING RESULTS

J. N. Galloway, J. M. Prospero, H. Rodhe, R. S. Artz, C. S. Atherton,
Y. J. Balkanski, H. G. Bingemer, R. A. Brost, S. Burgermeister,
G. R. Carmichael, J. S. Chang, R. J. Charlson, S. Cober, W. G. Ellis, Jr.,
C. J. Fischer, J. M. Hales, D. R. Hastie, T. Iversen, D. J. Jacob, K. John,
J. E. Johnson, P. S. Kasibhatla, J. Langner, J. Lelieveld, H. Levy, II,
F. Lipschultz, J. T. Merrill, A. F. Michaels, J. M. Miller, J. L. Moody,
J. E. Penner, J. Pinto, A. A. P. Pszenny, P. A. Spiro, L. Tarrason,
S. M. Turner, and D. M. Whelpdale*

ABSTRACT. In April, 1990, scientists from eight countries attended a workshop at the Bermuda Biological Station for Research to compare field measurements with model estimates of the distribution and cycling of sulfur and nitrogen species in the North Atlantic Ocean's atmosphere. Data sets on horizontal and vertical distributions of sulfur and nitrogen species and their rates of deposition were available from ship's tracks and island stations. These data were compared with estimates produced by several climatological and event models for five case studies: (1) sulfate surface distributions and deposition, (2) nitrate surface distributions and deposition, (3) vertical and horizontal distributions of reactive nitrogen species (NO_y), (4) spatial and temporal trends in DMS emissions, and (5) advections of sulfur and nitrogen into the North Atlantic Ocean's atmosphere. Highlights of the conclusions of the case studies were (1) few data existed to resolve seasonal and latitudinal variations in DMS flux to the North Atlantic Ocean's atmosphere, (2) measured concentrations and model results of nitrate and nss-sulfate deposition appeared to agree well for some locations but poorly for some months at other locations, (3) current models generally predicted NO_y concentrations that agreed with the measurements, and (4) estimates of the sulfur and nitrogen advection fluxes by even specific models agreed generally with estimates made by the synthesis of existing data. The case studies illustrated the need for measurement and modeling communities to interact not only to compare results but also to cooperate in improving the design of the models and of the field experiments.

1. INTRODUCTION

The emissions of sulfur and nitrogen to the global atmosphere have increased substantially over the past century because of anthropogenic activities, especially in North America and Europe. As a result, the North Atlantic Ocean is surrounded by large sulfur and nitrogen sources (Fig. 1). Aircraft measurements made during the Western Atlantic Ocean Experiment (WATOX) and the STRATOZ III expeditions document high concentrations of NO_x and SO_2 on the coastal fringes of the North Atlantic Ocean, implying significant fluxes of

---

*For affiliations, please see appendix.

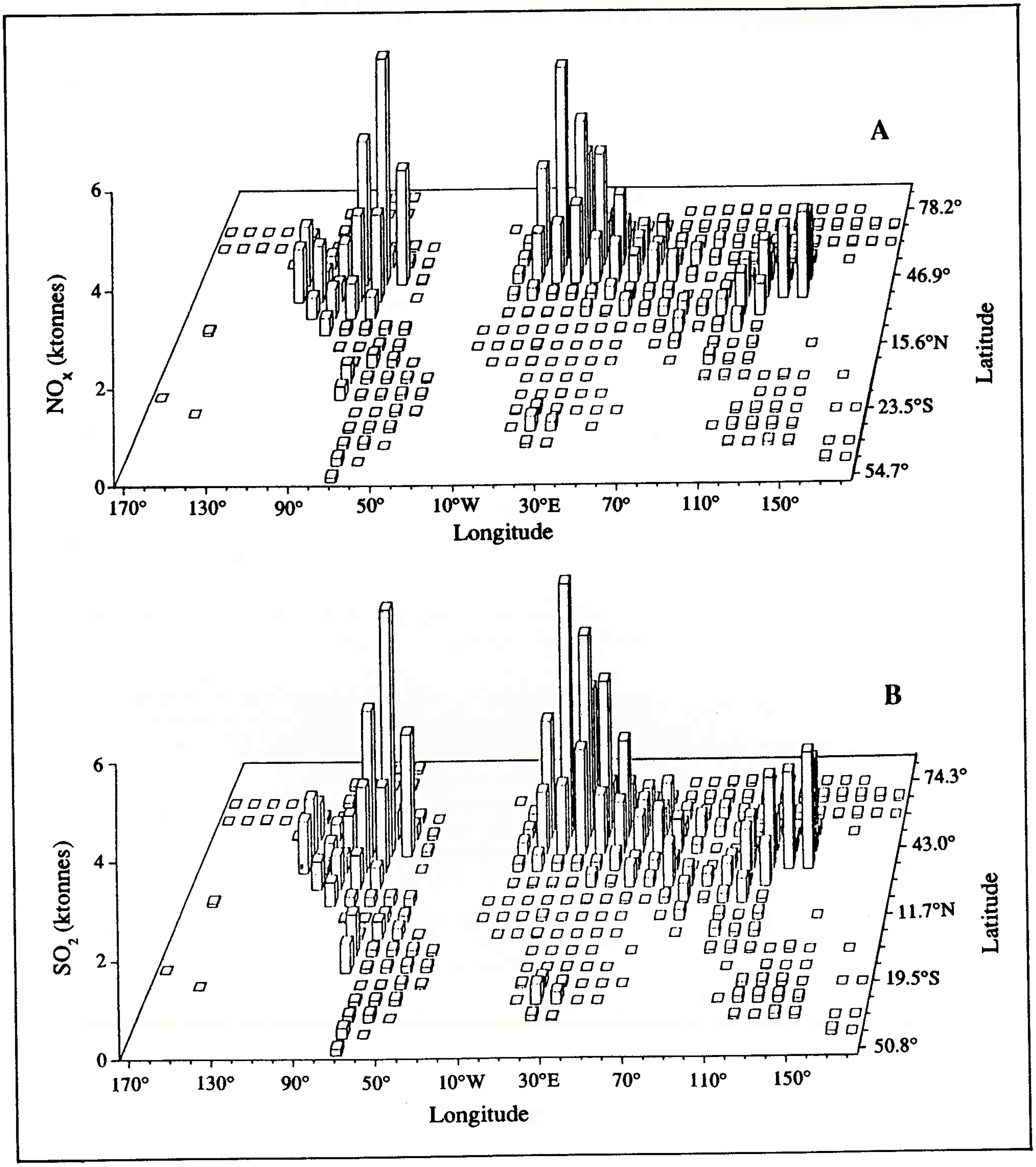

Figure 1.--Gridded emissions of (**A**) nitrogen oxides and (**B**) sulfur to the global atmosphere for 1980 (Galloway et al., 1992 from data in Hameed and Dignon, 1988).

both species (Luke and Dickerson, 1987; Drummond et al., 1988). Recent data from the Atmosphere-Ocean Chemistry Experiment (AEROCE) (see Prospero, 1989) sites within the North Atlantic Ocean indicate nitrate and sulfate levels several times above the natural background (Prospero et al., 1989; Galloway et al., 1989). The collected data are limited in time and space. However, models can be used to create a more general picture of the changes in sulfur and nitrogen in the North Atlantic Ocean's atmosphere. To test the models, we felt that it was important to compare them to the data bases.

This review assesses the understanding at the time we met of the cycling of sulfur- and nitrogen-containing compounds over the North Atlantic Ocean, by reviewing the measurement data bases and the estimates made with the help of global and regional chemical tracer models. This systematic comparison indicates the validity of the model estimates relative to the measured data. Such a comparison also identifies gaps in our knowledge and assists in the planning of future studies. This NOAA Technical Memorandum augments an article by the same authors that appeared earlier in *Global Biogeochemical Cycles* (see Galloway et al., 1992).

The material presented in this report is the result of the workshop "Sulfur and Nitrogen Cycling in the North Atlantic Ocean Atmosphere: Synthesis of Field and Modeling Results" held at the Bermuda Biological Station for Research during April, 1990. The objectives of the workshop were to:

1. Define the important research questions in sulfur and nitrogen cycling over the North Atlantic Ocean,

2. Review and compare the available data bases for sulfur and nitrogen species over the North Atlantic Ocean,

3. Assess the uncertainties in and the limitations of the sulfur and nitrogen data bases for the North Atlantic Ocean,

4. Suggest case studies for the joint attention of modelers and measurers,

5. Ascertain how modelers could assist in the design of field measurement programs.

Over the longer term, these cooperative efforts should address the following research questions:

1. What are the roles of sulfur and nitrogen species in the climate processes over the North Atlantic Ocean?

    - the relative importance of natural (i.e., mainly oceanic) and anthropogenic (continental) sources,

    - the direct impact of aerosol species on the radiation budget,

    - the indirect impact on the radiation budget through the modification of cloud characteristics and distribution.

2. What are the impacts of continental nitrogen oxides (NO_x) and related species on the natural oxidizing capacity of the North Atlantic Ocean's atmosphere?

    - the chemistry of aging continental air masses over the North Atlantic Ocean.

3. What are the impacts of the atmospheric deposition of oxidized and reduced nitrogen compounds on new production in the surface waters of the North Atlantic Ocean?

   - the importance relative to the upwelled nutrients on longer time scales (seasonal to annual) and space scales (on the order of 10^3 km),

   - the influence of episodic precipitation inputs on the phytoplankton species diversity on shorter time scales (hours to days) and space scales (on the order of 10^1 km).

Although these questions were not all fully addressed in the workshop, they provide the basic motivation for research in this area.

1.1 The Scientific Issues

Human influences on nitrogen and sulfur budgets over the North Atlantic Ocean have many environmental implications. Photochemical reactions involving NO_x produce ozone, a greenhouse gas and a pernicious pollutant; over some areas of the North Atlantic Ocean, the production of ozone is regulated largely by the availability of NO_x. The concentrations of tropospheric ozone at the northern midlatitudes have risen by approximately 1% per year over the past few decades (Logan, 1985) and this increase may reflect a parallel increase in NO_x emissions. Distributions of NO_x over relatively remote regions like the North Atlantic Ocean are particularly important to the global ozone budget since the ozone production efficiency per unit of NO_x increases with decreasing NO_x concentration (Liu et al., 1987). Even if NO_x levels over the North Atlantic Ocean are insufficient to promote vigorous ozone production, increases as low as 10 pptv above the natural background may mitigate the potential for ozone photochemical loss.

Because nitrogen is the limiting nutrient for marine biota, the deposition of nitrate and ammonium to the world's oceans may have implications for oceanic productivity and hence for the oceanic uptake of CO_2. The studies of the nitrogen budget in the euphotic zone off Bermuda suggest that atmospheric deposition is a small source of fixed nitrogen relative to its transport from the aphotic zone (Knap et al., 1986). However, algae blooms have been observed following rain events near Bermuda (Glover et al., 1988). In any case, the data base was too scant to resolve the issue.

The sulfur budget over the North Atlantic Ocean raises a different set of environmental issues. In contrast to nitrogen, sulfur is not a limiting nutrient for marine biota. Nevertheless, deposition of sulfur to the North Atlantic Ocean is important as a large-scale sink of atmospheric sulfur. Whelpdale et al. (1988) estimate that only about 10% of the sulfur exported from North America to the North Atlantic Ocean reaches Europe; most of the remaining 90% is deposited to the North Atlantic Ocean. The efficiency of the sulfur deposition to the North Atlantic Ocean may thus affect the potential for acid deposition in certain regions of northern Europe.

Sulfate aerosol plays an important role in the Earth's energy budget, both as a light-scattering agent and as a source of cloud condensation nuclei. Perturbations to atmospheric sulfate loadings may modulate planetary albedo either through changes in aerosol optical depth (Charlson et al., 1990) or through changes in the microstructure of clouds (Charlson et al., 1987). Attempts to detect a climatic signal associated with anthropogenic sulfur emissions in the Northern Hemisphere have yielded contradictory results (Schwartz, 1989; Wigley, 1989). However, more recent data supports the theory that there was a climatic forcing by anthropogenic $SO_4^=$ that is comparable in magnitude but opposite in sign to the greenhouse forcing by enhanced CO_2 (Charlson et al., 1992). If there were such a signal, its magnitude would depend critically on the relative contributions of biogenic and anthropogenic sources to sulfate budgets over the Northern Hemisphere's oceans (Galloway and Whelpdale, 1987; Savoie and Prospero, 1989) where the paucity of aerosol might produce the greatest effects on cloud microstructure (Charlson et al., 1987). Understanding the origin of the sulfate over the North Atlantic Ocean is a key issue in evaluating the potential for climate effects.

1.2 The Models Used

The distributions of reactive nitrogen and sulfur species in the atmosphere vary in space and time; any detailed simulation of these distributions requires computer models with 3-dimensional representations of transport and chemistry. Many models were in use or being developed; several were represented at the workshop, some characteristics of which are listed in Table 1. The spatial resolutions of the different models varied widely ranging from 80 km (the sulfur transport eulerian model [STEM-II] and the regional acid deposition model [RADM]) to 1100 km (the MOGUNTIA [Model of the Global Universal Tracer Transport in the Atmosphere]).

Models can be classified as either episodic or climatological. Episodic models simulate atmospheric distributions for particular time periods. Wind fields and other meteorological variables are taken from historical records of observations (observed episodic mode) or from model simulations (model episode mode). The output of these models can be directly compared with measurements made for a specific time and place.

Climatological models use meteorological inputs from general-circulation models. They can only simulate "typical" time periods (e.g., months) as described by the general-circulation models' meteorology. Any comparison with observations must focus on statistical features of distributions (namely, time-averaged values and variances).

1.3 Organization of the Report

This report has three major sections containing the overview, the case studies, and the conclusions and recommendations. The overview section provides the justification for investigating the sulfur/nitrogen cycling in the North Atlantic Ocean's atmosphere and then provides an overview of the physical dynamics of the North Atlantic Ocean's atmosphere. Finally, there are summaries of the data and measurements of sulfur and nitrogen cycling available at the time and a review of the models that could then be used in the North Atlantic Ocean's atmosphere.

The second section discusses five case studies. They deal with sulfur, marine DMS emissions, nitrate, reactive nitrogen, and the advection of sulfur/nitrogen from North America.

Table 1. Characteristics of models used in the comparisons with field observations

Models	Grid mesh	Meteorological fields	Key species	Chemical kinetics	Emissions	Maximum integral time	Temporal resolution
Eulerian: Global							
GFDL model	265 x 265 km 11 layers	GFDL GCM (on line operation)	Lumped NO_y		Fossil fuel (Hameed & Dignon, 1988), biomass burning	1 year	26 min
Harvard model	4° x 5° 9 layers	GISS output	NO_x, PAN, O_3; model generates OH internally	Detailed HC-NO_x photochemistry (Jacob et al., 1989)	Fossil fuel; NO_x, VOC, CO	1 month	4 hours
MOGUNTIA MPI model	10° x 10° 10 layers	Observed climatic winds	NO_x, HNO_3, O_3, OH	Parameterization (Crutzen & Gidel, 1983)	Natural, anthropogenic	years	1 month
Stockholm model	10° x 10° 10 layers	Observed climatic winds	SO_2, $SO_4^=$, DMS	Linear kinetic parameterization	Natural, anthropogenic	years	1 month
Eulerian: Northern Hemispheric							
Oslo model	300 x 300 km 10 layers	NMC output	SO_2, $SO_4^=$, DMS	Linear kinetic parameterization	EMEP, anthropogenic (Semb, 1985) natural oceanic DMS	1 month	6 hours

Table 1. (con't.)

Models	Grid mesh	Meteorological fields	Key species	Chemical kinetics	Emissions	Maximum integral time	Temporal resolution
Eulerian: North America, North Atlantic, Europe							
GCheM	3.5° x 5° 14 layers	CCM output	SO_2, $SO_4^=$, DMS, H_2O_2; O_3, OH prescribed	Simple gaseous, aqueous oxidation parameterization	NAPAP (North America), EMEP (Europe), oceanic DMS	1 month	2 hours
Eulerian: Regional United States							
RADM	80 x 80 km^2 6, 15 layers	MM4 meteorological driver	Detailed SO_x, NO_y, VOC, oxidants	Detailed gaseous, aqueous chemistry (Stockwell, 1986)	NAPAP	Aggregated seasonal	5 min
STEM-II	80 x 80 km 14 layers	Objectively analyzed, observed meteorology	Detailed SO_x, NO_y, VOC, oxidants	Detailed gaseous, aqueous chemistry (Atkinson et al., 1982)	NAPAP	1 month	1 hour
Lagrangian: Global							
LLNL model	4.5°x 7.5° 9, 12 layers	CCM output	NO_x, HNO_3, DMS, SO_2, $SO_4^=$, O_3, OH prescribed	Simple gaseous, aqueous oxidation parameterization	Fossil fuel (Hameed & Dignon, 1988), soil, lightning, biomass burning, DMS	1 month	1 month

Source: Partially taken from Galloway et al., 1992.

The conclusions and recommendations section identifies the state of knowledge and the gaps that existed and provides suggestions on how those gaps might be filled.

2. OVERVIEW

2.1 The Importance of Sulfur in the Atmosphere

Sulfur is one of the important minor elements found in the Earth's crust, behind the major elements comprising the main mass of the lithosphere, hydrosphere, and atmosphere, being fourteenth in atomic abundance. It is an essential element for life, for example, comprising 0.3-3% by weight of marine algae. The high abundance of $SO_4^=$ in seawater (29 mmol L^{-1}) and in most soils dictates that it is never a limiting nutrient in the ocean and is seldom limiting on land. One of the chief functions of sulfur in the biosphere is to provide 3-dimensional structure to structural protein through the two amino acids cysteine and methionine.

Sulfur occurs naturally in chemical compounds with oxidation states ranging from -2 (reduced compounds like H_2S and $(CH_3)_2S$) to the element to +4 (SO_2) and +6 (H_2SO_4, $SO_4^=$, etc.). These compounds are found in all three phases in the atmosphere, some as gases, some as solid aerosol substance, and some in the atmospheric aqueous phase.

There are both natural and anthropogenic sources of sulfur that are significant in the atmosphere. Dimethyl sulfide (DMS; $(CH_3)_2S$) from marine phytoplankton (algae) probably represents the largest natural flux and SO_2 from the burning of fossil sulfur comprises the main anthropogenic flux. SO_2 and H_2S from volcanoes are secondary but sporadically very important fluxes. Figure 1 shows estimates of the global fluxes that illustrate the current dominance of the anthropogenic flux from the Northern Hemisphere.

The atmospheric importance of sulfur stems mainly from its myriad environmental effects. Most arise because of the chemical reactions in the atmosphere of the reduced gaseous forms (DMS, H_2S, SO_2) to H_2SO_4 occurring as a component of aerosol particles. At the Earth's surface these effects are in evidence as follows:

1. $SO_4^=$ is the dominant anion in river water after HCO_3^-;
2. Acidity from H_2SO_4 can be important to soil chemistry, e.g., the solubility of aluminum;
3. H_2SO_4 can directly affect on land and aquatic biota;
4. The natural background acid/base balance is frequently close to the maximal sensitivity to perturbation by additional H_2SO_4.

Within the atmosphere, sulfate aerosol has both optical and cloud effects. The *direct* optical effects on solar radiation and on visibility are from the high efficiency that submicrometer particles have to optical scattering between wavelengths of 0.1-0.5 μm or longer. The typical scattering efficiency, given as the ratio of scattering extinction to submicrometer sulfate concentration, is 5 m^2 g^{-1} for low RH or about 10 m^2 g^{-1} for RH = 75%. As a result, sulfate is the dominant cause of reduced visibility in industrial regions and is also the main cause of reduction in solar irradiance (energy reaching the ground) in those regions. Besides producing a turbid sky, some scattered solar radiation is reflected out to space because about 10-20% of the light is scattered backward. Natural marine background aerosol concentrations are so low that even very small additions of anthropogenic aerosols have significant effects. Increases in extinction at solar wavelength in marine air occur at sulfate mass concentrations above about 0.5 μm^{-3}. Over the eastern United States, anthropogenic $SO_4^=$ concentrations of 1-10 $\mu g\ m^{-3}$ are calculated and measured to cause an annual average decrease of solar irradiance of about 7.5% (Ball and Robinson, 1982). Potential Northern Hemisphere effects have been estimated (Grassl, 1988) because of the dominance of anthropogenic sulfur over the U.S., Europe, and Asia.

Sulfate aerosol also affects clouds where, because of the hygroscopicity and water solubility of acidic sulfates, it is an important component of cloud condensation nuclei (CCN). Over many ocean regions, sulfate aerosol is the dominant component in CCN. This is true for those ocean regions where continental impacts are minimal and it is especially true for most of the southern oceans. The process of cloud nucleation provides an important pathway for acidic sulfate to enter cloud droplets and thereby produce rainwater acidity (Charlson and Rodhe, 1982).

$SO_4^=$ and $CH_3SO_3^-$ are probably the dominant anions in natural CCN, and $SO_4^=$ is probably the dominant pollutant CCN material. These substances are involved in climate, enigmatically, because the albedo of the most common type of cloud (marine stratus) is calculated to be dependent on the *number* concentration of CCN. A change of ±30% in marine CCN (only) is calculated to produce a *global* temperature change of $-/+1^{o}$ K. Quantification of the relationship between sulfur source strength (or even sulfate mass concentration) to CCN number concentration was not yet possible. Qualitatively, it had been known for decades that continental clouds have higher droplet populations than marine clouds. Most continental clouds are also polluted with anthropogenic $SO_4^=$. Thus it is possible that increased anthropogenic $SO_4^=$ mass concentration yields a higher CCN number concentration. However, there was no accepted theory for what controlled CCN number concentration and hypotheses were just being formulated (Baker and Charlson, 1990).

2.2 The Impacts of Nitrogen on the Marine Environment

2.2.1 Introduction

Well-documented increases in concentrations of carbon dioxide in the atmosphere, principally from anthropogenic sources (Broecker and Peng, 1982; Keeling, 1973), and the concomitant potential for long-term climate change through an enhanced greenhouse effect have led to a heightened awareness among both scientists and politicians of the need to understand the global carbon cycle. Oceans play an important role in moderating fluctuations in atmospheric CO_2 (Sundquist, 1985). They represent a net sink for atmospheric CO_2 and take up about half of the anthropogenic production. Therefore, an understanding of the mechanisms and patterns of the oceanic carbon cycle is necessary to assess adequately future changes in the ocean/atmosphere system.

The biological components of the oceanic carbon cycle in the illuminated upper ocean (the euphotic zone) are thought to be regulated by the availability of inorganic nitrogen (Eppley and Peterson, 1979) although other nutrients, such as phosphate and iron (Broecker and Peng, 1982; Martin and Fitzwater, 1988), have been suggested. The new-production hypothesis describes how the supply of exogenous nitrogen may regulate the amount of the organic matter exported from the euphotic zone on a multiannual time scale where a steady-state assumption is valid (Dugdale and Goering, 1967; Eppley and Peterson, 1979).

Under the new-production hypothesis, the nutrient supply to the primary producers in the illuminated upper ocean is divided operationally into "regenerated" sources and "new" sources. The regenerated nitrogen is derived from the biological activity of heterotrophs remineralizing the organic nitrogen back to usable inorganic forms within the euphotic zone. These regenerated nutrients are principally ammonia, urea, and perhaps some kinds of dissolved organic nitrogen. The new nitrogen is supplied from outside the euphotic zone, principally through the vertical mixing of nitrate from below the euphotic zone. The nitrogen fixation by marine cyanobacteria is probably a minor source of the new nitrogen (Carpenter, 1983) although recent measurements of higher rates may require a reevaluation of this conclusion (Carpenter et al., 1987; Martinez et al., 1983; Scranton et al., 1987).

The deposition of nitrogen from the atmosphere can be a significant source of nutrients, especially in the oligotrophic regions (Duce, 1986). However, atmospheric deposition is a relatively minor exogenous source in an open-ocean environment over a long time scale (Knap et al., 1986), even though on an event basis it may be significant (see below). In a coastal environment, atmospheric nitrogen has been shown to be important (Paerl, 1985). The production of biomass based on these exogenous nutrients is termed new production (Dugdale and Goering, 1967). With steady-state and other assumptions about nutrient transformations, the new production of biomass equals the losses of nitrogen from the euphotic zone. The passive sinking of organic particles is a major loss mechanism and has been the object of the most study. Other potential loss mechanisms are the vertical migration of zooplankton with their subsequent excretion at depth (Longhurst and Harrison, 1988) and the downward mixing of dissolved organic nitrogen (DON) when there is a euphotic zone maximum in DON concentration (Jackson, 1988).

In the ocean, nitrogen occurs primarily in six forms: dinitrogen, nitrate, nitrite, ammonia, DON, and particulate organic nitrogen (PON). Although there are substantial amounts of N_2 in the ocean, there is little nitrogen fixation and this gas is relatively conservative. Nitrate is the primary reduced inorganic nitrogen pool with concentrations up to 20-30 μmol L^{-1} in the deep Atlantic. As expected with a nutrient, surface waters are usually depleted compared to deep-sea values; over most subtropical areas, nitrate concentrations are below the detection limits of standard techniques (0.05 μmol L^{-1}) for most of the year. Both nitrite and ammonia are present at low concentrations (generally <1 μmol L^{-1}) because they are intermediate steps in the transformation between nitrate and organic nitrogen. Ammonia is readily assimilated by plants and bacteria and is the preferred inorganic form of nitrogen. Both DON and PON have maxima in surface waters where they are initially formed by phytoplankton and bacteria. The PON concentrations vary considerably both spatially and seasonally. Near Bermuda, PON ranges from 0.1-1.0 μmol L^{-1} and can be orders of magnitude higher in the highly productive waters farther north or near the continental margins. The concentrations of DON were uncertain as new techniques (Suzuki et al., 1985) were indicating much higher concentrations than those found by standard measurements (Jackson, 1988; Sugimura and Suzuki, 1988). The concentrations of DON in surface waters may have been comparable to concentrations of nitrate in deep seas (20-30 μmol L^{-1}) although there were no published measurements for the Atlantic using the new techniques. The transformations among forms of nitrogen are mostly biological and the fluxes of nitrogen are by a combination of biological and physical processes.

Any comparison of nitrogen rate processes in oceans with nitrogen sources from the atmosphere was confounded by the lack of good, concurrent data for both oceanic and atmospheric processes and by the controversies about oceanic measurements. Atmospheric inputs of biologically usable nitrogen (regardless of the form) are exogenous nutrient sources to the surface ocean. Logically they must be compared with the new-production rates for estimating their relative importance. Bermuda was one of the few places where this comparison could be done because of the presence of both long-term oceanic time-series measurements (from Hydrostation S and the Bermuda Atlantic Time-series Station [BATS]) and atmospheric measurements (from the WATOX and AEROCE programs). The atmospheric measurements and inputs are discussed further in other parts of this document; the discussion below focuses on the range of values for new production in the open ocean near Bermuda and briefly mentions just one published comparison of the atmospheric inputs for this site (Knap et al., 1986). The recent data from BATS are discussed in more detail to illustrate the importance of episodic events.

New production in the oligotrophic ocean near Bermuda has been estimated by a variety of direct and indirect methods (Table 2), all of which involve assumptions and methodologies that have some uncertainty. The most direct method for estimating new production is by measuring the flux of particles sinking out of the euphotic zone with sediment traps. Over long time periods, these losses must be balanced by exogenous inputs of nitrogen. The integrated new-production rates from the sediment traps are approximately 0.1-0.2 mol N m^{-2} yr^{-1}. The traps do not measure nitrogen fluxes from vertically migrating zooplankton (Longhurst and Harrison, 1988) or the downward mixing of DON (Jackson, 1988). They also have methodological problems of scale (short deployments, small areas), problems of overestimation from the inadvertent inclusion of zooplankton "swimmers" (Knauer et al., 1979; Michaels et al., 1990), and hydrodynamic problems of unknown magnitude (Gust, 1989).

Indirect calculations of new production usually take advantage of the stoichiometric relationships between elements in the organic matter: the Redfield ratios. By measuring changes in the oxygen concentrations through time, the required nitrogen production or consumption can be calculated. Jenkins and his coworkers (Jenkins and Goldman, 1985; Spitzer and Jenkins, 1989) use the 35-year time-series record from Hydrostation S for this purpose. Using a variety of independent techniques, they estimate minimum new-production rates of approximately 0.5 mol N m^{-2} yr^{-1}. Their techniques have the advantage that they are averaged over decadal time and large space scales. Jenkins and his colleagues also compare these values to models of the physical mixing of nitrate from below the euphotic zone and find agreement between the model predictions and their new-production estimates.

A final indirect method of estimating new production is by its relationship with primary production. The oligotrophic environment is thought to have

Table 2.--Nitrogen flux estimates for the Sargasso Sea near Bermuda

---

Hydrostation S oxygen fluxes, nitrate fluxes (Jenkins and Goldman, 1985; Spitzer and Jenkins, 1989):

MINIMUM NEW production = 0.5 mol N m^{-2} yr^{-1}

BATS particle fluxes (Altabet, 1989; S. E. Lohrenz; Center for Marine Science, University of Southern Mississippi, Stennis Space Center, MS 39529; personal communication, 1990):

NEW production = 0.1 mol N m^{-2} yr^{-1}

Carbon fixation rates (Menzel and Ryther, 1961; S. R. Smith; Bermuda Biological Station for Research, 17 Biostation Lane, Ferry Reach GE 01 Bermuda; personal communication, 1990):

TOTAL production = 0.6-1.1 mol N m^{-2} yr^{-1}

BATS production data (S. E. Lohrenz; Center for Marine Science, University of Southern Mississippi, Stennis Space Center, MS 39529; personal communication, 1990):

TOTAL production = 1.4 mol N m^{-2} yr^{-1}

Recycling (Glibert, 1982):

N % recycling = 90%-99% (new = 0.14-0.01 mol N m^{-2} yr^{-1})

---

a large amount of recycling compared to a nutrient-rich ocean (Eppley and Peterson, 1979). The measured nitrogen recycling rates (the uptake of ammonia versus nitrate) are on the order of 90-99% of the total production at various oligotrophic Atlantic sites (Glibert, 1982); the remaining 1-10% of the production would be exported. Total primary production rates estimated from the carbon-fixation rate vary from 0.6-1.4 mol N m^{-2} yr^{-1} (Menzel and Ryther, 1961; S. E. Lohrenz; Center for Marine Science, University of Southern Mississippi, Stennis Space Center, MS 39529; personal communication, 1990; S. R. Smith; Bermuda Biological Station for Research, 17 Biostation Lane, Ferry Reach GE 01, Bermuda; personal communication, 1990), implying a new-production rate of only 0.01-0.14 mol N m^{-2} yr^{-1}.

Knap et al. (1986) use atmospheric inputs of nitrogen measured over a three-year period (1982-1984) in Bermuda to estimate the importance of atmospheric sources to oceanic new production. Their average annual deposition rates are only about 1.2-6% of the annual new-production rates that Jenkins and Goldman (1985) estimate; however, the episodic deposition rates are substantially higher. The largest event they report in that period results in a deposition of 860 μmol m^{-2}, which is 50% of the average daily new production estimated from the long-term average. Knap et al. conclude that atmospheric inputs are not important in long-term nitrogen budgets of open oceans. However, new production as estimated from other techniques is up to an order of magnitude lower and atmospheric inputs would be very large by comparison. Future comparisons of atmospheric inputs with oceanic new production must take into account the methods used to estimate the new production and the uncertainties associated with each method. Resolution of the discrepancies in new-production rates is an area of active research in the oceanographic community and must be resolved before these kinds of comparisons are adequate.

2.2.2 Episodic events

A comparison of long-term average values conceals some very important patterns that may influence ocean processes on the time and space scales that organisms actually experience. Time-series measurements of oceanic properties reveal a striking amount of temporal and spatial heterogeneity, including the presence of episodic events contributing significantly to the annual average. The magnitude of these episodic events is apparent in the first year's data from BATS (Fig. 2).

Monthly sampling for BATS began in October, 1988, at a station 45 nm southeast of Bermuda. The first year's data showed a pronounced spring bloom during the February, 1989, cruise (Michaels et al., 1990; A. Michaels; Bermuda Biological Station for Research, 17 Biostation Lane, Ferry Reach GE 01, Bermuda; unpublished data, 1990). As a result of the deep-winter mixing (a 250-m mixed layer), the near-surface nitrate concentrations were over 0.2 μmol L^{-1}. There was a pronounced increase in the chlorophyll concentration with a shallow maximum and oxygen supersaturation to a depth of 250 m. Particulate organic carbon and nitrogen concentrations were elevated compared with the previous months and the primary production rates and sinking fluxes measured by the sediment traps showed the highest values at this time. By the next cruise in late March, nitrate concentrations in the upper euphotic zone had decreased to below detection limits. The chlorophyll concentrations had decreased and a chlorophyll maximum had developed at the base of the euphotic zone. High concentrations of particulate organic carbon and nitrogen had disappeared and production and flux rates were back to average values. This bloom was present as a single cruise anomaly in the BATS data set, with the oxygen supersaturation and the residual chlorophyll maximum the only evidence in subsequent samples of the enhanced biological activity.

By examining changes in the oxygen anomaly (the difference from saturation in ml L^{-1}) and the ambient nitrate concentrations, we could estimate the amount of new production that may have occurred during this bloom event. The oxygen concentration was below saturation throughout the euphotic zone on the mid-December cruise. The January profile showed a mixture of undersaturated and slightly supersaturated profiles. The February bloom profile showed supersaturation of oxygen down to a depth of 250 m. If we assumed that bubble injection and other physical processes could not cause a supersaturation in excess of 0.1 ml L^{-1} (W. J. Jenkins; Woods Hole Oceanographic Institution, Woods Hole, MA 02543; personal communication, 1990), the integrated oxygen anomaly over 0.1 ml L^{-1} should have represented biological activity. This integrated oxygen stock was 26.3 L m^{-2}, which was equal to approximately 0.14 mol N m^{-2}. This was an underestimate of the actual new production since much of the oxygen produced escapes into the atmosphere (Jenkins and Goldman, 1985); the estimate of bubble-injected oxygen was conservative. The actual new production in this event may have been higher than 0.29 mol N m^{-2}.

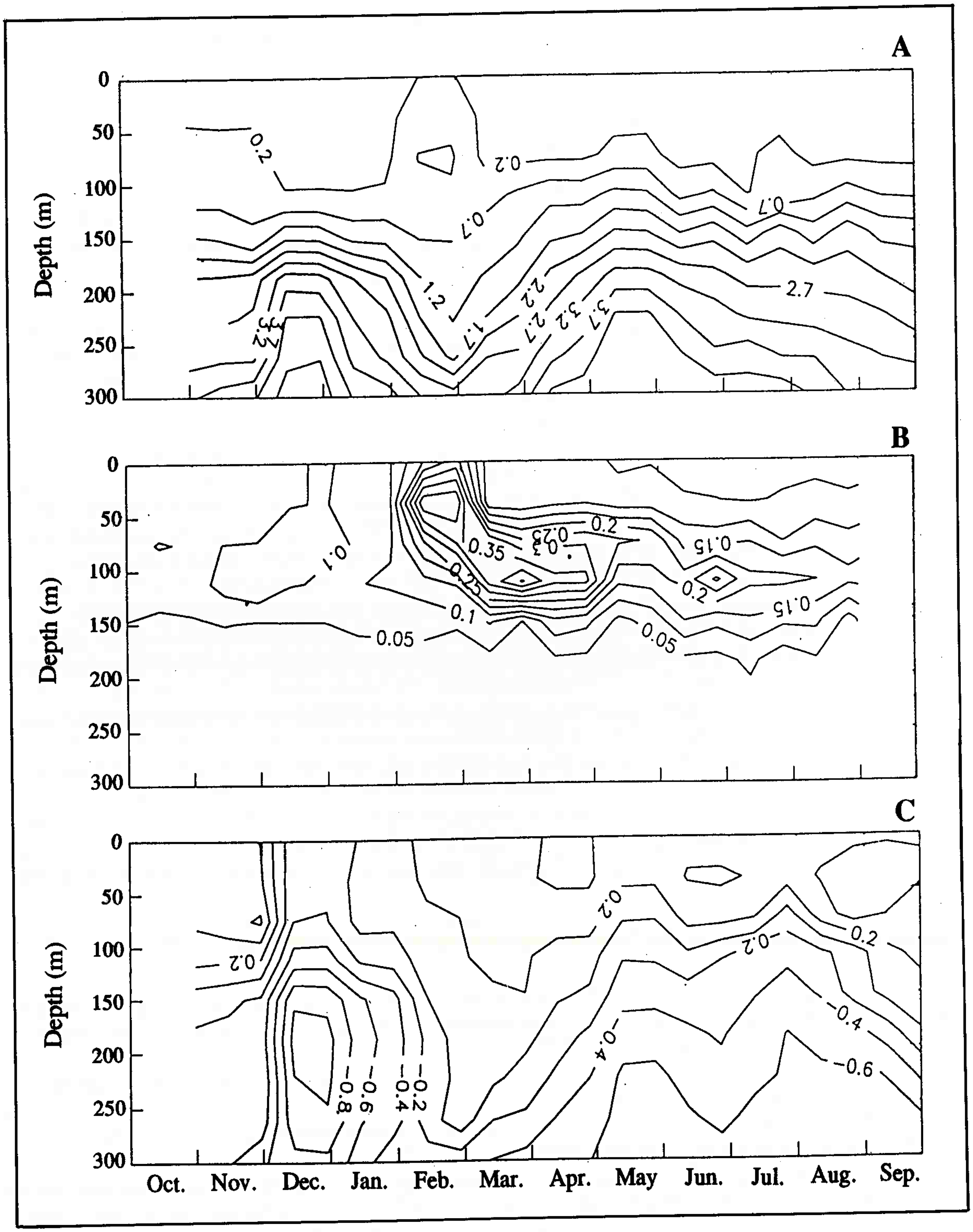

Figure 2.--Time-series of **(A)** nitrate (μmol L^{-1}), **(B)** chlorophyll a (μg L^{-1}), and **(C)** oxygen anomaly (ml L^{-1}) at the Bermuda Atlantic Time-series Station from October, 1988, to September, 1989.

The ambient nitrate concentration in February was around 0.5 μmol L^{-1}. The nitrate concentration of water with the same density as the February mixed layer was greater than 1.0 μmol L^{-1} both before and after the bloom. If the mixed layer began with a uniform 1.0 μmol L^{-1} of nitrate, approximately 0.04 mol L^{-1} m^{-2} would have been consumed in the upper 100 m by the time of the February cruise. Most of the remaining nitrate (0.044 mol L^{-1} m^{-2}) would have been used by the March cruise. This nitrate use would also represent a minimum estimate as the kinetic effects (e.g., the continued inputs of nitrate) were ignored. These minimum new-production rates by oxygen evolution and nitrate consumption were 17-28% of the annual average new-production estimate of Jenkins and Goldman (1985). Less conservative estimates of the oxygen production suggested that more than half of the annual production could have been associated with this event.

A major implication of an episodic event of this nature is that the annual mean is a poor reflection of the nitrogen cycle at any specific place and time. Subtracting this event from the annual mean (Jenkins and Goldman, 1985) results in a daily average new-production rate of 600-1,100 μmol N m^{-2} day^{-1}. Other types of episodic events are also known to occur and, for most days, the daily rate is undoubtedly lower. By this calculation, large atmospheric deposition events such as those recorded by Knap et al. (1986) may have been the dominant nitrogen sources when they did not co-occur with other oceanic episodes. These nitrogen inputs would have been used by the phytoplankton and might have stimulated a short-lived bloom in the surface waters. This kind of bloom was observed by Glover et al. (1988) following a rainfall. Although the authors discount the rain as a source of the surface nitrate that stimulated the bloom (using the Knap et al. [1986] citation of annual averages), the actual amount of excess nitrate is within the range of measured episodic inputs for Bermuda. These blooms are probably restricted to the surface mixed layer and would be visible in satellite images of ocean color also restricted to measuring the upper ocean. The organisms that bloomed in these episodes and the community processes that led to particulate exports may also have differed from the usual taxa and processes. These variations in the community structure will have significant effects on the composition of sinking particles (Michaels and Silver, 1988) and the amount of carbon and other elements that are concomitantly transported. It is likely that the intersection of the episodic nature of an ocean and the atmosphere is where the true importance of the atmospheric deposition to the oceanic nitrogen cycle will be found.

2.3 Meteorology Overview

2.3.1 Climatological distributions

Describing meteorological patterns in the Atlantic Ocean region has been an important area of scientific study for over two hundred years. The need to advise marine and air traffic in the region and to track major weather features moving towards the European continent has been the main impetus for this work. More recently, the effectiveness of these systems in transporting trace materials (especially acidifying pollutants) into and across the North Atlantic area has become an area of scientific interest. One advantage is that the North Atlantic has the longest running record of marine meteorological measurements, which were first begun in the 1850s (Maury, 1857). This record has been continued to this day with data from ships, from islands, from coasts, and now from satellites.

From these climatologies, it can be seen that the North Atlantic Ocean area is dominated by three semipermanent weather features:

1. The Icelandic low-pressure system,
2. The Bermuda-Azores high-pressure area,
3. The northeast trade-wind regime.

These systems fluctuate in strength and position through the year; their wintertime positions are shown in Figure 3. The Icelandic low is a series of moving low-pressure centers that dominate the northern North Atlantic, with an average position near Iceland in the winter. In contrast, during the summer months, the Bermuda-Azores high moves north and broadens and strengthens over its winter manifestation as the Icelandic low weakens. With this movement, the northeast trades also extend further north, tend to be more persistent, and reach peak velocities during the warmest months. Also important is the formation and movement of tropical disturbances, tropical storms, and hurricanes; these occur irregularly from June to November. During their lifetimes these systems can change the predominant meteorological situation (Tucker and Barry, 1984).

Some meteorological factors are specific to the transport question and include information on winds, both surface and upper level, and the statistics of precipitation amounts and perhaps air temperatures. Masses of data on these factors are included in atlases (Meserve, 1974; Isemer and Hasse, 1985). An example of the information available can be found in chart 148 of Isemer and Hasse, where the resultant surface winds are plotted for January based on a 20-year record. Other data, such as precipitation frequency, are also available (see chart 101, Isemer and Hasse). Some data are now available not only in the form of charts but also as computer-accessible data archives (Slutz et al., 1985).

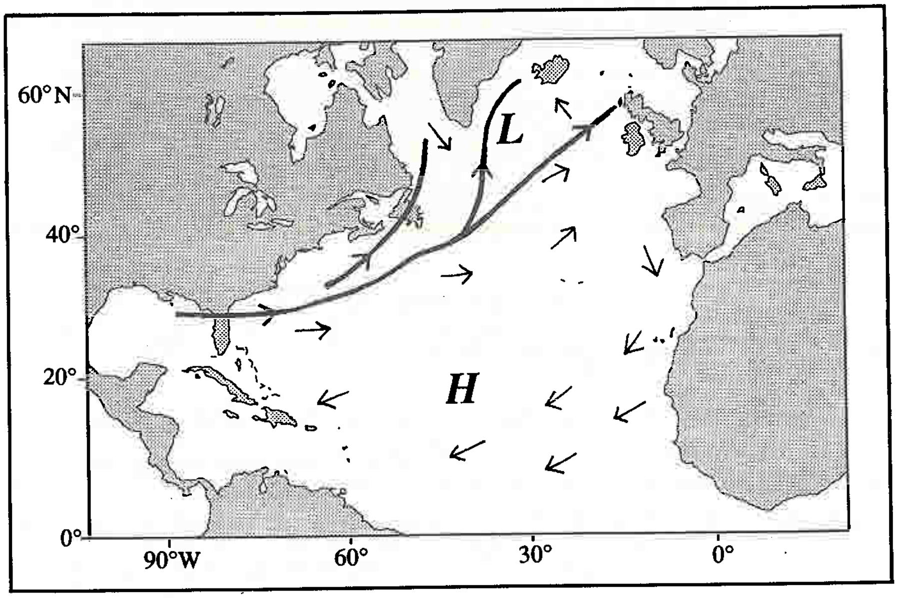

Figure 3.--Surface meteorology in winter in the North Atlantic. The L and H identify the Icelandic low and the Bermuda-Azores high, respectively. The thick lines indicate the principal storm tracks; the light arrows show the mean wind direction.

2.3.2 Trajectory techniques and the use of trajectory analyses

Atmospheric transport is strongly dependent upon the details of winds in the area at the time of interest. Motions on a wide range of space and time scales are relevant and the problem is complex even for the simplest case of inert-gas species. In general, mean transport is not carried out by the mean horizontal wind. The exception is in regions of very steady winds (for example, the trades) where the streamlines of the wind give a clear indication of the transport that can be expected. More typically, because of shear and diffluence in the wind field, initially compact parcels of air pollutants can be separated into many discrete blobs; vertical motion in convective cloud systems can rapidly move pollutants into a different wind regime. Chemical reactions, often times enhanced in the heterogeneous environment of clouds, change the composition of parcels.

Air-parcel trajectory analysis is a technique that can be used to assess possible source regions and transport paths for particular periods and sites. Typically, back trajectories from a site are calculated for times when sampling of concentrations or deposition is underway. Trajectory analysis can take into account some, but not all, of the phenomena that are important in long-range transport (Miller, 1987). We discuss here some aspects of such analysis as it is applied to transport to remote ocean areas.

The meteorological data required for retrospective trajectory analysis in open-ocean areas are usually obtained from routinely available global analyses of wind and temperature data. This is in contrast to continental areas, which are generally well covered with *in situ* meteorological data and where analyses tailored to transport calculations can be used. In isobaric trajectory calculations, the winds on the analysis surface, quasi-horizontal layers of constant atmospheric pressure, are used. In isentropic trajectory analyses, winds follow a hypothetical surface of constant potential temperature; this is the way air moves in the absence of mixing, latent-heat release (i.e., condensation or evaporation), or other diabatic processes. Fully 3-dimensional trajectory analyses require explicit estimates of vertical velocity, which are only available in a dynamical model--however, none of the results discussed here uses this approach.

These techniques have limitations that must be kept in mind. Foremost is that trajectory analysis is inherently qualitative. That is, the fact that a trajectory passes over a potential source area implies, but does not guarantee, that the source may have contributed to the observed air chemistry. The accuracy of trajectories is limited by the adequacy of the basic meteorological data used and by assumptions fundamental to the technique; accuracy decreases rapidly back in time with increasing path length. Nevertheless, trajectories provide a convenient way to use meteorological data in interpreting concentration and deposition observations.

2.3.3 Results for the North Atlantic sites

Several large ensembles of trajectories have been compiled for sites in the North Atlantic area. Of particular interest are the analyses by Miller and Harris (1985) in which isobaric back trajectories from Bermuda for the period 1975-1981 are divided into six azimuthal sectors and plotted on a histogram. The importance of flow from the North American continent is indicated in their results by the dominant peak in the northwest sector. The authors also present a histogram for trajectories for days with rainfall; although the northwest is the most common sector in the "all days" set, its dominance in this selected set is significantly reduced. The seasonal variations of these patterns are also discussed.

In work that was as yet unpublished, Merrill (J. T. Merrill, Center for Atmospheric Chemistry Studies, The University of Rhode Island, Narragansett, RI 02882-1197) had compiled isentropic trajectories for the North Atlantic sites discussed at the workshop. Trajectories were calculated twice a day for the years 1984-1988. For trajectories arriving at a specific site (e.g., Bermuda), a calculation was made of the number of hours spent by each trajectory over a geographical grid. Merrill et al. (1989) use a superposition technique developed by Poirot and Wishinsky (1986). The contours of trajectory passage probability (Fig. 4) indicated the areas with the highest number of trajectory

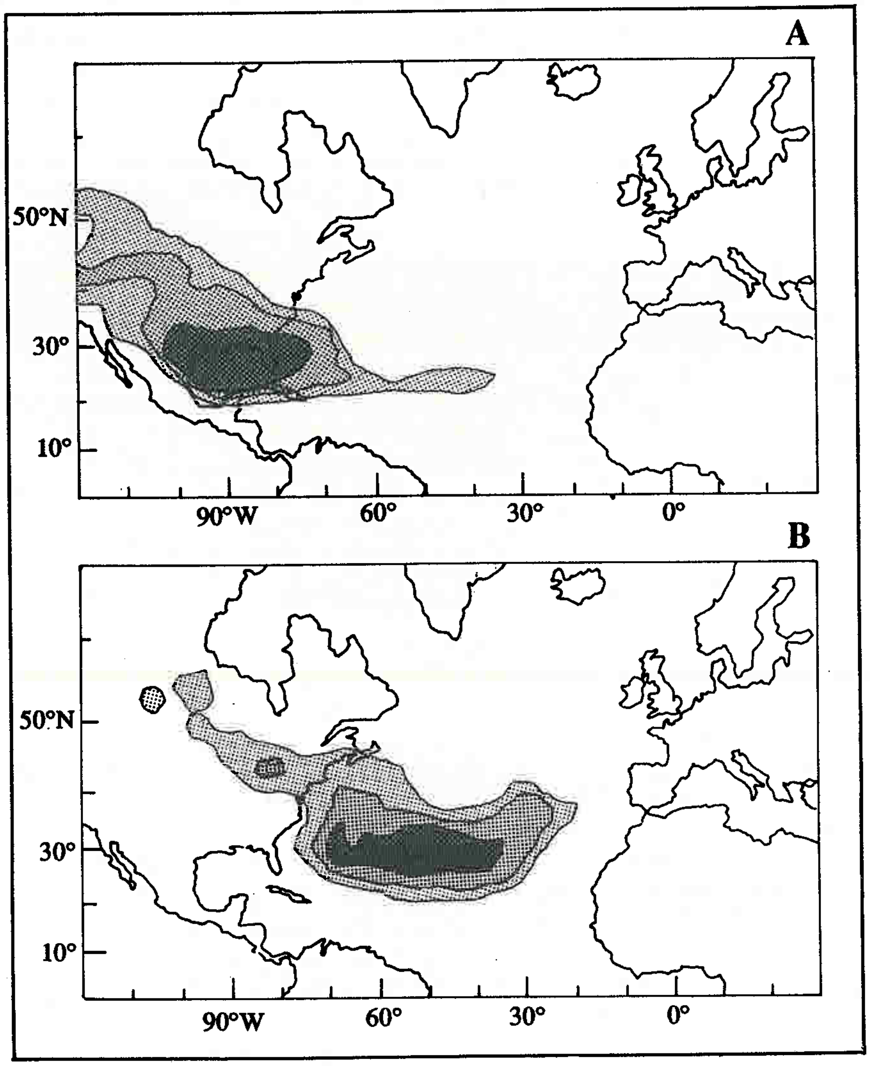

Figure 4.--Cumulative probabilities (40% , light stippling; 60%, medium; and 80%, dark) of the airflow passage to Bermuda on 300 K potential temperature surfaces during (**A**) January-March, and (**B**) July-September, 1984-1988.

passage hours for the Bermuda trajectories. Thus in the winter months (Fig. 4A), the air reaching Bermuda was most likely to have passed over interior areas of North America and the Gulf of Mexico. In the summer months, on the other hand, the flow was more often from open-ocean areas southeast and east of Bermuda (Fig. 4B). The trajectories shown were calculated on the 300-K isentropic surface, which intersects the boundary layer near the latitude of the island. The trajectories extended back for ten days; for substances with atmospheric residence times shorter than this, the areas closer to the site were the most relevant.

The corresponding trajectory probability fields for the other sites showed differing patterns. At Barbados where the trade-wind flow is steady, there was less variation from season to season and the flow was more or less directly from east to west; however in the summer months, the curvature in the pattern indicated that both Europe and Africa were likely continental source areas. At Izania in the Canary Islands, the station was in the free troposphere and the winter flow path was somewhat similar to the winter pattern for Bermuda, showing flow from west to east from the southeastern areas of North America, Mexico, and the Gulf. In the summer months, the flow was slower and more from the north, indicating that areas in the open Atlantic Ocean were the most probable sources. Only a short record was available for Mace Head, Ireland, because of temperature variability. A selection had to be made of the potential temperature surface that was the most relevant, i.e., that was the lowest lying above the surface near the site. Plots made for such an analysis for the period of July, 1988, to December, 1989, indicated a fairly straight west-to-east flow toward Mace Head, with the highest-probability areas extending over interior regions of North America, generally from 45° N to 60° N. The easterly flow, generated by a clockwise flow around the Siberian High, might at times have been important.

Problems and prospects for extensions of these techniques.

Trajectory analysis can be combined with chemical-concentration or deposition data to provide insights on the long-range-transport process. Moody and Galloway (1988) use an informative approach. Isobaric back trajectories from Bermuda selected for rain days are grouped by cluster analysis, and the authors show that a significant part of the chemical-concentration variance can be explained by the trajectory pattern.

The probability analysis technique discussed in the preceding section can be augmented to include chemical data: semiquantitative mass-transport probability fields can be generated by weighting trajectories that arrive during high-concentration periods more heavily than those that arrive during low-concentration periods. Merrill and Graustein (1989) discuss the use of this approach for North Atlantic sites for radionuclides indicative of continental sources. A more sophisticated approach called quantitative trajectory bias analysis (Keeler and Samson, 1989) is difficult to apply over the ocean because of the lack of routine estimates of rainfall distributions.

No technique of trajectory analysis could account for the inherent nonlinearity of the chemical processes that were important for some species. The air might have passed through the high-probability regions most of the time, but the low-probability areas might have been significant. If the mixing of air parcels created a critical assemblage of reactants some distance from the site, environmentally important reaction products might have reached the site from areas that were not often "upwind." Consequently, concentrations of certain substances could have peaked during atypical conditions; such circumstances could have accounted for a large fraction of the annual variation in concentration or deposition. Only 3-dimensional chemical-transport models could be expected to deal with such complexities. However, the models were seldom run with event-specific meteorological fields that covered the entire North Atlantic Ocean.

2.3.4 Precipitation in the observations and in the models

Precipitation observations on islands and coasts.

The precipitation amount measured on an island or coastline is not necessarily equal to that falling on the surrounding ocean. Islands, especially those surrounded by reefs or other shallow water areas, present both a thermal and dynamical anomaly to the air flowing over the sea. The dynamical influence can produce orographic uplift. However, even islands with low relief cause a convergence on the upwind side and a divergence on the lee side, because of the island's mechanical drag, that may be as much as a thousand times greater than that on even a fully developed sea. Further, the surface-level air is near saturation, especially in subtropical areas, and only weak upward motion is needed to induce cloud formation and precipitation.

There have been numerous studies of the influence of islands on cloud and precipitation distributions. In general, island rainfall is more nearly representative of ocean rainfall when the islands have low topographic relief and when they are situated in areas dominated by convective (as opposed to stratiform or frontal) precipitation systems (Reed, 1980). Although Bermuda has limited relief, the extent of shallow water exceeds the area of the island itself by a large factor. Therefore it is not surprising that the climatological total annual precipitation estimates for Bermuda, which range from about 1100-1500 mm, significantly exceed estimates for the surrounding ocean areas where the value may be 800-900 mm.

Challenging simulations of rainfall distributions over the ocean.

It had been generally believed that precipitation was not well simulated by large-scale circulation models. This deficiency was related to fundamental problems of cloud simulation in global models. Although the latter had recently received much attention, quantitative comparisons of simulated and observed precipitation distributions had not. Global-scale models were usually run at moderate spatial resolutions, and the resulting very large grid areas inevitably contained a heterogeneous mixture of surface conditions, thermodynamic and radiative environments. Consequently, only grid-area precipitation amounts could be simulated and these represented an average of rates within the grid area. The purpose in discussing this was not to criticize models but rather to draw attention to the limitations in the simulation of a process that was vitally important to the deposition estimates.

Only recently had basin-wide estimates of precipitation amounts been published that were generally regarded as representative and reliable. For example, the estimates of Elliot and Reed (1984) from marine weather observations represent the precipitation field away from islands. Their estimates agree quite well with those of Jaeger (1983; the January and July distributions are shown in the GESAMP [1989] report): the oceanic rainfall distribution is constrained by the global water balance in Jaeger's analysis. In the latter, the dry zone extending west from Africa is larger, and the gradient toward higher precipitation values west and north is concentrated in a narrower area. However, the basin-wide total precipitation is similar in these two compilations.

Those working with model simulations of chemical transport should avail themselves of reliable climatological precipitation distributions to refine the interpretation of their results. Further, histograms of deposition amounts from events contributing to monthly totals should be used in conjunction with the totals in comparisons between simulations and meteorological and chemical observations.

2.4 Measurements Overview

2.4.1 Introduction

The sulfur and nitrogen data bases in the North Atlantic Ocean's atmosphere are resources that can be used not only to determine the cycling of sulfur and nitrogen in the marine atmosphere but also to test various model formulations. For both purposes, the data bases should characterize the spatial and temporal variabilities of sulfur and nitrogen species. This section of the paper reviews the spatial and temporal extent of the data bases that were available and their variabilities and identifies areas where additional information was needed to evaluate and improve the accuracy of the existing models.

2.4.2 The existing data bases

Four categories of data bases were defined for convenience: coastal, island, aircraft, and shipboard; the shipboard data were limited to oceanic DMS. Although the data bases used in the comparisons in this paper do not go beyond 1989, data from the islands continue to be taken into the 1990s.

The coastal data bases included precipitation-chemistry/wet-deposition data from three networks: the National Acid Precipitation Assessment Program (NAPAP) in the eastern United States, the Canadian Air and Precipitation Monitoring Network (CAPMoN) in eastern Canada, and the Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (known as the European Monitoring and Evaluation Programme or EMEP) in western Europe. Some gas and aerosol data were available from occasional studies at some sites.

The island data bases included a fair amount of precipitation-chemistry/wet-deposition data, a small amount of aerosol-chemistry data, and almost no vapor-phase-species data (Fig. 5; Table 3). There were precipitation-chemistry/wet-deposition records for 1.5 years at Barbados (AEROCE); approximately 9 years at Bermuda (WATOX/AEROCE); and 5 years at Adrigole, Ireland (WATOX). The longest aerosol-species data record was the one for 5 years from Barbados (AEROCE). Records less than 3 years were available from other islands and were supplemented at Bermuda by occasional short-term (few weeks) intensive

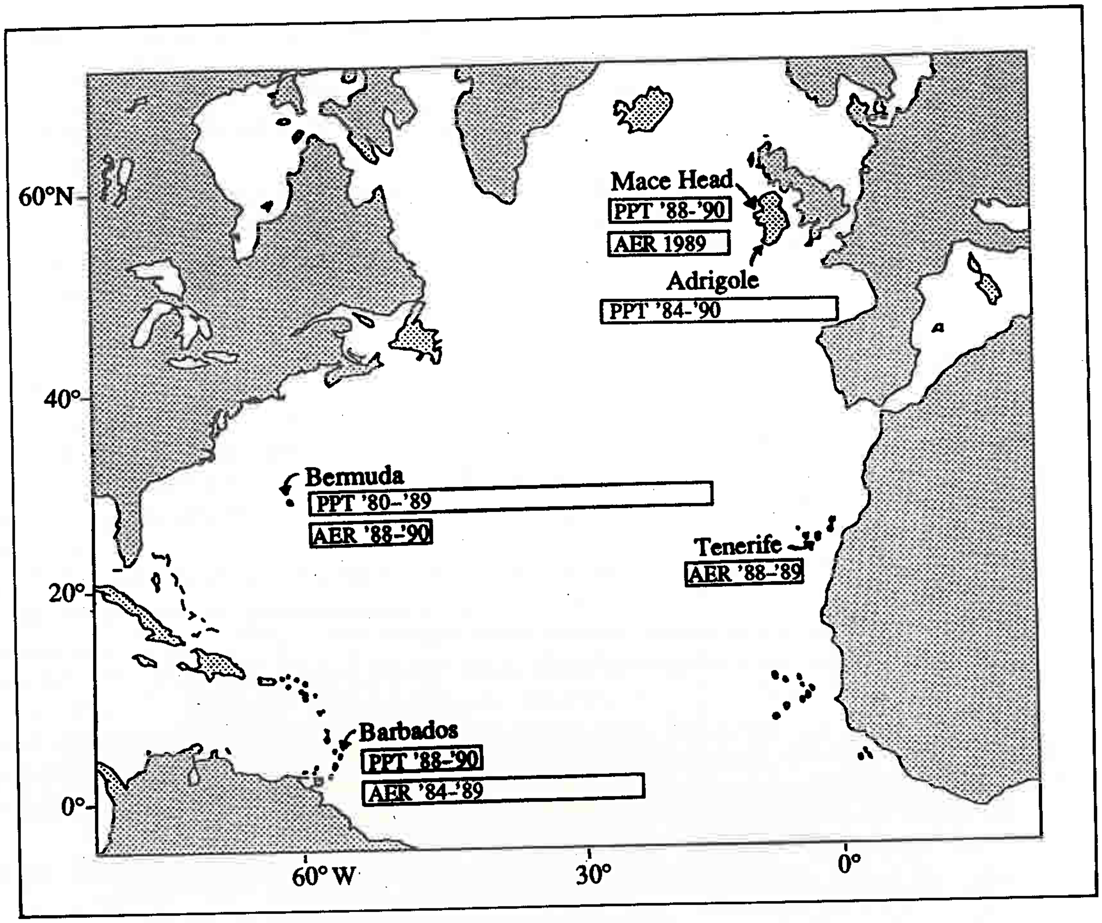

Figure 5.--Sites of surface data bases and the temporal extent (shown by the length of the rectangles) of the data on the aerosol and precipitation compositions from North Atlantic Ocean's islands (see also Table 3). As of August, 1992, sampling was continuing at all sites, except Adrigole, Ireland.

studies. Sampling times varied from essentially continuous for some of the intensive gas-phase measurements to integration times of as long as a week for the aerosol species. Precipitation was generally sampled either daily or by event.

The ship-based data were available from several cruises, including intensive surveys in coastal regions off the east coast of the United States, near Bermuda, in Scottish coastal waters, and along latitudinal and longitudinal transects covering much of the North Atlantic Ocean (Fig. 6). The types of sulfur and nitrogen data available are summarized in Table 4.

The aircraft data bases were derived from the STRATOZ III mission around the perimeter of the North Atlantic Ocean and several WATOX intensives off the east coast of the United States. Flight tracks are shown in Figure 7 and the types of data that were available are listed in Table 5. Sampling times ranged from continuous to several hours for various species.

Table 3.--Sulfur and nitrogen data bases for the North Atlantic Ocean islands

Location	Phase	Species	Dates
		Barbados	
Ragged Point*	aerosol, precipitation	$CH_3SO_3^-$, nss-$SO_4^=$, NO_3^-, NH_4^+	1984-1989, 1988-1990
		Bermuda	
Harbour Radio Tower**	precipitation	nss-$SO_4^=$, NO_3^-, NH_4^+	1980-1989
High Point**	gas	SO_2, NO_x, HNO_3	8/82, 2/83
	aerosol, precipitation	nss-$SO_4^=$, NO_3^-, NH_4^+	8/82, 2/83; 1982-1984
St. Davids*,**	aerosol, precipitation	$CH_3SO_3^-$, nss-$SO_4^=$, NO_3^-, NH_4^+	1989-1990, 1988-1990
Tudor Hill*	aerosol, precipitation	$CH_3SO_3^-$, nss-$SO_4^=$, NO_3^-, NH_4^+	1988-1990, 1988-1990
		Ireland	
Adrigole**	precipitation	nss-$SO_4^=$, NO_3^-, NH_4^+	1984-1990
Mace Head*	aerosol, precipitation	$CH_3SO_3^-$, nss-$SO_4^=$, NO_3^-, NH_4^+	1988-1989, 1988-1990
		Tenerife	
Izania*	aerosol	$CH_3SO_3^-$, nss-$SO_4^=$, NO_3^-, NH_4^+	1988-1989
Punta del Hidalgo*	aerosol	$CH_3SO_3^-$, nss-$SO_4^=$, NO_3^-, NH_4^+	1989-1990

NOTE: As of August, 1992, sampling continued at all sites, except Adrigole.

*AEROCE sites
**WATOX sites

2.4.3 Summary of the data bases

The 1989 average concentrations of sulfur and nitrogen species in precipitation at island sites in the North Atlantic Ocean ranged from about 0.2 to 6 μmol L^{-1} (Fig. 8); in aerosol the average concentrations ranged from slightly over 2 to 25 nmol m^{-3} (Fig. 9). These concentrations in precipitation and aerosol were substantially less than in the populated regions of the world. Although these lower concentrations provided challenges for the analysts, the precision and accuracy of these values were commonly less than ±20%.

The annual concentrations of sulfur and nitrogen species in precipitation and aerosols provided indications of the magnitude of the concentrations over space and time but provided nothing on the temporal variability or on how time varied as a function of space. To provide this information, we used long-term records of aerosols from Barbados (1984-1989) and precipitation composition from Bermuda (1980-1989). The seasonal variabilities, monthly averages of NO_3^- concentrations in aerosol, and monthly averages of the rate of NO_3^- wet deposition for the individual years are shown in Figure 10 for aerosols at Barbados

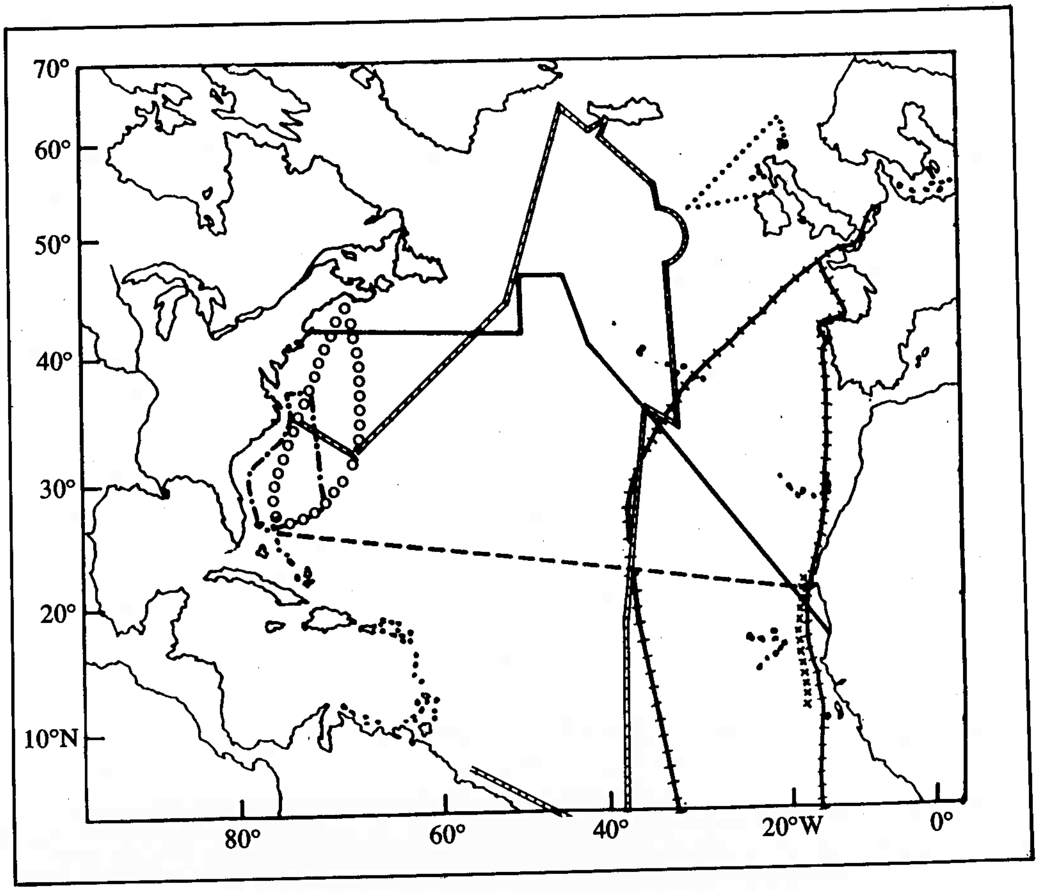

Figure 6.--Cruise tracks of ships on which samples were taken that supplied the necessary data for the shipboard data bases (see also Table 4): The NOAA ships consisted of the R/V Cape Florida and Columbus Iselin, (1985, 1986; dashed line with dots), the R/V Researcher (August-September, 1986; dashed line), the R/V Knorr (April-May, 1984; solid line), the R/V Mt. Mitchell (summer, 1988; railroad tracks), and the R/V Challenger (June-July, 1987; dotted line). The German R/V Polarstern made three cruises: January-April, 1983 (Xs), and March-April, 1987, and in September-October, 1988 (cross-hatched line). Only rain was measured on the cruise ship Oceanic (Os) during her summer cruises from 1982-1985.

and Figure 11 for precipitation at Bermuda. For nitrate in aerosols at Barbados, there were two types of temporal variability. There was a seasonal variability on the order of 2-16 nmol m^{-3} with a maximum in spring and a minimum in winter. This pattern was consistent with the transport patterns from Africa (Savoie et al., 1989). In addition to seasonal variability, there was substantial monthly variability. For any one month, the concentrations of nitrate in aerosols could vary up to a factor of four; although there appeared to be some consistency to the spring maximum, the month during which the maximum occurred could vary from April to June. This type of temporal variability made it very difficult for modelers to predict an "average" behavior of nitrate in aerosols at Barbados. The same type of intermonth and interannual variability was evident for nitrate wet deposition at Bermuda. The situation was even more complicated because of the confounding influence of the variability of the

Table 4.--Data bases established from ship samples

Location	Species	Date
	Nitrogen	
R/V Mt. Mitchell	NH_4^+, NO_3^-, HNO_3, amines, a-acids, NO, NO_2, NO_y, PAN	Summer, 1988
R/V Polarstern	NO_3^-, NH_4^+ NH_4^+, NO_3^-, HNO_3, NO, NO_2, NO_y, PAN	Aug, 1989 Sep-Oct, 1988
R/V Researcher	NO_3^-, HNO_3	Aug-Sep, 1986
R/V Cape Florida, R/V Columbus Iselin	NH_4^+, NO_3^-	4 seasons, 1985-1986
R/V Knorr	NH_4^+, NO_3^-, rain	Apr-May, 1984
	Sulfur Data Bases	
R/V Mt. Mitchell	SO_2, MSA^-, nss-$SO_4^=$, rain*	Summer, 1988
R/V Polarstern	MSA^-, DMS, nss-$SO_4^=$ MSA^-, nss-$SO_4^=$ MSA^-, DMS DMS, SO_2, nss-$SO_4^=$	Aug, 1989 Sep-Oct, 1988 Mar-Apr, 1987 Jan, Apr, 1983
R/V/ Challenger	DMS	Jun-Jul, 1987 Jul, 1985
R/V Researcher	nss-$SO_4^=$, rain*	Aug-Sep, 1986
R/V Cape Florida, R/V Columbus Iselin	DMS, SO_2, MSA^-, nss-$SO_4^=$, rain*	4 seasons, 1985-1986
R/V Knorr	DMS, MSA^-, nss-$SO_4^=$, rain*	Apr-May, 1984

*Major sulfur and nitrogen species were measured.

precipitation amounts. The dashed line (with the Xs) represents the mean of the nitrate deposition calculated over the 1981-1989 period, simply the average of all the individual years. The dotted line (with the open star in a solid circle), however, represents the deposition calculated using the climatological monthly precipitation amount determined over a 50-year period (Mackey, 1957). Clearly, the average deposition, as determined from the 9-year record at Bermuda, still varied by a factor of two from the climatological deposition in some months. This type of interannual variability in both the composition of precipitation and the precipitation amount made it more difficult for climatological modelers to duplicate the "average" deposition of nitrate on Bermuda.

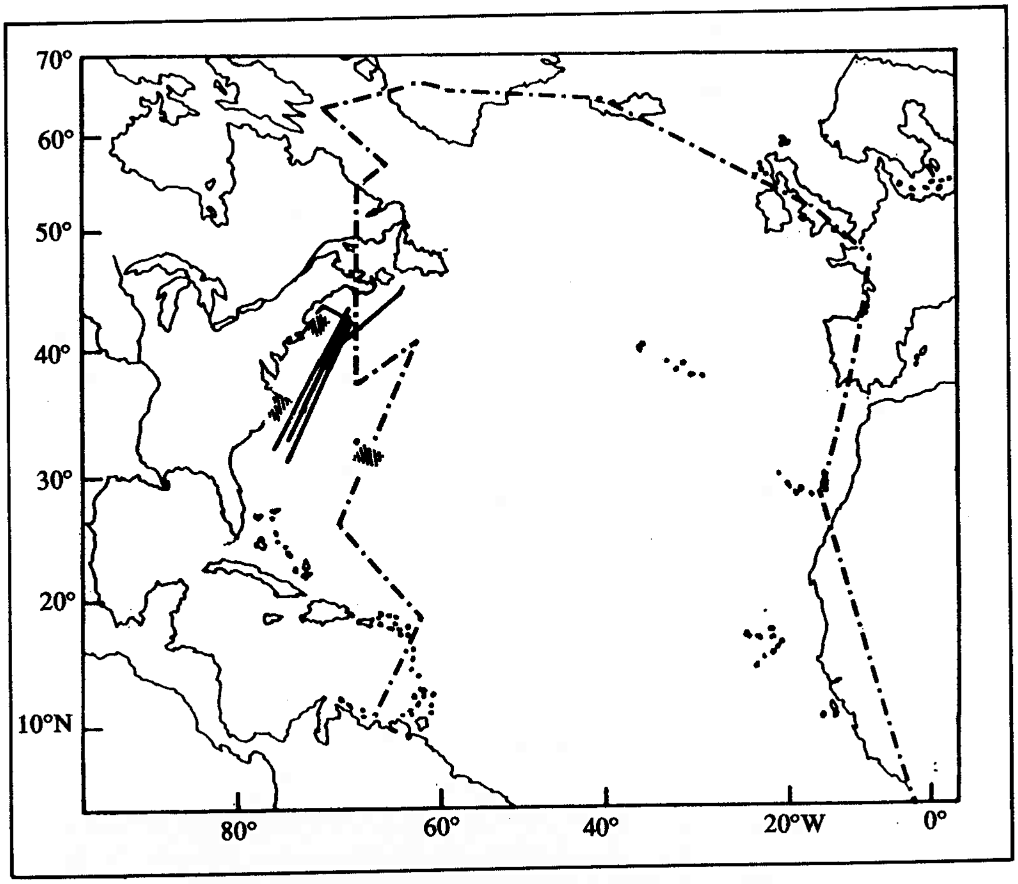

Figure 7.--Flight tracks of the aircraft on which samples were taken that supplied the necessary data for the aircraft data bases (see also Table 5): the STRATOZ III aircraft (spring, 1984; dashed line with dots), the WATOX P-3 aircraft (winter, 1986; solid lines), and the WATOX King Air (summer, 1988; winters, 1985, 1986; slashed rectangles).

In addition to the temporal and spatial variabilities at the surface, another degree of variability is introduced when the atmosphere is treated as a 3-dimensional system by examining the vertical distribution of sulfur or nitrogen species. Figure 12 shows the vertical distribution of SO_2 and nss-$SO_4^=$ between 0-2 km during several of the intensive experiments of WATOX. In most cases, concentrations decreased with altitude as might be expected. In all cases, there was substantial variability among measurement periods. For example, concentrations of SO_2 on both the ground and in the boundary layer ranged from about 10-220 nmol m^{-3}. In the free troposphere they ranged from about 4-100 nmol m^{-3}. This degree of variability meant that it would be very difficult to test the vertical profiles produced by the climatological models--it would require a large amount of data. Rather, such tests should be performed with episodic models.

2.4.4 Data uncertainties and limitations

In general, the quantitative estimates of uncertainties were poor. This was especially true for aircraft and ship-based data sets since these studies had been conducted independently by different groups at different times. No

Table 5.--Data bases established from aircraft samples

Program	Location	Species	Time
		Nitrogen and Oxidant Data Bases	
WATOX NAEC* and Bermuda	Marine boundary layer and free troposphere	NO, NO_x, NO_y, HNO_3, NH_4^+, NO_3^-, O_3	Summer, 1988
NAEC	Marine boundary layer and free troposphere	NO, NO_x, NO_y, HNO_3, PAN, NO_3^-, O_3, H_2O_2	Winter, 1986
Bermuda	Marine boundary layer and free troposphere	HNO_3, NO_3^-, O_3	Winter, 1986
NAEC	Marine boundary layer and free troposphere	NO, NO_x, HNO_3, NO_3^- NO_3^-, O_3	Winters, 1985, 1986
Bermuda	Marine boundary layer and free troposphere	NO, NO_x, NO_y, HNO_3, NO_3^-, O_3	Winter, 1985
STRATOZ III	Multiple	NO, NO_x, NO_y, PAN, O_3	Spring, 1984
		Sulfur Data Bases	
WATOX NAEC and Bermuda	Marine boundary layer and free troposphere	SO_2, $SO_4^=$, $CH_3SO_3^-$	Summer, 1988
WATOX NAEC	Marine boundary layer	DMS, SO_2, $SO_4^=$	Winters, 1986, 1985
Bermuda	Marine boundary layer and free troposphere	DMS, SO_2, $SO_4^=$	Winters, 1986, 1985
STRATOZ III	North Atlantic	SO_2, $SO_4^=$	Spring, 1984

*North Atlantic east coast.

mechanism existed for a long-term intercomparison or a standardization of sulfur or nitrogen species measurements. A sense of the order of magnitude of possible biases in chemical-measurement methods, including sampling artifacts, might have been gained from the results of continent-based "shootouts" conducted for some nitrogen species.

It was the group's consensus that, on the atmosphere side, *chemical*-sampling analytical uncertainties were minor compared to the uncertainties in dry-deposition fluxes (especially for submicrometer particles) and rainfall amounts and rates. With regard to oceanic sources, the major uncertainties were related to the use of different models for calculating the sea-to-air DMS flux. To facilitate comparisons in the future, the depth of sampling and the temperature should be reported in addition to $[DMS]_{SW}$ and wind speed in all studies that attempt to estimate DMS flux.

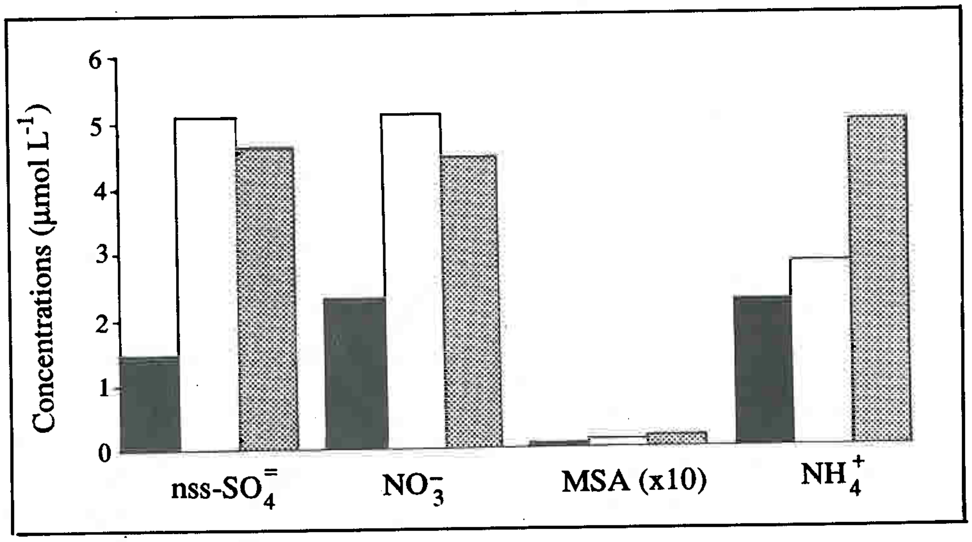

Figure 8.--The 1989 average concentrations of sulfur and nitrogen species in precipitation at three AEROCE sites: Barbados (solid), Bermuda (open), and Ireland (stippled).

A final limitation we identified was the lack of any data for NH_3 gas over the North Atlantic Ocean.

2.4.5 Conclusions

The concentrations of the sulfur and nitrogen species in the North Atlantic Ocean's atmosphere varied substantially both spatially (3-dimensionally) and temporally. Except for the precipitation composition at Bermuda and the surface-aerosol composition at Barbados, the existing data records were insufficient to quantify the temporal variability. The fact that they existed for only two islands was indicative of the lack of spatial coverage. Given the low probability of forming new islands in the North Atlantic Ocean, long-term measurement programs should be initiated on those islands that are available and ship programs should be used to "interpolate" between the long-term data bases for the islands.

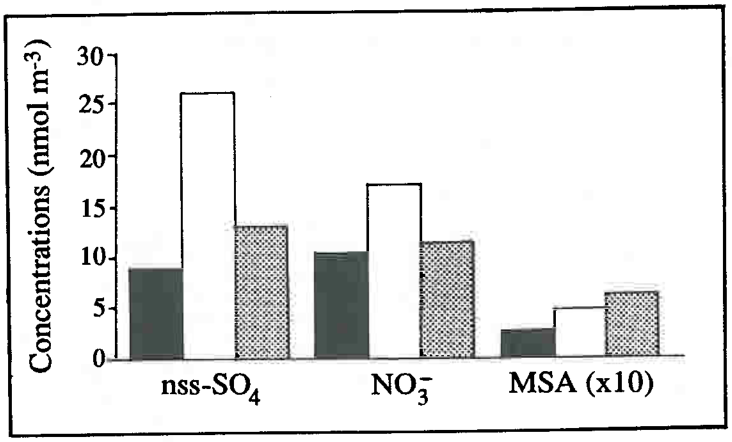

Figure 9.--The 1989 average concentrations of sulfur and nitrogen species in aerosols at three AEROCE sites: Barbados (solid), Bermuda (open), and Ireland (stippled).

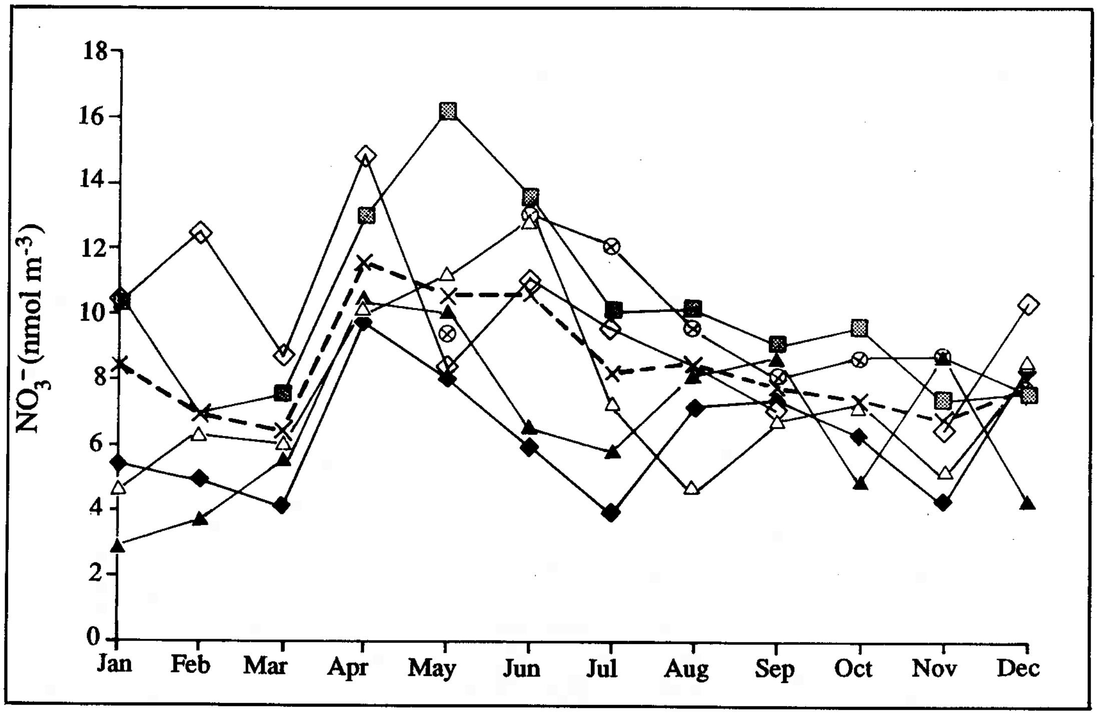

Figure 10.--Temporal trends of aerosol NO_3^- monthly average concentrations for 6 years (Galloway et al., 1992) (1984, X in circle; 1985, open square; 1986, solid diamond; 1987, open diamond; 1988, solid triangle; 1989, stippled square) and average over all years (dashed line, Xs) at Ragged Point, Barbados.

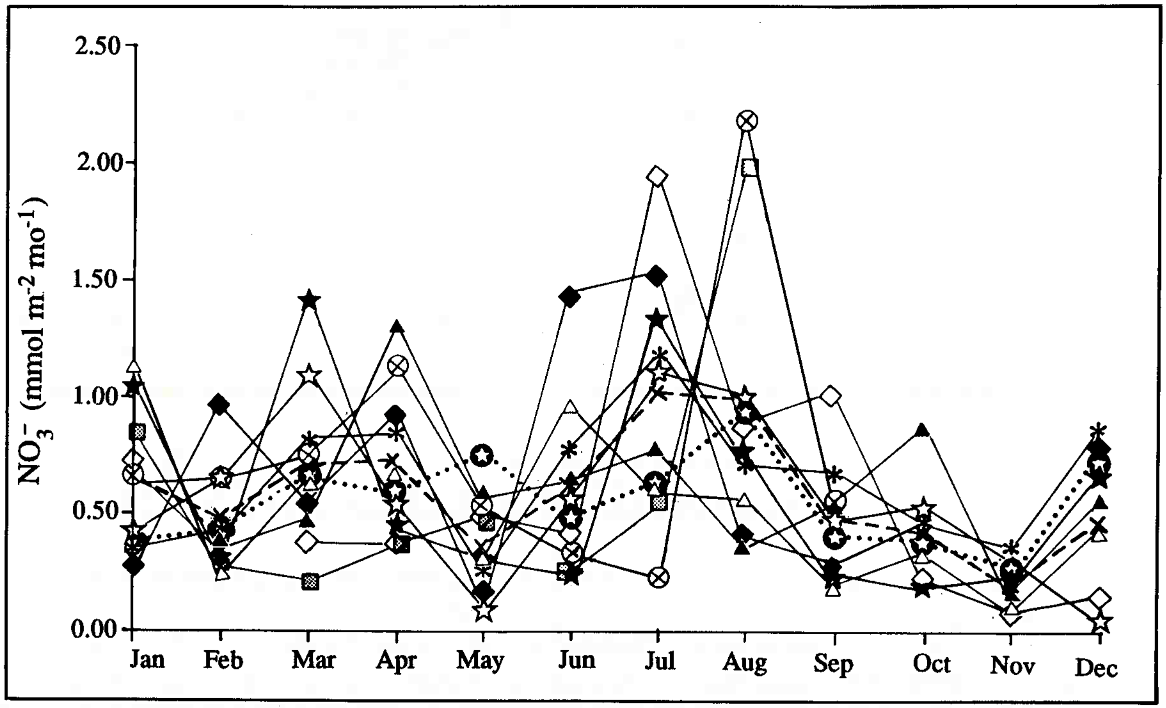

Figure 11.--Temporal trends in NO_3^- monthly wet-deposition (1981, solid star; 1982, open star; 1983, asterisk; 1984, X in circle; 1985, open triangle; 1986, solid square; 1987, open square; 1988, solid triangle; 1989, stippled square) (Galloway et al, 1992); average over all years (dashed line with X); monthly average wet deposition using climatological data on precipitation amounts (dotted line, open star in closed circle) for Harbour Radio Tower, Bermuda.

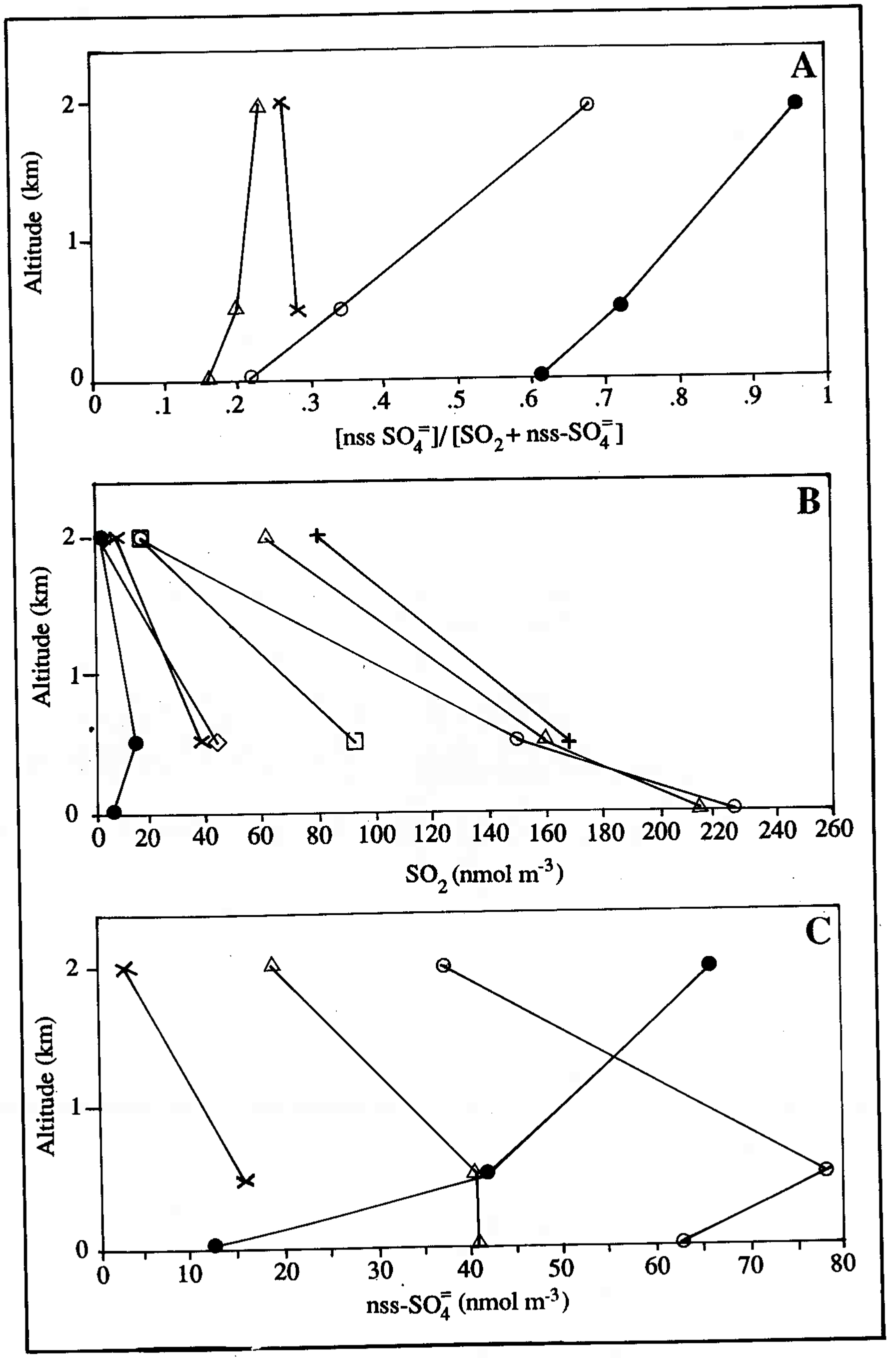

Figure 12.--Altitudinal variabilities of (**A**) [nss-$SO_4^=$]/[nss-$SO_4^=$ + SO_2] ratio, (**B**) SO_2, and (**C**) nss-$SO_4^=$. Concentration data are from Galloway et al. (1990, solid circle), Thornton et al. (1987, open diamond), Whelpdale et al. (1987, X), Luria et al. (1987, open square), Galloway et al. (1984, open circle), Hastie et al. (1988, open triangle), and Luria et al. (1988, plus sign) (Galloway et al., 1990).

Measurement programs on ships and islands would not have helped our understanding of the transport and transformation processes that occur above the marine boundary layer; aircraft programs were needed for such data. By their nature, aircraft programs cannot be continuous. Consequently, aircraft studies must be integrated with long-term island programs.

Full-scale atmospheric-chemistry programs require the measurement of many species at many locations over extended time periods. Such programs are inevitably limited by resources; consequently, priorities must be established and strategies developed. The modeling community can play an important role by participating in the design of field programs.

One strategy would be to focus on regions where there are large concentration or deposition gradients. Large gradients are evidence that atmospheric and deposition chemistries are being strongly controlled by meteorological factors or by chemistry. Field experimenters generally like to see large concentration variations in their measurements because such data are evidence of dynamic processes. Models can tell us where and when we are most likely to encounter such gradients. In addition, are there other key species that need measuring and on what time scales are these measurements needed?

These questions were difficult to answer at the time. It would have required the continued cooperation of modelers and field experimenters to answer them in an efficient and expeditious manner. This workshop was part of the process of facilitating such cooperation.

2.5 Overview of the Trace-Gas Models Applied to the North Atlantic Ocean's Atmosphere

2.5.1 Introduction

Atmospheric scientists face a major challenge in their attempt to understand the causes and effects of the changes in the cycles of major biogeochemicals in the atmosphere over the North Atlantic Ocean. This knowledge is important because the chemical composition of the atmosphere and, particularly, the presence of certain trace species can greatly influence health, weather, climate, and agriculture.

To understand the tropospheric biogeochemical cycles of the North Atlantic Ocean better, it is necessary to know the following:

1. The spatial and temporal distribution of sulfur and nitrogen species;
2. The processes that control the cycles of these species;
3. The role of these species in climate processes;
4. The present and future impact humans have on the cycles.

The answers to these questions must be obtained through combined laboratory, field, and modeling studies. Modeling plays an essential role in unraveling the answers to these questions because it provides a link between the results of field experiments and our understanding of the chemical and physical processes of trace species in the troposphere. Modeling analyses are necessary because field-measurement programs, even with extensive spatial coverage, can only encompass a minute portion of the troposphere for short periods and laboratory studies focus on only a limited number of processes under highly idealized conditions. Verified models can be used to project the state of the troposphere at different times and under different conditions.

Modeling analyses can guide the designs of experiments. For example, models can 1) provide information on the concentrations of species in the troposphere (e.g., OH, H_2O_2, PAN) and, thus, suggest which sensors should be used (or developed); 2) estimate the temporal and spatial distributions of trace species, thereby indicating what sampling strategies should be used; and 3) estimate the variabilities and lifetimes of trace species, thus suggesting optimum sampling frequencies.

The structures of the tropospheric models were inherently process oriented instead of cycle oriented. Models had to reflect that the cycles of trace species are controlled by transport, chemistry, dry-deposition (surface removal), wet-removal, and primary-source processes. Furthermore, the cycles approach focussed on a description of the long-term average mass balance of a species, whereas the dynamic models could show extreme excursions from the mean behavior. Thus, to develop meaningful models, the chemical and physical processes affecting the cycle had to be mathematically characterized.

Comprehensive models that could fully treat all the complexities of the physical and chemical processes affecting sulfur and nitrogen in the North Atlantic Ocean had not yet been developed when we met. Rather, depending on the application, the models had to make tradeoffs between the levels of detail included in the meteorology, the chemistry, the temporal and spatial resolutions, and the times of integration. Eight models were represented at our meeting; their characteristics are summarized in Table 1 (p. 6). These models were either episodic or climatological. The episodic models yielded chemical species distributions for specific "real-world" days (e.g., June 18, 1989). Wind fields were based either on observations or on winds calculated from weather-forecast models. The episodic models could also describe climatology for specific time periods (June, July, August, 1980-1990) if they were run for a sufficiently long time.

In contrast, the climatological models described only the statistical characteristics (i.e., average values and, in many cases, variabilities). Wind fields were based on observations (the MOGUNTIA) (Zimmermann, 1987) or on simulations from general-circulation models (GCM). Some models had temporal resolutions of one day or less (the Lawrence Livermore National Laboratory [LLNL] model, the Geophysical Fluid Dynamics Laboratory [GFDL] model, the Harvard model, the Oslo model) although others (e.g., the MOGUNTIA) had a resolution of one month. It was important to recognize that GCM-based models yielded results that could be compared with mean time periods (e.g., an average June or an average year) but that were not necessarily representative of specific time periods (e.g., June, 1989, or the year 1989).

The tropospheric chemistry models could be further classified according to whether they were coupled directly to meteorological models (on-line) or decoupled from (run outside of) the meteorological models (off-line); whether they used fixed spatial-coordinate reference systems (Eulerian) or coordinate systems that made moving points or parcels their reference points (Lagrangian) and whether they used regional, hemispherical, or global spatial coverages

(Table 1). All models at the workshop were off-line; four models were episodic and four were climatological; two of the episodic models were regional, one was hemispheric, and one was global.

The models also differed according to which species were explicitly treated. Sulfur was treated in the STEM, the Stockholm version of the MOGUNTIA (referred to hereafter as the Stockholm model), the RADM, the Oslo model, the Battelle Global Chemistry model (GCheM), and the LLNL model. Nitrogen was analyzed in the STEM, the Max Planck Institute-Mainz version of the MOGUNTIA, (referred to hereafter as the MPI model), the Harvard model, the RADM, the GFDL model, and the LLNL model.

Because of computational limitations, models that incorporated high resolutions and complex chemistries were usually restricted to relatively small regions. Conversely, global scale models usually had to resort to longer grid sizes and simplified chemistries.

2.5.2 The STEM-II model

The STEM-II was a 3-dimensional Eulerian transport/chemistry/removal model that calculated chemical distributions in the troposphere of some sixty chemical species, including the major SO_x, NO_x, NO_y, H_xO_y, and reactive hydrocarbons species (Carmichael et al., 1986, 1991). This model was designed to analyze chemical transport and removal on regional scales (i.e., spatial scales of thousands of kilometers with an 80-X-80-km grid) under episodic flow conditions (days to weeks). The major features of the STEM-II included emissions from point and area sources; transport by convection and turbulent diffusions; spatially and temporally varying winds, temperatures, water vapors, precipitation, and cloud fields; transformations of chemical species by gas- and liquid-phase chemical reactions; removal at the surface by dry deposition; and removal through detailed cloud- and precipitation-scavenging processes. Applications of the model were focused on acid deposition and oxidant formations in the eastern United States.

2.5.3 The MOGUNTIA

The basic model, the MOGUNTIA, was developed at the Max Plank Institute for Chemistry in Mainz; it covered the whole globe with a horizontal resolution of 10^o longitude by 10^o latitude and had 10 layers in the vertical between 1000 hPa and 100 hPa. Advection was based on climatological monthly mean winds; transport processes occurring on smaller space and time scales were parameterized as eddy diffusion (Zimmermann, 1987, Zimmermann et al., 1989). A diagnostic cloud model provided vertical transports in deep convective clouds; the input parameters were large-scale temperature, humidity, and estimated convective precipitation (Feichter and Crutzen, 1990).

The Mainz version of the MOGUNTIA.

This version, the MPI model, was used to study the tropospheric nitrogen cycle. The chemical mechanism in this model was simple (Crutzen and Gidel, 1983) but it explicitly calculated hydroxyl concentration. Five species were transported and integrated in time: NO_x, HNO_3, O_3, H_2O_2, and CO. Four species had specified temporal and spatial variations: CH_4, H_2O, O_2, and M. Ten species were put in steady-state balance: CH_2O, O^1D, OH, HO_2, CH_3O_2, CH_3O_2H, HCO CH_3O, NO_3^-, and CH_3. We calculated the steady-state species algebraically and placed the algebraic solutions in five predictive equations that were then solved numerically. We also calculated NO and NO_2 from NO_x using photochemical, steady-state approximations.

The Stockholm version of the MOGUNTIA.

This version (the Stockholm model) was used to study the tropospheric sulfur cycle. It used the same basic model transport description as the Mainz version. The parts of the atmospheric sulfur cycle included in the model were 1) the emissions of dimethylsulfide (DMS) and SO_2, 2) the oxidation of DMS by OH to SO_2 and directly to $SO_4^=$, 3) the oxidation of SO_2 to $SO_4^=$, and 4) the wet and dry depositions of SO_2 and $SO_4^=$ (Fig. 13). Three species were carried prognostically in the model: DMS, SO_2, and $SO_4^=$. The main objectives of the modeling were to estimate distributions of various sulfur species in the troposphere on time scales of months or longer, to estimate the relative importance of natural and anthropogenic emission processes, and to test the hypotheses regarding transformation and deposition processes.

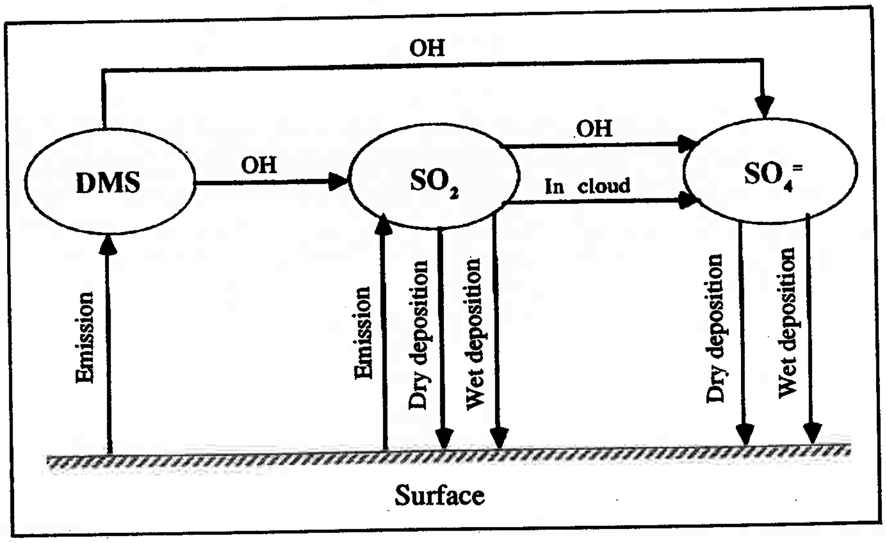

Figure 13.--A schematic description of the atmospheric sulfur cycle implemented in the Stockholm model.

2.5.4 The Harvard model

The Harvard group was developing a 3-dimensional, global chemical-tracer model based on meteorological information from the "fine-resolution" NASA/GISS (Goddard Institute for Space Science) general-circulation model. The chemical-tracer model has a resolution of 4° latitude x 5° longitude with nine layers in the vertical extending from the surface to 10 mb; the time step was 4 hours.

The long-range objective in developing the chemical-tracer model was to describe the global distributions of O_3, CO, NO_y, sulfate, and other trace species in the troposphere. The model in this case would have to account properly for an exchange with the stratosphere, for a range of chemical processes in the troposphere, and for the deposition to the surface. It would have to simulate correctly the spatial redistribution of trace species. This objective was to be approached through a series of intermediate steps. The first studies (Prather et al., 1987; Jacob et al., 1989) focussed on CFCs and ^{85}Kr, two long-lived trace gases with sources in the northern midlatitudes. These studies demonstrate that a chemical-tracer model can adequately simulate the exchange between hemispheres and the transport between midlatitudes and tropics. Further, chemical-tracer model studies of ^{222}Rn and ^{210}Pb (Balkanski et al., 1989) test the abilities of a chemical-tracer model to simulate the regional transport of trace gases and aerosols in various parts of the world (North America, the Indian Ocean, the Pacific Ocean). A first photochemical study using CH_3CCl_3 as a tracer (Spivakovsky et al., 1990) shows that global OH levels in a chemical-tracer model are correctly predicted to within 25%. The Harvard group's efforts were to include global simulations of CO and of the tropospheric sulfur cycle and regional simulations of NO_y and O_3 over North America and the western Atlantic Ocean.

2.5.5 The Regional Acid Deposition model

The RADM, was an extremely complex Eulerian modeling system designed to simulate numerous chemical and physical processes that were important in the distribution of tropospheric trace gases and the resulting dry and wet deposition of these gases. The RADM subdivided the troposphere over the northeastern United States and southeastern Canada into a 35 x 38 horizontal grid (each grid was 80 x 80 km^2) with 6 or 15 vertical levels (from the surface to 100-mb pressure level). The domain size and associated vertical and horizontal resolutions of RADM could be easily changed as could the submodels used to parameterize individual physical and chemical processes.

Time-varying trace-gas concentrations were calculated in each model-grid cell by solving a species-continuity equation. Advection, diffusion, and dry deposition were calculated every 300 or 600 seconds. Changes in trace-gas concentrations from chemical reactions and emissions were computed using smaller time steps. Concentration changes due to cloud processes were computed using a chemically or scavenging-limited time step that was then imposed on the grid-averaged concentrations at intervals or one hour or less.

The transport and diffusion of trace gases and particles were calculated using meteorology from the Mesoscale Model Version 4 operating in a 4-dimensional data-assimilation mode. The vertical turbulent transport of trace species in the absence of clouds was parameterized with an eddy diffusiveness based on atmospheric stability and wind shear. Dry-deposition fluxes were computed for 13 species by multiplying trace-species concentrations in the lowest model level by species-specific deposition velocities that were parameterized in terms of atmospheric stability, land type, season, insolation, and surface wetness. Effects of clouds, including subgrid-scale vertical redistribution, aqueous chemistry, and trace-gas and particle scavenging, were parameterized using a simple 1-dimensional cloud model and a local equilibrium scavenging and aqueous-chemistry submodel. Cloud distributions and characteristics were parameterized in terms of precipitation rates and vertical profiles of temperature and moisture.

The gas-phase chemical-reaction mechanism contained 140 reactions among 60 species including 40 organics. In RADM 2.0, 20 photolysis-rate coefficients were determined from a radiative-transfer model for the clear atmosphere with average turbidity and a seasonally adjusted stratospheric ozone column. Clear-air photolysis rates were functions of heights, latitudes, and zenith angles. The corrections for the presence of clouds differed for above-cloud, in-cloud, and below-cloud regions and depended on average condensed-water contents, thicknesses, and fractional areas of cloud coverage.

Emission data bases derived from 1980 and 1985 inventories provided hourly emissions of thirty species in the RADM 2.0 domain. Area sources were emitted into the lowest model layer and point sources were emitted at an effective height, including plume rise, for each point source. Diurnally varying, average, seasonal emission rates that differed for weekdays or weekends were specified from the emission inventories.

2.5.6 The Oslo model

This model provided representative estimates of concentrations and depositions of sulfur. The model was episodic, used a temporal resolution of 6 hours, and could be integrated over different periods (Iversen, 1989). The model contained two components, SO_2 and particulate $SO_4^=$, with a linear reaction rate depending on latitude and season in accordance with the general photochemical activity. This was an Eulerian model with the scheme of Smolarkiewiez (1983) for horizontal and vertical advection. The dry deposition took into account aerodynamic resistance in the surface boundary layer. The wet scavenging was formulated through scavenging ratios and was separated between in-cloud and subcloud scavenging efficiency. Vertical eddy diffusion was parameterized as a function of static stability and wind shear. Emissions were instantly mixed vertically to a locally defined mixing-layer height. On the subgrid scale, 15% of the emissions were deposited inside the emission grid square, 5% of which was in the form of secondary particulate sulfate.

The governing equations were written with dry potential temperatures as the vertical coordinates. This coordinate choice diminished the numerical errors in the horizontal and vertical advection terms because 1) the vertical winds were smaller than when using quasi-horizontal surfaces; 2) the surfaces of the constant potential temperatures were tightly packed in layers with large gradients (stratosphere, fronts, stable atmospheric boundary layer); and 3) the horizontal gradients were much weaker. The model had been applied to four specific months with input from National Meteorological Center data obtained through the National Center for Atmospheric Research (NCAR). The months were October, 1982; January, March, and July, 1983. A meteorological preprocessor calculated all additional parameters needed in the dispersion calculations and included a complete physical package for precipitation and diabatic heating. The concentration fields for sulfate calculated by the Stockholm, LLNL, and Oslo models are presented in Figure 14.

2.5.7 The Battelle Global Chemistry model

The GCheM was a 3-dimensional, time-variant kinematic model of atmospheric pollutant behavior. It was based on an Eulerian reference frame, applying a latitude-longitude-sigma coordinate system. The computation mesh had a flexible resolution and domain; thus relatively small geographical areas could be

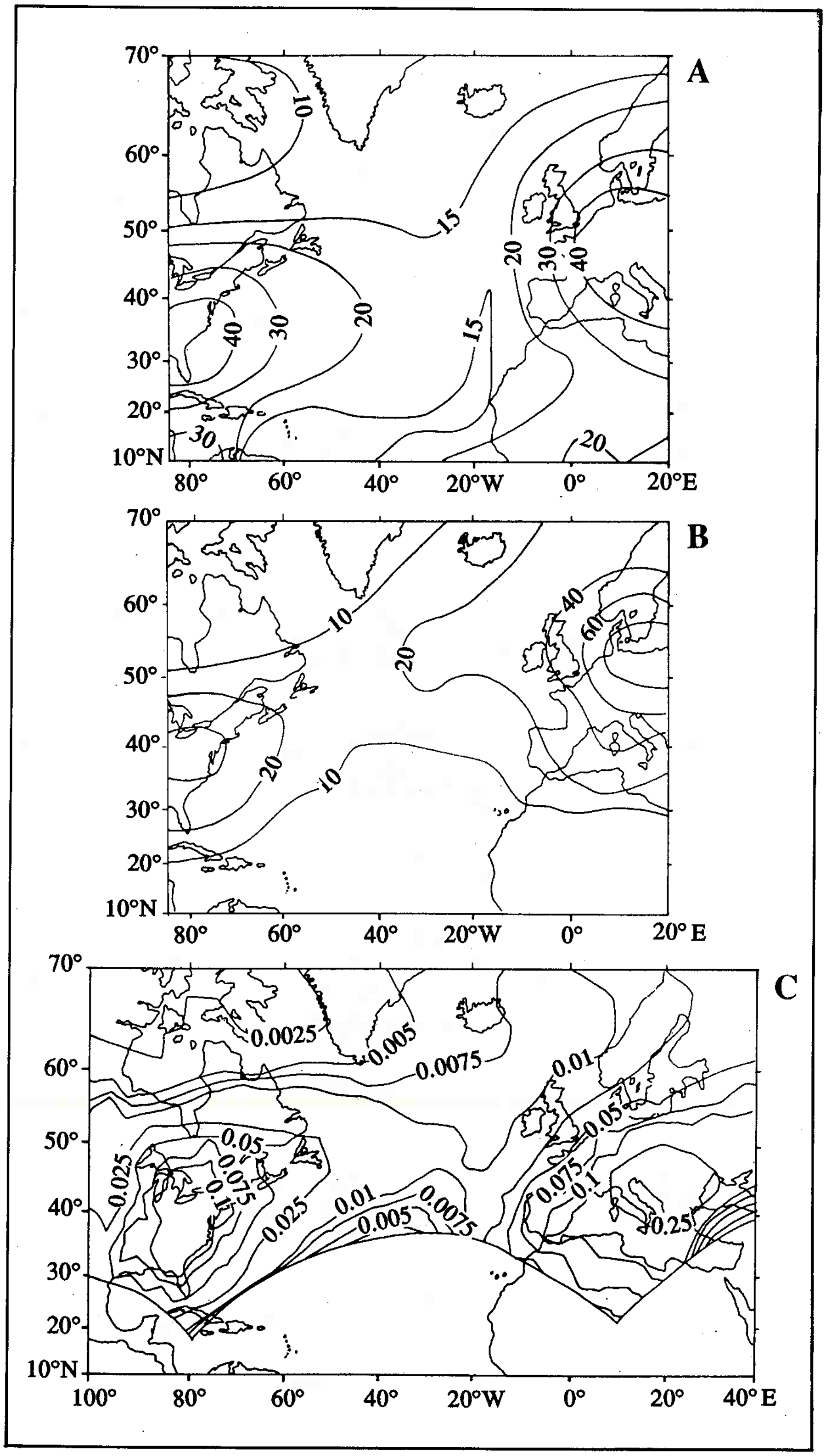

Figure 14.--Sulfate concentration predictions from (**A**) Stockholm model at 250 m (nmol m^{-3}), (**B**) LLNL model at surface (nmol m^{-3}), and (**C**) Oslo model at 40 m (μmol m^{-3}) for January when all sources were considered (Galloway et al., 1992).

selected for detailed computations while still enabling total global simulations when desired.

The GCheM code was modular, thus allowing a large degree of flexibility in the simulation of reaction chemistry and wet- and dry-removal processes. The code's structure allowed for direct computation of pollutant behavior in several media besides air (e.g., rain, cloud water, snow, etc.); thus aqueous-phase conversion and wet removal could be treated conveniently and naturally. GCheM applied a finite-element technique to integrate fluid-flow components of the governing equations. Chemical and physical transformation steps were being integrated using an exponentially assisted procedure.

2.5.8 The Geophysical Fluid Dynamics Laboratory model

The GFDL model was a global transport model with 11 vertical levels (31.4 km, 22.3 km, 18.8 km, 15.5 km, 12.0 km, 8.7 km, 5.5 km, 3.1 km, 1.5 km, 0.5 km, and 0.08 km), a horizontal grid size of approximately 265 km, and a time step of approximately 26 minutes. For transport, the model used the 6-hr time-averaged winds and the self-consistent precipitation provided by a parent general-circulation model with no diurnal cycle; emissions of gaseous and particulate reactive-nitrogen compounds were transported as a single species, NO_y. The emissions that were not deposited in a particular source region were available for long-range transport in the model. The fraction of NO_y available for transport was specified by basing the model's precipitation-removal and dry-deposition parameterizations on the measured yearly wet deposition over North America and the measured partitioning of individual nitrogen species at several locations in the United States. Although these parameterizations were based on observations in North America, the simulated deposition over Europe and remote regions of the Northern Hemisphere agreed well with the observed values. Simulations had already been completed for global emissions from fossil-fuel combustion (Levy and Moxim, 1987, 1989a, 1989b) and for stratospheric injection (Kasibhatla et al., 1991).

2.5.9 The Lawrence Livermore National Laboratory model

The LLNL model (also called GRANTOUR, c.f. Walton et al., 1988) was a Lagrangian parcel model that could be run either off-line using the wind and precipitation fields from a general circulation model, or interactively, in a mode that allowed alterations of wind and precipitation fields consistent with the currently calculated species or aerosol concentrations. The model had been used to study effects of smoke from a nuclear war on climate (Ghan et al., 1988), the effects of an asteroid impact on climate (Covey et al., 1990), the cycle of reactive nitrogen in the troposphere (Penner et al., 1991b), the sulfur cycle in the troposphere (Erickson et al., 1991), the effects of smoke from biomass burning on cloud reflectivity and climate (Penner et al., 1991a), ^{222}Rn and ^{210}Pb distributions (Dignon et al., 1989), and O_3 photochemistry in the troposphere (Atherton et al., 1990). The model was typically run with 50,000 constant-mass air parcels the dimensions of which averaged 100 mb x 330 km x 330 km. If the centroid of a parcel came within 50 mb of the surface, its species concentrations were subject to a dry-deposition rate that was proportional to a species-dependent deposition velocity. Also, each species was removed proportionally to the rate of precipitation at a given grid location times a species-dependent and precipitation type-dependent scavenging coefficient. The model used a simplified chemistry; OH and O_3 fields as well as photolysis and reaction-rate coefficients were specified during runs for a perpetual January or a perpetual July. We ran the reactive nitrogen simulations reported here using 12-hour averaged wind and precipitation fields from the NCAR community climate model (CCM). The CCM had a 4.5 x 7.5-degree average resolution with 9 vertical layers. The model's sources of reactive nitrogen included fossil-fuel burning, soil microbial activity, biomass burning, lightning, and production in the stratosphere from the oxidation of N_2O. The treatment of chemistry incorporated the major reactions that cycle NO_x ($NO + NO_2$) to HNO_3. The ratio of NO to NO_2 was determined using the photostationary state relation. For the sulfur simulations reported below, we used CCM-1 12-hour averaged wind and precipitation fields. The CCM-1 had a horizontal resolution similar to that represented in the CCM but had 12 vertical layers. For sulfur, we included sources from fossil-fuel burning and oceanic dimethylsulfide emissions. The representation of chemistry included the reaction of DMS with OH to form SO_2. SO_2 was converted to $SO_4^=$ with a six-day e-folding lifetime.

3. THE CASE STUDIES

3.1 The Sulfur Case Study

For the sulfur case study, we compared predictions from three models--the Oslo model (Iversen, 1989), the Stockholm model (Langner and Rodhe, 1990), and the LLNL model (Erickson et al., 1991; Walton et al., 1988)--to data collected by the AEROCE, Global Precipitation Chemistry Project, and WATOX programs. In particular, we compared values for two single months: January and July. First, we examined the predictions for the deposition of SO_2, $SO_4^=$, and S as given by the three models. Second, we compared the model calculations to the actual measurements of $SO_4^=$ concentrations in aerosol and wet deposition from Mace Head (Ireland), Bermuda, and Barbados and in aerosol only from Tenerife (Spain). These comparisons illustrated how these models simulated the sulfur cycle and why there were differences in the results from these models. They also provided guides for new or improved measurement and modeling studies that would further our understanding of the sulfur cycle.

3.1.1 The relevant model characteristics

The three models that we examined treated the physical and chemical processes differently. Two models, the Stockholm and LLNL, were climatological; their meteorologies represented statistically typical Januarys or Julys. Both had global domains. The third model, the Oslo model, used actual meteorological fields analyzed by the National Meteorological Center to simulate January and July, 1983. This model's domain extended over most of the Northern Hemisphere. Thus, although the Stockholm and LLNL models' results were best compared only to "average" or "typical" measurements, the Oslo model could be compared to the specific data collected during the simulated time.

The sulfur-emission inventories in the models differed not only in their total amounts but also in their distributions. The Oslo model's emissions included 60 Tg S yr^{-1} for the Northern Hemisphere from anthropogenic sources; the global DMS source was 39 Tg S yr^{-1}. The Stockholm model contained global sulfur sources of 80 Tg S yr^{-1}, 40 Tg S yr^{-1}, 12 Tg S yr^{-1}, 7 Tg S yr^{-1}, and

5 Tg S yr^{-1} for fossil-fuel combustion, DMS emissions, volcanoes, biomass burning, and biogenic land sources, respectively. The LLNL model had a global fossil-fuel source of 63 Tg S yr^{-1} and a natural DMS source of 15 Tg S yr^{-1}.

Sulfur emissions and the subsequent chemical transformations also differed between models. The Oslo model assumed that DMS was emitted in the form of SO_2 although both the Stockholm and LLNL models assumed that DMS was emitted directly and then reacted with the hydroxyl radical OH. The Stockholm model prescribed 3-dimensional monthly mean OH fields calculated using the NOx-HC chemistry in the MPI model. In the LLNL model, monthly mean OH fields were prescribed based on results from the LLNL 2-dimensional model that had been checked against the methyl-chloroform data.

Once the sulfur was emitted, the Oslo model assumed that the SO_2 was transformed to $SO_4^=$ at a linear rate that was a function of latitude and season in accordance with the atmosphere's photochemical activity; the rate ranged from 6×10^{-7} s^{-1} to 4×10^{-6} s^{-1}. The LLNL model directly converted SO_2 to $SO_4^=$ via a process that had an e-folding time of six days. The Stockholm model converted SO_2 to $SO_4^=$ through two different processes. In the first, OH reacted directly with SO_2; thus, as concentrations of OH increased from winter to summer, so should the amounts of SO_2 converted to $SO_4^=$ in this process. In the Stockholm model, SO_2 was also incorporated into clouds and then transformed to $SO_4^=$. This process, a function of height and latitude, was most important in the lower troposphere; it had a minimum e-folding time of four days in the tropics and midlatitudes.

The treatment of wet and dry deposition affected the results of our case study. The three models used similar dry-deposition velocities: 0.8 cm s^{-1}, 0.6 cm s^{-1}, and 0.5 cm s^{-1} for SO_2 and 0.1 cm s^{-1}, 0.2 cm s^{-1}, and 0.1 cm s^{-1} for $SO_4^=$ in the Oslo, Stockholm, and LLNL models, respectively. (In the LLNL model, the specified deposition velocities were multiplied by 1/2 to account for a stable boundary layer at night.) All three models parameterized wet deposition using scavenging ratios. The Oslo model contained both "in cloud" and "sub-cloud" scavenging processes, each of which used a 3-dimensional parameterization. The parameterization was based on empirically determined scavenging ratios and was primarily dependent on the temporal and spatial distributions of precipitation. In the Stockholm model, wet deposition was also calculated using empirically determined scavenging ratios together with zonally averaged precipitation fields. Scavenging of SO_2 and $SO_4^=$ occurred in the LLNL model at a vertical level, j, at a rate, r,

$$r = S_i \times P_j \,, \qquad (1)$$

where P_j was the precipitation rate in cm h^{-1} and S_i, the species scavenging coefficient.

3.1.2 A comparison between the three models' results

We examined the models' results for January and July. Predicted distributions of particulate-sulfate concentrations in surface level air are shown in Figure 14 (p. 37). (Please note that the surface level is different for each model and refers to 250 m for the Stockholm model, the actual surface for the LLNL model, and 40 m for the Oslo model.) Figures 14A and B represent the climatological distributions of particulate sulfate for typical January weather according to the Stockholm and LLNL models; Figure 14C depicts January, 1983, as calculated by Oslo model.

The three models predicted quite similar sulfate-concentration patterns. Maximum concentrations occurred over continental areas with a low concentration band over the mid-Atlantic Ocean. Maximum concentrations were larger over Europe than over North America because of larger fossil-fuel sulfur sources. The Oslo model predicted higher maximum concentrations over Europe and North America than did the Stockholm and LLNL models. Over central Europe, the positions of maximum air concentration corresponded to the maximum emission areas for the Stockholm and Oslo models but they were displaced towards the north for the LLNL model. All three models also predicted a trough of roughly 10-20 nmol m^{-3} over the mid-Atlantic Ocean.

The climatological models (the Stockholm and LLNL models) showed smoother gradients than did the Oslo model, which used meteorology for a specific month. So, for example, the Oslo model showed a SW/NE tilt for the North American contours that reflected the particular weather situation of January, 1983.

We compared the model calculations for surface air concentrations and wet depositions for three selected areas: over North America, over the mid-Atlantic Ocean (50^{o}N, 40^{o}W), and over Europe (Table 6). The selected continental points represented the regions of maximum predicted concentration values. The point over the mid-Atlantic was over the trough region where the influence of biogenic oceanic sources could have been more evident.

The Oslo and Stockholm models predicted similar SO_2 concentrations. (The RADM and STEM-II also predicted similar maximum SO_2 concentrations over North America: roughly 250 nmol S m^{-3}.) The LLNL model's predictions for SO_2 were lower than those from the Oslo or Stockholm models. This might have been

Table 6.--Comparisons of SO_2 and $SO_4^=$ model results

	Air Concentrations (nmol S m^{-3})						Wet Deposition (μmol S m^{-2})		
	SO_2			$SO_4^=$			$SO_4^=$		
	Stockholm	LLNL	Oslo	Stockholm	LLNL	Oslo	Stockholm	LLNL	Oslo
				North American Maximum					
January	200-400	135	250-500	40-50	>40	100	1200	3000	1000-2500
July	200-300	>125	250	60	>40	100	1800	3200	2500
				Mid-Atlantic Trough					
January	15	2.4	10	15	15	15	700	200	400
July	15	4.0	15	20	10	15	700	100	300
				European Maximum					
January	750	260	500-750	>60	> 80	250	1800	2970	5000
July	400	320	500	150	>120	250	2700	3200	2800-5000

Source: Galloway et al., 1992

partly because the LLNL model's predictions were calculated for the surface level but the Stockholm and Oslo models' results were calculated for higher levels (250 m and 40 m, respectively).

The three models showed a better agreement for $SO_4^=$ in air. The concentrations over the mid-Atlantic Ocean agreed particularly well. They were at least one order of magnitude smaller than the maximum continental concentrations. For the particular point selected in the table (50°N, 40°W), the relative contributions of anthropogenic sources in relation to those of biogenic sources were estimated to be 50%.

The wet-deposition values depended strongly on precipitation fields. The Stockholm and LLNL models considered climatological precipitation although the Oslo model calculated its own precipitation from actual meteorological data. Such different treatments of precipitation, a field characterized by its spatial and temporal variabilities, could have accounted for part of the differences in the wet deposition shown by each model (for example, the Oslo model predicted higher deposition values over Europe than the Stockholm or LLNL model did).

In general, the predicted distributions of sulfur concentrations and deposition over the North Atlantic Ocean agreed fairly well between the models except for SO_2, which had lower values in the results from the LLNL model (Table 6). Additionally, the predictions from the Oslo model, which used actual meteorology, were within the range defined by the climatological models.

3.1.3 Discussion of the measurements

An inherent problem that limits the usefulness of a model-measurement comparison is the difficulty of relating a point measurement to the result of a model presented as an areal average estimate. Implicit in the gridded model output is spatial averaging, which is not directly comparable to a single measured value. In general, the fewer the measurements, the less representative they are. These observations were temporally, and presumably spatially, highly variable. Measurements from a longer record of observations would have provided more information about their context, e.g., whether they were average, extreme, etc.

The reactive nitrogen case study was the worst equipped to deal with this issue since the measurement data were only for a particular location and time. No spatial or temporal averaging was possible.

Precipitation measurements from the official weather station on each island provided our network observations of precipitation with climatological contexts. We used these climatological data to extrapolate from a limited number of measurements in the comparison of the modeled-versus-measured nss-$SO_4^=$ deposition discussed below.

We estimated the accumulated monthly nss-$SO_4^=$ deposition used in the comparison with the accumulated monthly deposition of the climatological (the LLNL and Stockholm) models by multiplying the monthly volume-weighted average concentration of nss-sulfate by the climatological monthly precipitation. The time periods covered 4/20/80-8/14/89 for Harbour Radio Tower, Bermuda; 11/16/88-7/12/90 for Mace Head, Ireland; and 12/18/88-6/20/90 for Ragged Point, Barbados. The accumulated monthly deposition values based on the measurements and those from each model for the grid cell containing each site are discussed in the next section.

There was also a question about how representative the aerosol concentrations were when compared with the model outputs. The actual observations might have underestimated the reality. The aerosol samplers were sector controlled to minimize the influence of local sources. At each AEROCE site, when winds at tower height were blowing across an island, no aerosol samples were taken. This reduced sample collection time to less than 100%. At Barbados, winds were out of sector less than 10% of the time on average. However, at Mace Head and Bermuda, out-of-sector winds were more frequent and the sector-controlled measurements were biased. Since tower-level winds at Mace Head were not sampled when they came from the east (crossing Ireland), an important fraction of aerosol-laden air masses from Europe could have been missed. These exclusions of winds resulted in an aerosol signature that was more representative of aerosol concentrations over the North Atlantic Ocean. Since the models simulated all flow conditions, we had to consider the nss-$SO_4^=$ aerosol observations at Mace Head reported in Table 7 as biased concentrations that underestimated the real conditions for that site. Because of this problem, the AEROCE sampling protocol was changed; future measurements were to be collected for both in-sector and out-of-sector wind flow. Similarly, the Bermuda measurements might have been biased. However, since the two measurement sites were at opposite ends of the island (Harbour Radio Tower and Tudor Hill), measurements could be corrected for the sector exclusion when comparing with models.

3.1.4 A comparison between climatological model results and measurements

(nss-$SO_4^=$) in aerosol.

Table 7 shows model results and measurements of surface nss-$SO_4^=$ in air for the stations included in this case study. When the months included in the measured averages in Table 7 were considered, only Barbados had a record long enough to compare with the model results. Predictions from the Stockholm model were quite accurate in January and within a factor of 2 in July; however, those from the LLNL model were a factor of 3 to 4 lower. A portion of the differences between the model estimates for Barbados could have been related to the differences in the magnitude of the natural emissions, which were almost a factor of 3 higher in the Stockholm model. About half of the nss $SO_4^=$ was derived from marine DMS (Savoie et al., 1989). Also, the higher concentrations predicted by the Stockholm model for Barbados in the summer were consistent with increased reaction rates for SO_2 + OH because of the increased OH in the summer. For the other stations with shorter records, the models predicted concentration values that were generally within a factor of 2 of the measured values, but this apparent agreement might have been fortuitous since all these stations had records of less than two years.

Wet deposition of nss-$SO_4^=$.

Figures 15-17 show the results from the Stockholm and LLNL models versus the measurements of wet deposition of nss-$SO_4^=$ for Harbour Radio Tower, Bermuda; Mace Head, Ireland; and Ragged Point, Barbados. For the Bermuda station, both models predicted values that were within a factor of 2 of the mean

Table 7.--Climatological model results versus measurements of aerosol nss-$SO_4^=$ concentrations (nmol m^{-3})

	Models		Measurements		
	Stockholm	LLNL	Mean ± S.D.	Range	Number of months
			Mace Head, Ireland		
January	25	26	40	---	1 (1989)
July	60	19	42	---	1 (1989)
			Harbour Radio Tower, Bermuda		
January	34	18	23	---	1 (1989)
July	34	11	31	19-44	2 (1988, 1989)
			Barbados		
January	15	3.5	17 ± 5	---	6 (1984-1989)
July	15	5.4	24 ± 12	---	6 (1984-1989)
			Tenerife		
January	15	5.4	9	3-15	2 (1988, 1989)
July	20	18.4	19	18-20	2 (1988, 1989)

Source: Galloway et al., 1992.

measured values although the Stockholm model predicted higher values than the LLNL model. In Figure 15, one can see that the variability in the wet deposition produced in the Stockholm model was clearly weaker than that measured at Bermuda. This may have been partially because zonally averaged precipitation fields were used to calculate wet deposition. The comparisons with other stations (Figs. 16 and 17) were very tentative because of short sampling periods. The observations covered less than two years, therefore they may have differed significantly from a long-term mean. So, agreements between the models and the observations that did not seem to be completely favorable at first glance may have been caused by year-to-year variations in the data. As we discuss in a later section, the wet deposition of NO_3^- on Bermuda varied from year to year, usually by at least a factor of 2 and by more than a factor of 4 for August. Figure 16 shows that the LLNL model was high in January and low in July relative to the measurements; the Stockholm model was within a factor of 2 for most months but was similarly high in January. If there had been substantial year-to-year variations in the data, the agreement between the models and the data could have been improved further (especially for months with large discrepancies, such as January). Likewise, if the data in Figure 17 had shown similar year-to-year variations, the agreement between the results from the Stockholm model and the observations would have been much stronger (the LLNL had already done fairly well for both January and July).

(SO_2).

As shown in Table 6 (p. 41), the LLNL model predicted surface SO_2 concentrations in source regions that were about a factor of 2 to 4 lower than the Stockholm model. Over the North Atlantic Ocean, the limited measurements of SO_2 available were not long term. A comparison with the measured SO_2 concentrations reported in the literature (Warneck, 1988) showed a range of

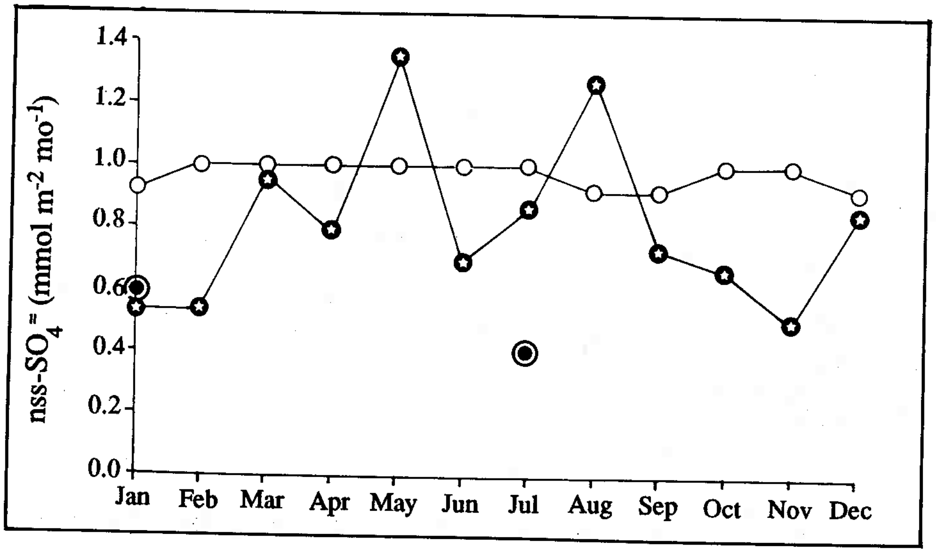

Figure 15.--Monthly nss-$SO_4^=$ wet deposition from the Stockholm model (open circle), the LLNL model (dot in open circle), and Harbour Radio Tower, Bermuda, records based on collected storms from 1981-1989 (open star in solid circle) (Galloway et al., 1992).

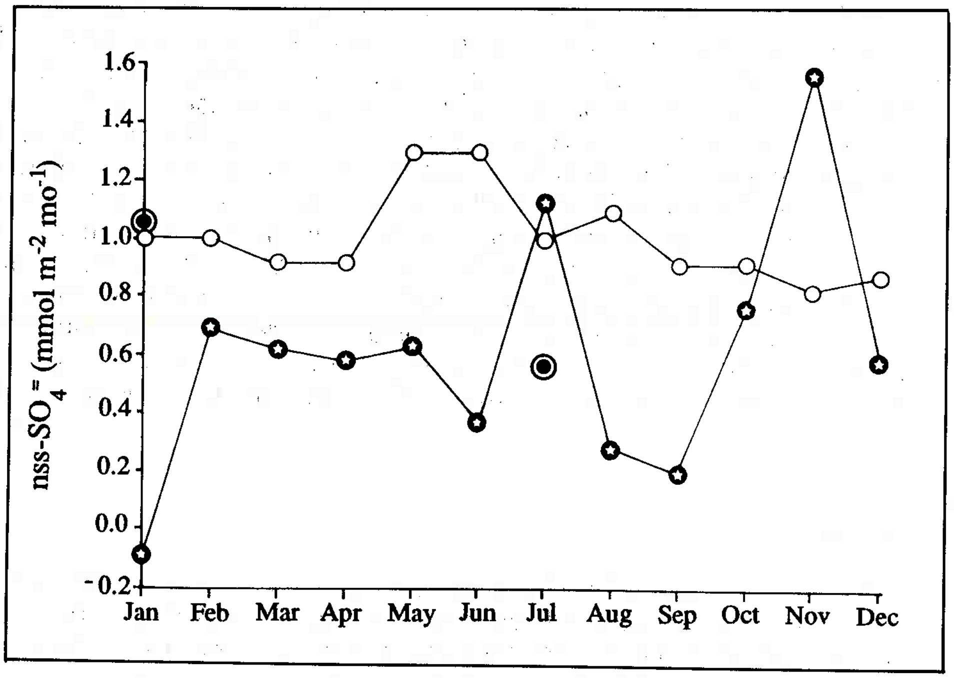

Figure 16.--Monthly nss-SO_4 wet deposition from the Stockholm model (open circle), the LLNL model (dot in open circle), and Mace Head, Ireland, records for November 16, 1988, to July 12, 1990 (open star in solid circle) (Galloway et al., 1992).

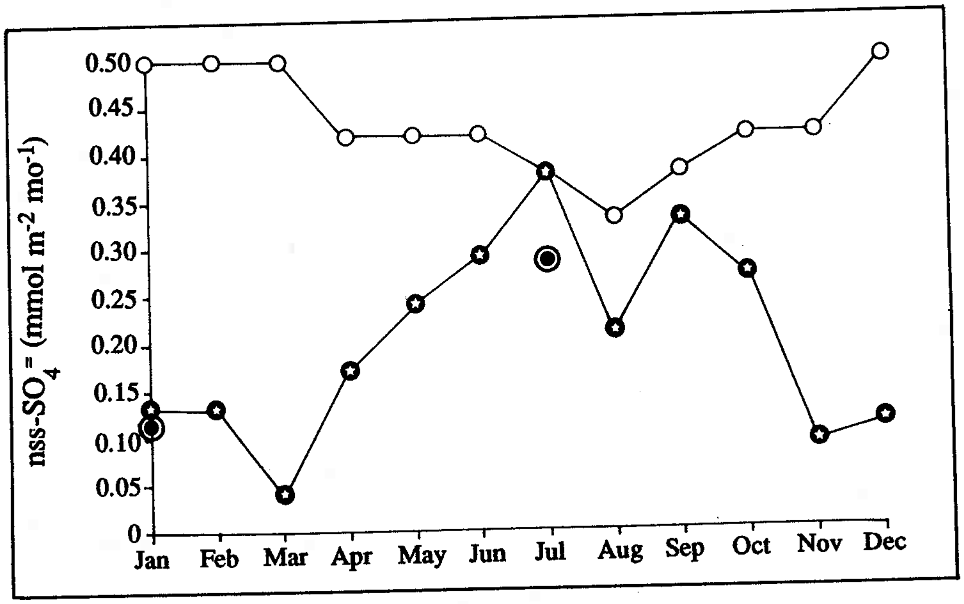

Figure 17.--Monthly nss-SO_4 wet deposition from the Stockholm model (open circle), the LLNL model (open circle with dot), and Ragged Point, Barbados, records for December 18, 1988, to June 20, 1990 (open star in solid circle) (Galloway et al., 1992).

1-4 nmol m^{-3} for limited sampling. During a cruise of the NOAA R/V Mt. Mitchell, an average value of 2 nmol m^{-3} SO_2 was measured in the southeastern part of the North Atlantic Ocean (Pszenny et al., 1990b). The LLNL model's results for this region were close to the limited measured values although the Stockholm model's results were a factor of 5 or more too high. Results from the RADM and STEM II models were similar to the Stockholm model's for the coast along the northeastern United States but not for along the mid-Atlantic region. These differences between the models might have been related to how efficiently SO_2 was dry deposited and how quickly SO_2 was converted to $SO_4^=$. The LLNL model appeared to have a more efficient deposition process than did the Stockholm model. Additionally, the LLNL model's concentrations were actually surface-level quantities and the Stockholm model's concentrations were calculated for 250 m. Vertical profiles in the LLNL model showed an increase in height for SO_2 from 1000 mb to 900 mb. These differences, together with the differences in source strengths, might explain the discrepancies between the two models.

3.1.6 Future work

This sulfur case study clearly illustrated how the measurement and modeling communities could help each other improve their understanding of the global sulfur cycle. Below we detail the recommendations from the modelers to the measurers, and vice-versa, as well as some resources modelers could provide one another.

Temporally and spatially representative measurements were critically needed to compare with results from the climatological models. As this study showed, it was quite difficult to compare a monthly output from a climatological model to a single month of measurements. It would have been a much more valid comparison if we had been able to use data for a specific month collected over five to ten years. This would have greatly reduced much of the influence that the statistical outliers and extreme events had on the data. In contrast, the episodic models required measurements that directly coincided with the simulation periods. Long-term measurements would have helped to assess the how representative the simulation period was.

A good spatially resolved network of measurements was also necessary. For this case study, only one site had a long record of $SO_4^=$ aerosol concentrations (Barbados) or deposition (Bermuda). At least three to five more stations with long-term sampling records would have greatly assisted our model interpretations. When the models predicted 3-dimensional fields, 3-dimensional data fields should have been used for the comparisons; for this, we would have needed data on vertical profiles as well as surface measurements.

Additional information to characterize the situation in which the measurements had been taken would also have helped us determine how representative the measurements were. Future measurement data should include information about averages, extremes, and pertinent meteorological information (such as the length of an event, timing of a storm, etc.). If measurements are only taken during specific time periods (for example, only when onshore winds are blowing), the expected bias should be indicated.

Our study also showed that, in the future, modelers can provide useful information to one another when the data are not available. For example, the SO_2 concentration fields predicted by the Stockholm and Oslo models differed significantly from those predicted by the LLNL model. Clearly, SO_2 should have been spatially and temporally sampled over both the ocean and source regions. However, with only limited SO_2 measurements, the analyses of concentrations predicted by the episodic Oslo model combined with those of the regional models (STEM and RADM) provided useful information about probable SO_2 fields. These bridges between regional and global models and between climatological and episodic models should be increasingly valuable. Future discussions about emission inventories, treatments of chemical and physical processes, definitions of such terms as surface level, and the resulting predictions will greatly aid modelers in interpreting their results.

Another category of recommendations we discussed were those concerning the assistance that modelers could provide measurers. An average of model runs (i.e., the average of ten different runs for a January model scenario) would have provided an excellent comparison to measurements that had also been averaged for the same month from different years (e.g., ten different Januaries). Modelers could also provide guidance on where to locate sampling stations. For example, in the sulfur study, all the models predicted a "trough" in the mid-Atlantic Ocean where the concentrations were minimal. Because the conditions there were far removed from any anthropogenic sources, the area could be a valuable location for remote sampling.

Finally, in the future, measurers and modelers need to inform each other about the temporal and spatial resolutions and the how representative their measurements or model outputs are. Besides averages, useful comparisons can be made as distributions of quantities, such as fluxes and precipitation, by both modelers and measurers.

3.2 The Current Model Treatment of Marine DMS

The ocean, through the sea-to-air flux of DMS, is a significant source of sulfur to the atmosphere of the North Atlantic Ocean. This is particularly important in the remote regions of the North Atlantic where the influence of SO_2 emissions from the burning of fossil fuels is minimal.

Many models had been constructed to facilitate our understanding of how sulfur cycles in the atmosphere of the North Atlantic Ocean. These models needed to parameterize the fluxes of marine biogenic sulfur as DMS at their lower boundaries as well as the anthropogenic sources of sulfur from continental regions. Our group, consisting of people who measured sulfur gases, examined how current atmospheric models were treating marine DMS emissions. We also made several recommendations about how we believed DMS emissions should be modeled.

3.2.1 The Oslo model

The Oslo group used two approaches to incorporate marine DMS into their model: both methods were based on a global flux of 39 Tg S yr^{-1} (Andreae and Raemdonck, 1983). Contributions of the North Atlantic to this flux were proportioned on a global-ocean-area basis. This area was corrected for ice coverage, but there was no parameterization for seasonal variations in DMS emissions. Method 1 distributed DMS emissions homogeneously over the polar stereographic grid (8 ktonnes S grid $square^{-1}$ yr^{-1}). Method 2 attempted to differentiate between bioproductivity regions (i.e., open ocean, zero flux, and coast), the Gulf Stream, and the Sargasso Sea (12 ktonnes S grid $square^{-1}$ yr^{-1}).

3.2.2 The LLNL model

The LLNL model parameterized fluxes based on a relationship between daily solar radiation reaching the ocean surface and the surface fluxes of DMS reported by Bates et al. (1987). This relationship was determined from measured DMS concentrations from which a flux was calculated as determined below (Equation 2) and the daily solar radiation taken from the Smithsonian Meteorological Tables. The LLNL model used this relationship and the sunlight at each grid point as determined by the CCM-1 to prescribe the DMS flux at each grid point. The flux parameterization is described in detail by Erickson et al. (1990).

3.2.3 The RADM

The current RADM did not incorporate marine DMS emissions into its lower layer.

3.2.4 The Stockholm model

In this model, the global flux of DMS was taken to be 40 Tg S yr^{-1} (Andreae, 1986). The Stockholm group assumed a latitudinal dependence of DMS emissions according to the data of Bates et al. (1987) and differentiated between winter and summer seasons.

3.2.5 The air-sea transfer of gases

The flux of gases across an air-sea interface driven by the supersaturation of a species in one phase was given by:

$$F = V_p(C_g/H - C_w) \ , \tag{2}$$

where V_p was the piston or exchange velocity; C_g, the concentration in air; H, Henry's Law constant of gas in seawater; and C_w, the concentration in water.

In the special case of DMS, $C_g/H << C_w$ so that

$$F = - V_p \times C_w . \tag{3}$$

The piston velocity, V_p, was generally parameterized as a function of the diffusivity, D, of the individual gas; wind speed, μ; and seawater temperature, T. The diffusivity of DMS is estimated by Bates et al. (1987) and Andreae (1986). We used the dependence of V_p on wind speed from Liss and Merlivat (1986) (Fig. 18) based on various field data and experiments as the current best estimate. (Recent SF6 tracer experiments lent further support to this relationship [P. Liss; Environmental Sciences School, University of East Anglia, Norwich NR4 7TJ, England; personal communication, 1990]).

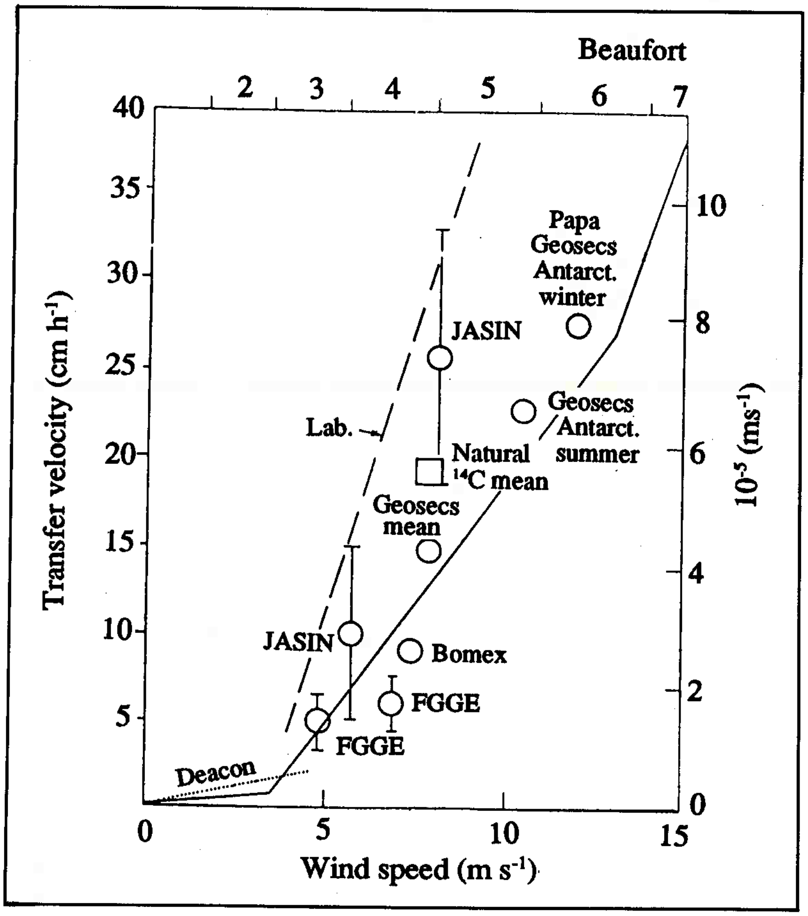

Figure 18.--Oceanic measurements of liquid-phase gas transfer velocity (v_p) plotted as a function of wind speed measured at a height of 10 m and the corresponding Beaufort scale number. The dotted line represents predictions based on the Deacon smooth surface model; dashed line, the results for intermediate wind speeds from wind-tunnel studies;full line is the three-phase relationship based on lake studies extrapolated using information from models and wind-tunnel experiments. Equations for the three phases for a gas with SC = 600 and at 20^0 are: $V_p = 0.17\mu$ for $\mu < 3.6$; $V_p = 2.85\mu - 9.65$ for $3.6 < \mu > 13$; $V_p = 5.9 \mu - 49.3$ for $\mu > 13$ (Liss and Merlivat, 1986).

Equation 3 could be used to calculate a local flux if both Cw and wind speed were measured. The climatological models required, however, long-term average fluxes that could only be calculated if Cw was independent of wind speed. Leck and Rodhe (1991) find no systematic correlation between Cw and meteorology, implying that Cw may be controlled by biological processes the rate terms of which are poorly known. High winds might also have driven down Cw so that Vp and Cw were anticorrelated, making the product of the means less then the mean of the products. Limited data from one episode showed that, following a high wind lasting about 24 hours, Cw decreased by about 20% (S. Turner; Environmental Sciences School, University of East Anglia, Norwich NR4 7TJ, England; personal communication, 1990).

Figure 19 illustrates a "paper exercise" to demonstrate how sensitive the flux calculation could be with regard to the value of the wind speed used in determining the piston velocity. Figure 19A describes the hypothetical wind regimes for February to October that we used to calculate a piston velocity for

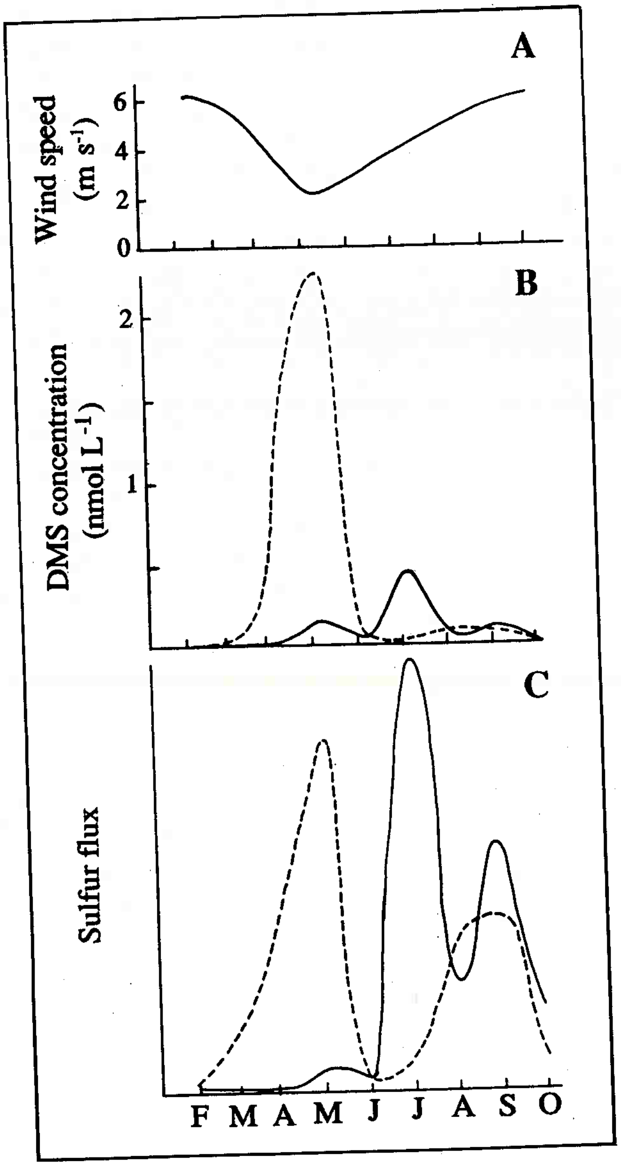

Figure 19.--**(A)** Wind speeds, **(B)** DMS concentrations, and **(C)** sulfur fluxes from two hypothetical stations (dotted line, dashed line) in proximity to one another for February to October.

each month according to Liss and Merlivat (1986). We made no corrections for changes in the diffusiveness of DMS with water temperature but this did not significantly influence the calculated fluxes. The DMS concentrations in surface water at two geographically close stations with very different hydrologies in Figure 19B were based on real data. Applying the piston velocities to these concentrations resulted in the fluxes depicted in Figure 19C. This shows that a factor-of-5 difference in the measured concentrations in May and in July could still result in equal fluxes with only a doubling of wind speed. In this case, the calculation was particularly sensitive because the May winds represented a theoretically smooth surface regime and those in July, a rough surface regime.

3.2.6 The available data

DMS concentrations are highly variable in both time and space (Andreae and Raemdonck, 1983). Correlations of DMS surface-water concentrations with chlorophyll or primary productivity are so weak that variations in chlorophyll account for only 30% of the variations of DMS (i.e., the production of DMS by phytoplankton is strongly species-specific) (Andreae, 1986). DMS has a strong seasonal cycle with maximum concentrations in the summer season and relative changes of factors of 2 to 4 (Bates et al., 1987). Turner et al. (1988) report a difference of up to a factor of 55 between winter and summer DMS concentrations in the nearshore waters of the European shelf and Leck and Rodhe (1991) report a seasonal factor of 100 in the surface waters of the brackish Baltic Sea.

Measurements of surface-layer DMS in the North Atlantic Ocean were sparse in both geographical and seasonal coverage. Although some authors had reported fluxes as well as concentrations, only the concentrations had been measured. These combined with either measured or climatological winds were used to derive fluxes. Because of the different parameterizations of Vp as a function of wind speed as well as the lack of fluxes reported for some data sets, we chose to review only concentrations. Since fluxes were being "modeled," we recommended that the modelers explicitly incorporate the flux parameterizations into their models using mean oceanic concentrations and winds appropriate to their models.

Both the climatological and episodic models of the transport and deposition of sulfur in the North Atlantic Ocean's atmosphere required seasonally resolved DMS input fluxes at their lower boundary. Since shelf and coastal regions are generally more productive than open-ocean waters, we compiled data sets for each. Also, because of the high natural variability of DMS in coastal regions, we included coastal data from both the Atlantic and Pacific Oceans.

3.2.7 Data interpretation

As a basis for calculating open-ocean fluxes, we constructed the best-estimate seasonal cycles of Cw shown in Figure 20 from the data in Table 8. This shows the maximum, minimum, and mean concentrations for different times of the year with peaks in the spring and possibly autumn, a pattern also seen in other data sets. We used this limited data set to construct a best-estimate curve for the seasonal variations of DMS concentrations. The impact of high DMS concentrations was minimized because they were highly transient and

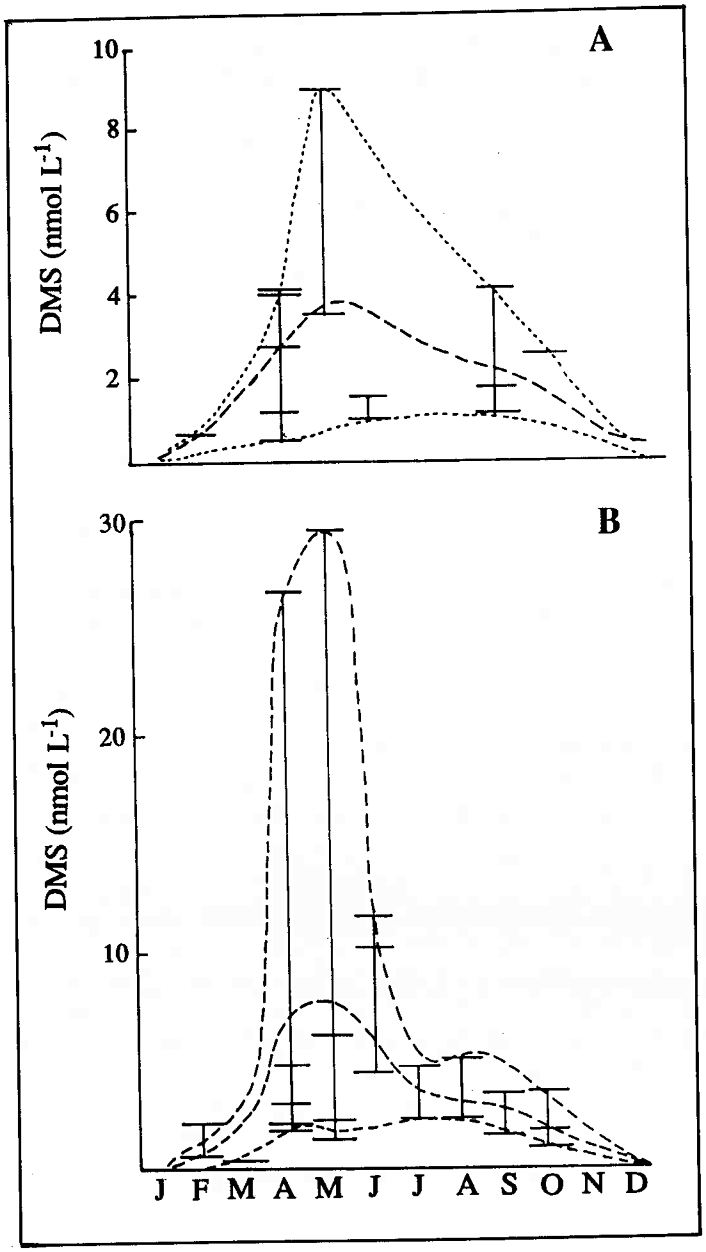

Figure 20.--Best estimates of DMS concentrations (**A**) over open waters of the North Atlantic Ocean and (**B**) for coastal and shelf regions of the North Atlantic and Pacific Oceans (see Table 8). Dashed lines represent maximum and minimum envelopes of expected concentrations, solid lines represent best-estimate, seasonal, mean DMS concentrations.

maintained for only a few days or weeks over small areas. We had insufficient data to infer any latitudinal variations but the Pacific data from Bates et al. (1987) suggest increasing seasonal differences with increasing latitude. Hence, the curve in Figure 20A probably represented an average seasonal amplitude for the region between 10° and 57°N. Particular care should be exercised in interpreting the curve for winter months as there were no data and low DMS concentrations could still have supported significant fluxes if high wind speeds were used to calculate piston velocities (see Fig. 19 and discussion).

The shelf and coastal data from Table 8 are depicted in Figure 20B, which again indicates a spring peak. A comparison of Figures 20A and B shows that the ranges of DMS concentrations in nearshore waters in spring/summer could be far greater than in the open ocean. As in Figure 20A, we constructed a best-estimate curve but the majority of the data were from approximately 50°N and might have considerably biased the average. Any attempt to generalize for

Table 8.--DMS concentrations in the surface waters of the open Atlantic Ocean and the Atlantic and Pacific Oceans' coastal and shelf areas (nmol S L^{-1})

Date	Concentration*	Location	Author
		Open Atlantic Ocean	
Feb 02-13	0.7 (141)	24-40°N, 70°W	Berresheim et al., 1991
Apr 05-07	1.3 (6)	10-20°N, 30°W	Burgermeister et al., 1990
07-09	1.2 (9)	20-30°N, 30°W	Burgermeister et al., 1990
09-12	1.8 (10)	30-40°N, 30°W	Burgermeister et al., 1990
	4.7 (73)	40-49°N, 22-70°W	Burgermeister et al., 1990
26-30	3.0	40-47°N, 22-43°W	Church et al., 1991
28-May 01	3.7 (47)	24-40°N, 70°W	Berresheim et al., 1991
	2-4 (12)	41-48°N, 42-69°W	Church et al., 1991
May 01-09	4-8 (12)	40°N, 57-45°W	Church et al., 1991
Jun 10-11	1.4 (4)	SE of Bermuda	John Dacey, 1990**
Sep 04-06	4.1 (50)	25-40°N, 70°W	Berresheim, 1987**
19-26	1.0 (22)	17-44°N, 30-13°W	Staubes et al., 1990
26-30	0.8 (12)	17°N-3°S, 30°W	Staubes et al., 1990
30-Oct 09	2.5 (6)	ca. 30°N, 75-80°W	Berresheim, 1987**
Oct 12-26	3.1 (17)	Tropical	Bingemer, 1984
12-26	2.1 (44)	Temperate	Bingemer, 1984
		Atlantic and Pacific Ocean's coastal and shelf areas	
Feb 03-06	2.1 (81)	25-40°N, 75-80°W	Berresheim et al., 1991
	0.7 (24)	32-49°N, US West Coast	Bates et al., 1987
Apr 16-17	4.8 (6)	British Channel	Burgermeister et al., 1990
23-26	1.9 (67)	25-40°N, 75-80°W	Berresheim et al., 1991
May	2.1 (243)	32-49°N, US West Coast	Bates et al., 1987
Jul	6.8	North Sea	Turner et al., 1988
	2.5 (30)	North Sea	Leck and Rodhe, 1991
Aug	2.3	US West Coast	Andreae, 1986
Sep 07-13	3.4 (37)	25-40°N, 75-80°W	Berresheim et al., 1991
Oct	3.5 (2)	25-30°N, 80°W	Berresheim et al., 1991
08-11	7.7 (15)	North Sea Channel	Barnard et al., 1982

*Numbers in parentheses are numbers of samples taken.

**J. Dacey; Woods Hole Oceanographic Institution, Woods Hole, MA 02543; personal communication, 1990; H. Berresheim; School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332; personal communications, 1990.

nearshore waters was necessarily more hazardous than to do so for the open ocean since DMS production is very locally influenced (e.g., nutrients, salinity, stratification, etc.). As for the open ocean, data for the winter months were very limited and latitudinal variations in DMS production might have been highly significant.

The global models were not very significantly effected by coastal emissions because coastal areas are considerably smaller than open-ocean areas. Regional models or areas, such as Northern Europe, however, could have been significantly influenced by coastal DMS emissions.

3.2.8 Recommendations

Except for the data of Berresheim et al. (1991), too few data existed to resolve satisfactorily the seasonal variations in DMS for the North Atlantic Ocean; data from the central North Atlantic Ocean were also extremely sparse. More DMS measurements need to be taken in the future to characterize seasonal cycles. Future measurements should also be taken in the central North Atlantic Ocean over several seasons to determine if DMS fluxes are similar to Pacific fluxes and if the extrapolation of Pacific data is reasonable.

The covariance of oceanic DMS concentrations and piston velocities (i.e., wind speed) should be determined to test the validity of using Equation 3 to calculate mean fluxes from mean Cw multiplied by a Vp determined from climatological wind speed.

In conclusion, although this attempt to estimate seasonal cycles for DMS in the North Atlantic Ocean was very limited, it was apparent that some attempt had to be made to improve the information available to the modeling community.

3.3 The Nitrate Comparison

3.3.1 Introduction

This case study compared predicted and measured surface distributions and deposition fluxes of reactive nitrogen compounds (primarily nitrate) in the North Atlantic basin. Because multiyear time-series information was available for wet deposition at Bermuda and for surface aerosol concentrations at Barbados, we used these data to provide a context within which we compared predictions from the climatological models. Variations on monthly, seasonal, and annual time scales were examined. We also compared model results with both aerosol and wet-deposition data from Mace Head, Ireland. Although only one year of data was available for Mace Head, the results from this station provided a different perspective because of its location at a high latitude and close to the European continent.

The three climatological models used in this study were the LLNL model (Penner et al., 1990, 1991a), the MPI model (Feichter and Crutzen, 1990; Zimmermann, 1987; Zimmermann et al., 1989), and the GFDL model (Levy and Moxim, 1989b). As noted before, the models differed in their spatial resolutions and meteorology as well as in their parameterizations of wet- and dry-removal processes. Model similarities and differences pertinent to this case study are discussed in this section.

Table 9.--Sources of the reactive nitrogen treated in the models (Tg N yr^{-1})

	LLNL		MPI		GFDL	
	Strength	Seasonal variation	Strength	Seasonal variation	Strength	Seasonal variation
Fossil-fuel combustion	22	No	20	No	21	No
Biomass burning	6	No	5	Yes	8	Yes
Biogenic soil emissions	10	Yes	10	Yes	--	n/a
Lightning	6	Yes	5	Yes	--	n/a
Stratospheric injection	1	No	--	n/a	--	n/a

Source: Galloway et al., 1992

The LLNL and MPI models included chemical reaction schemes to partition reactive nitrogen (NO_y) into HNO_3 and NO_x; the GFDL model transported NO_y as a single species and assumed a partitioning of NO_y based on the available data to assign dry-deposition velocities over land and ocean. The reaction scheme in the LLNL model was simplified by incorporating only the major reactions between NO_x and HNO_3 and by assuming latitudinally averaged OH concentrations and photolysis rates. The MPI model's chemistry was more complete and calculated OH concentrations using a CH_4, CO, and NO_x reaction scheme. In this sense, the MPI model was more like the Harvard one although it did not yet include PAN. Total NO_y was predicted by the GFDL model whereas for the LLNL and MPI models we used the predicted HNO_3 concentrations. Since none of the models treated particulate-phase nitrate separately, in this comparison we assumed that the predicted HNO_3 could be compared with the concentrations of nitrate collected at the measurement sites despite the fact that the latter included a combination of gas- and particulate-phase nitrate.

The sources of reactive nitrogen and the deposition velocities used in each model are listed in Tables 9 and 10, respectively. The GFDL model's simulations included only sources from fossil-fuel combustion and biomass burning although the LLNL and MPI models' simulations also included natural sources. The globally averaged source strength for each source type was approximately the same for these simulations although the distribution of the sources

Table 10.--Deposition velocities of reactive nitrogen used in the models (cm s^{-1})

		MPI		GFDL	
	LLNL	Land	Sea	Land	Sea
NO	0.05	0.0	0.0		
NO_2	0.25	1.0	0.1		
HNO_3	0.5	1.0	2.0		
NO_y				0.3	0.1

Source: Galloway et al., 1992

within each model might have differed somewhat. Because the assumed partitioning for the GFDL model was developed from the partitioning observed over land (where NO_x concentrations are larger than HNO_3 concentrations), the deposition velocities used in this model and in the LLNL and MPI models should have been quite similar over the source regions. However, the different deposition velocities we used for HNO_3 over the sea were expected to lead to differences in the removal rates over the Atlantic.

The meteorology used in each model was developed from quite different sources. The LLNL model was driven by wind and precipitation fields derived from the NCAR CCM general-circulation model (Pitcher et al., 1983). The GFDL model used fields from the GFDL ZODIAC/GASP general-circulation model (Manabe and Holloway, 1975; Manabe et al., 1974). The MPI model, on the other hand, used observed but monthly averaged winds (Oort, 1983) and monthly averaged precipitation rates (Jaeger, 1983). The fields from each of the general circulation models were compared with observed climatological winds and were in general agreement with these observations (e.g., Manabe and Holloway, 1975; Manabe et al., 1974; Pitcher et al., 1983); however, we did not compare the wind fields and precipitation patterns in detail and expected that there might have been significant differences that impacted upon the predicted concentration and wet-deposition fields.

The data used in this case study included results from aerosol and wet-deposition samples. The aerosol samples were collected daily on 20 cm x 25 cm Whatman 41 filters at a rate of approximately 1 m^3 min^{-1} during onshore wind conditions. (As noted below, model results were not selected on the basis of wind direction; this could have introduced some uncertainty into the analyses.) The samplers were on the climatologically determined windward shores of the coastal sites. The filters were mounted on towers 16-20 m above ground level (except at Mace Head from August, 1988, to June, 1989, when the filter was at a nominal 2 m above ground level). Cellulose filters, such as the Whatman-41, do not normally adsorb gas-phase HNO_3; however, the collection efficiency for HNO_3 was expected to increase progressively as the sea-salt concentration built up on the filter. Consequently, the nitrate data reported for these filters was regarded at a minimum as nitrate aerosol and at a maximum as total nitrate (i.e., aerosol nitrate and HNO_3). The measurements of HNO_3 in the marine boundary layer yielded highly variable results but the mean ratio of HNO_3 to nitrate appeared to be about 0.3 or less based on recent unpublished data presented at this meeting and on earlier works reported in the literature (Huebert, 1988; Savoie and Prospero, 1982). Thus variabilities in the collection efficiency of HNO_3 by the Whatman-41 should not have greatly affected the nitrate-data values we used. We did not expect any significant concentrations of PAN in the marine boundary layer at these sites although this conclusion seemed at odds with the WATOX data reported in the reaction-nitrogen case study for the Bermuda site (see Section 3.4). The concentrations of nitrate were invariably much higher than the blank levels and the analytical sensitivity.

Precipitation samples were collected daily with an automated wet-only collector at Mace Head, Ireland, and one at Barbados, both AEROCE sites. The altitudes of the collectors were the same as for the aerosol samplers discussed above (i.e., 16-20 m above ground level). However, unlike the aerosol samplers, the precipitation collectors were not sectored but operated independently of surface wind direction. At Bermuda, because of the nine-year record provided by WATOX, we used the data from Harbour Radio Tower on the northeastern portion of the island. Details on collection and analytical techniques are summarized by

Galloway et al. (1989). The precipitation samples were collected from December 18, 1988, to June 30, 1990, at Ragged Point, Barbados; from April 20, 1980, to August 14, 1989, at Harbour Radio Tower, Bermuda; and from November 16, 1988, to July 12, 1990, at Mace Head, Ireland.

3.3.2 Results of the comparisons

Barbados: Nitrate concentrations in aerosols by year, 1984-1989.

Data used for this comparison were obtained from daily filter samples collected from 1984 to 1989. Because of the strong trade-wind regime, winds were in the sampling sector over 90% of the time.

Measured monthly mean concentrations ranged from 2.86-16.3 nmol m^{-3} (Fig. 21). In some months there was considerable variability from year to year. Maximum concentrations were in April, May, and June; concentrations tended to be most variable during this time but concentrations measured in January through March were also quite variable. Concentrations tended to be least variable during August through December, especially during August and September.

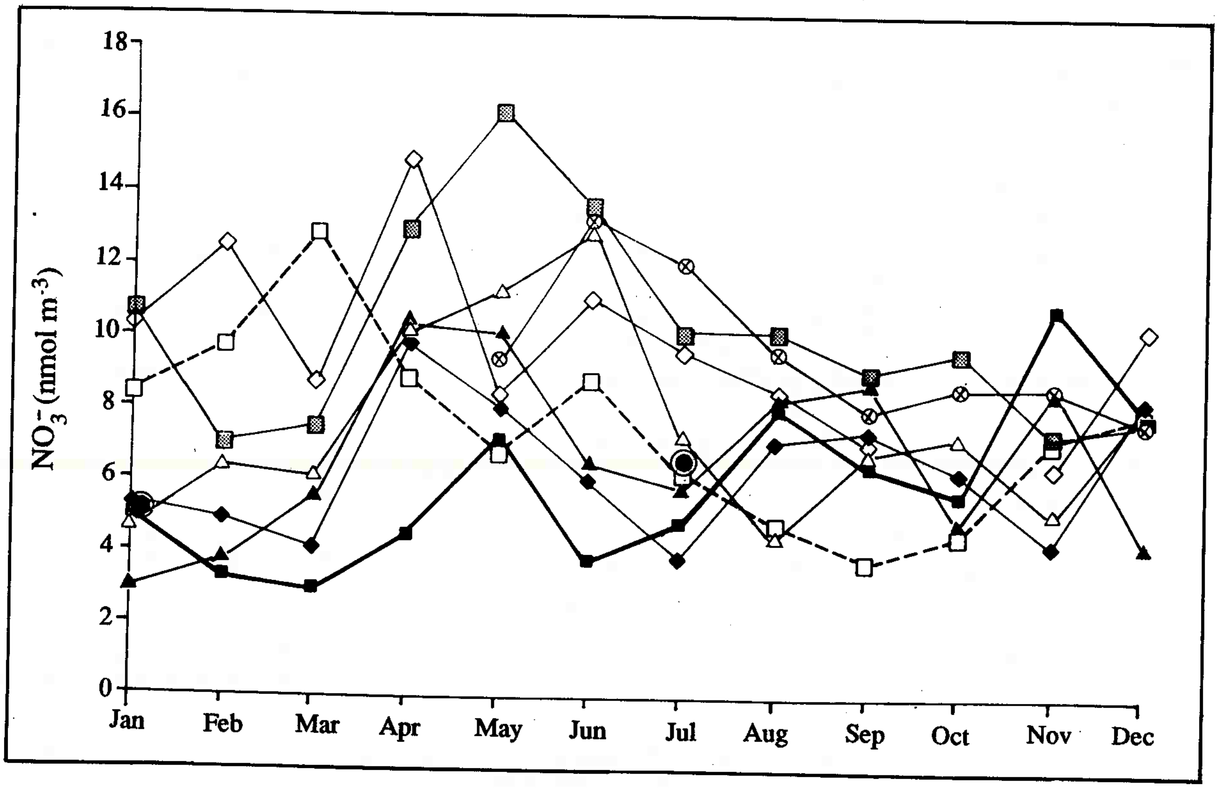

Figure 21.--Mean monthly aerosol nitrate concentrations from Ragged Point, Barbados, over six years (1984, X in open circle; 1985, open triangle; 1986, solid diamond; 1987, open diamond; 1988, solid triangle; and 1989, stippled square) compared to nitrate concentrations predicted by the MPI (dashed line, open square), GFDL (heavy line, solid square), and LLNL (dot in open circle) models (Galloway et al., 1992).

Previous studies by Savoie et al. (1989) suggest that more than half the nitrate aerosol is derived from anthropogenic sources; lead-isotope studies by Hamelin et al. (1989)) indicate that European sources play a significant role in this regard. The ratio of nitrate to nss-sulfate is very high during the winter and early spring; along with other evidence, this suggests that biomass burning could be a major source. The seasonality is consistent with the burning cycle in Africa (Delmas, 1982).

For the GFDL model, the simulated yearly average concentration of total reactive nitrogen (NO_y) was about 30% less than the yearly average concentration when all observations were considered. Although the simulated seasonal cycle agreed reasonably well with observations from 1986 and 1988, it underestimated the late spring maximum seen in the observations and generated an annual maximum in the fall. The differences could have been partially due to the GFDL model's omission of the lightning source and soil biogenic emissions.

The LLNL model results for Barbados yielded means for January and July that were about 30% lower than the measured values for these months. July concentrations were slightly higher than January values because of both larger OH concentrations (which converted NO_x to HNO_3 in the model) and larger sources in the Northern Hemisphere. (The model had both higher lightning and higher soil-microbial sources during this summer.) However, the model results fell within the range of the measured concentrations. Because this model tried to describe all sources of reactive nitrogen, its predicted concentrations should have been close to those measured. The model concentrations would have been higher if, for example, larger lightning sources had been used (Penner et al., 1991a).

The MPI model's results were generally in the envelope formed by all the individual years of data. A significant feature of the MPI model's simulation was a strong maximum in spring although the simulated maximum in March was one to three months before the observed maximum. The MPI model's simulation generated a minimum in September that was not evident in the real data. Compared to individual years of data, the model simulated a large annual cycle but the month-to-month changes in the model were relatively gradual. The annual cycle range was similar to that for the GFDL model.

Most differences in the model-predicted results might have been rationalized by the differences in the sources included in each model and the deposition velocities used. The GFDL and MPI models' simulations yielded large month-to-month and annual variations that were broadly consistent with the measurements. However, substantial disagreements pointed to the need for more detailed analyses. In particular, it would have been desirable to compare the meteorology used for the predictions with that associated with any particular year's data in order to assess the factors that contributed to any agreement or to the lack thereof.

Bermuda: Nitrate wet deposition by year, 1980-1989.

Monthly wet-deposition data for nitrate at Harbour Radio Tower, Bermuda, were available for May, 1980, through August, 1989. The data for 1982-1984 and 1988 were compared to estimates from the MPI, GFDL, and LLNL models (Fig. 22). The wet-deposition rates were calculated using monthly volume-weighted average

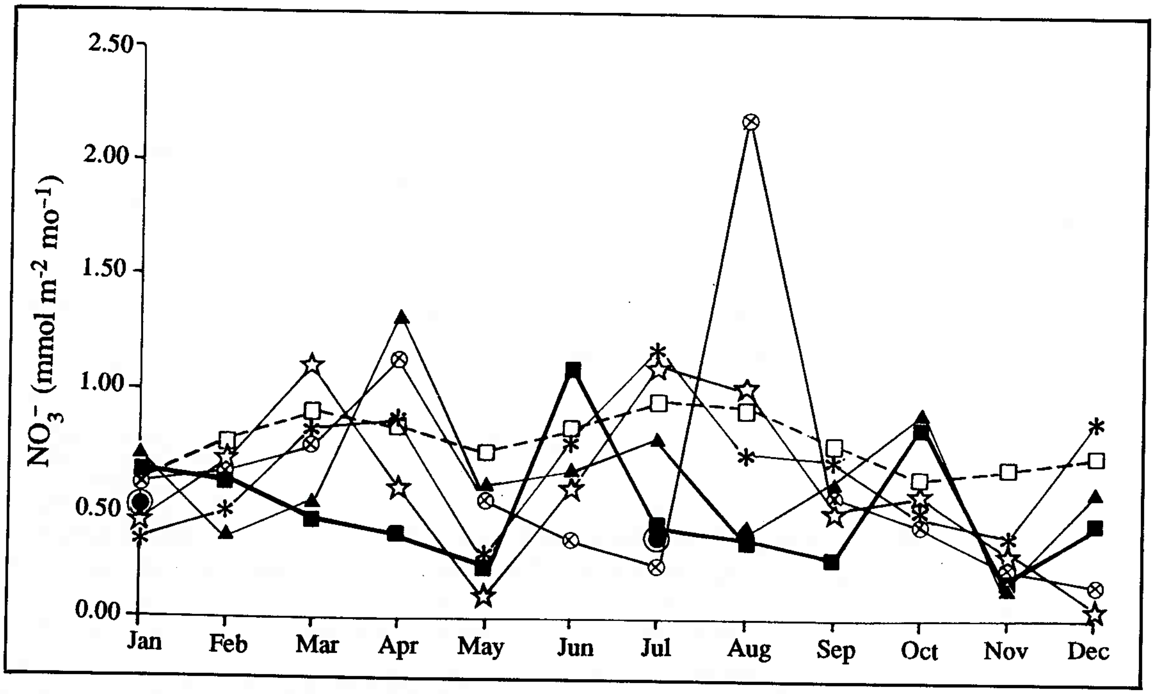

Figure 22.--Mean monthly wet deposition of nitrate from Harbour Radio Tower, Bermuda, over four years (1982, open star; 1983, asterisk; 1984, X in circle; and 1988, solid triangle) compared to predictions from the MPI (dashed line, open square), GFDL (heavy line, solid square), and LLNL (dot in open circle) models (Galloway et al., 1992).

concentrations (sampling and analytical techniques are given in Galloway et al., 1989) and the total amount of precipitation measured at the U. S. Naval Air Station, which is 2 km from the precipitation-collection site. Over the year, the wet-deposition rates varied from 0.1-2.4 mmol m^{-2} mo^{-1}.

The yearly wet deposition simulated by the GFDL model was 20% less than that observed for Bermuda and the missing lightning source was not expected to make up the difference. Both the observed and the model time series were highly variable and neither appeared to have a strong seasonal signal. However, except in June, model deposition values for spring and summer were generally less than observed deposition values.

The average wet-deposition value for July from the LLNL model was remarkably close to that from the GFDL model. The LLNL model's predicted deposition for January was very close to the measured mean value for the same month but the predicted value for July was lower than the measured values for most years for which we had data. Again, the LLNL model predicted little variation between winter and summer seasons. The similarity between the LLNL and GFDL models' predictions of deposition was consistent with the agreements in the predicted surface concentrations of HNO_3 and NO_y in air from these two models, respectively. These agreements were somewhat surprising because the LLNL model included lightning and soil-microbial sources as well as the fossil-fuel and biomass sources that were incorporated in the GFDL model. In the LLNL model's simulations, fossil-fuel sources provided only about 50% of the calculated concentrations in winter and 70% of the concentrations in summer. In fact, when both models were run with only fossil-fuel sources, they differed in predicted concentrations by about a factor of 2 at this site. This was a serious discrepancy that needed to be resolved.

The MPI model broadly reproduced the pattern of the wet-deposition data. Both in the model simulation and the data, there were maxima in early spring, in mid-summer, and in December with a corresponding minima between the peaks. However, on a year-to-year basis, the data showed great variability. On the other hand, the modeled concentrations were slightly high, the month-to-month changes in the model were smoother than in the data, and the amplitude of the yearly cycle was smaller in the model than was observed for any given year.

In summary, the various models' predictions for deposition at Bermuda agreed well. This was surprising because the predicted concentrations in the surface air at this site varied by about a factor of 2. This agreement might have occurred because the predicted wet deposition resulted from a process that occurs throughout the tropospheric column and depended on predicted precipitation as well as concentrations. The model predictions were quite close to the measured deposition, particularly in months where the observed variability was low; the predictions in general appeared low in months where the observed variability was high. The measured high concentrations may have been caused by a few intense events (which would be difficult to reproduce with a large-scale climatological model) or there may have been an "island effect" not represented in the models that enhanced precipitation.

Mace Head: A comparison of nitrate concentrations and deposition

Although there was only one year of data available from the Mace Head site, we tried a comparison. Figure 23 shows a plot of the observed versus the model-predicted NO_3^- wet-deposition values at Mace Head. Figure 24 shows a plot of the observed versus model-predicted, monthly averaged, aerosol NO_3^- concentrations at Mace Head.

The aerosol sampler at Mace Head was on the west coast of Ireland (about 75 km northwest of Galway) and was activated only when the winds were from the west. This was a problem for us when we compared the data to the model results because the model results had not been sorted according to wind direction (except as noted below). Because of the wind climatology, the sampler was active only about 50% of the time. Nonetheless, useful samples were obtained on 19-27 days of every month except November and December, at which time samples were obtained on only 8 and 11 days, respectively. Thus, there was a possibility of significant biasing when the model results were compared with the data from these two months, especially when one considered that out-of-sector winds (i.e., winds from the east) might have carried high concentrations of pollutants from Europe. However, as our comparisons showed, this did not appear to have been the case.

The monthly mean aerosol nitrate concentrations at Mace Head varied over a wide range, <1-43 nmol m^{-3} (see Fig. 24). Highest concentrations were during the late spring and summer. Concentrations were very low during the late fall and winter, even lower than those at Bermuda or Barbados.

At Mace Head, NO_3^- deposition values varied from 0.3 to 1.3 mmol m^{-2} mo^{-1} with no pronounced seasonal signal (Fig. 23). (The climatically weighted data did show a strong signal.) This lack of a seasonal pattern differed from what

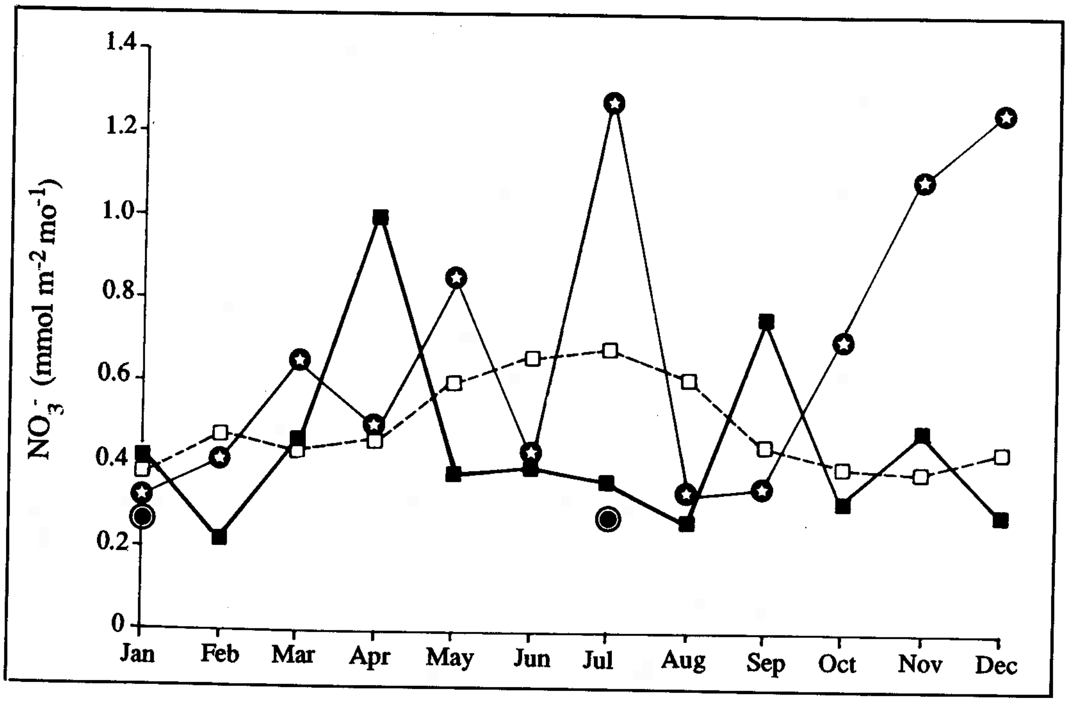

Figure 23.--The mean monthly wet deposition of nitrate (open star in closed circle) measured at Mace Head, Ireland, from November 16, 1988, to July 12, 1990, compared to predictions from three models: the MPI model (dashed line, open square), the GFDL model (heavy line, solid square), and the LLNL model (dot in open circle) (Galloway et al., 1992).

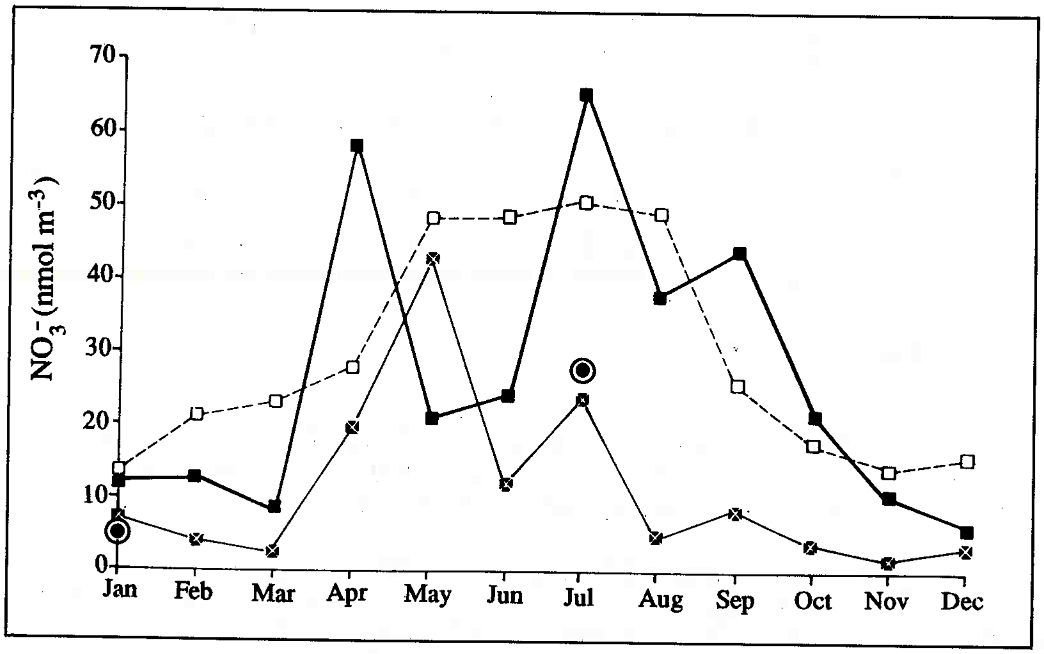

Figure 24.--Mean monthly aerosol nitrate concentrations (open X in solid square) measured at Mace Head, Ireland, in 1989 compared to predictions from three models: the MPI (dashed line, open square), the GFDL (heavy line, solid square), and the LLNL (dot in open circle) (Galloway et al., 1992).

Table 11.--Variabilities of NO_3^- concentrations in aerosols and precipitation at Ragged Point, Barbados, and Mace Head, Ireland

	c	r	r/c	δ	δ/c
	Barbados aerosol concentrations (nmol m^{-3})				
Data					
5-year averages	8.4	5.2	0.62	1.59	0.19
1985	7.8	8.4	1.09	2.39	0.31
1986	6.3	5.8	0.92	1.81	0.29
1987	9.8	8.4	0.85	2.31	0.24
1988	6.7	7.5	1.12	2.42	0.36
1989	10.2	9.3	0.92	2.73	0.27
Model					
GFDL	5.9	8.0	1.35	2.23	0.38
MPI	7.5	9.0	1.20	2.51	0.35
	Barbados wet deposition (μmol m^{-2} mo^{-1})				
Data					
1989	0.45	0.93	2.09	0.26	0.59
Model					
GFDL	0.048	0.09	1.89	0.037	0.78
MPI	0.18	0.16	0.89	0.049	0.27
	Mace Head aerosol concentrations (nmol m^{-3})				
Data					
1989	11.2	41.3	3.69	11.7	1.05
Model					
GFDL	27.1	57.3	2.11	19.2	0.71
MPI	28.9	37.3	1.29	15.1	0.52
	Mace Head wet deposition (μmol m^{-2} mo^{-1})				
Data					
1989	0.57	1.07	1.88	0.37	0.66
Model					
GFDL	0.45	0.78	1.74	0.21	0.48
MPI	0.50	0.30	0.60	0.11	0.22

Source: Galloway et al., 1992

was observed for aerosols (Fig. 24) possibly because of the impact of seasonal variations of precipitation amounts on NO_3^--deposition rates and the scavenging of gas-phase nitrogen compounds by the precipitation.

The yearly average deposition obtained with the GFDL model and the measured yearly total wet deposition agreed reasonably well, within 25% (Table 11) (W. Moxim; Geophysical Fluid Dynamics Laboratory, Princeton University, Princeton, NJ 08520; personal communication, 1990). There was qualitative agreement (within a factor of 2) between the GFDL model's time series and the observed surface nitrate concentrations. The GFDL model's deposition time series were highly variable and entirely out of phase with the data (Fig. 23). To remain compatible with the sector-selected concentration data, we used the model surface concentrations for the grid box to the west of the box that contained both Mace Head and a portion of the Irish fossil-fuel emissions. The results were still overestimates since the model concentrations were selected for all wind directions.

The LLNL model's results for the aerosol nitrate concentrations at Mace Head were significantly higher for July than for January; these results agreed quite well (within 50%) with the measured values. At this latitude, the differences in the prescribed OH concentrations in the model in January and July might have accounted for the predicted seasonal variation.

Despite the differences in the predicted concentrations for the aerosol nitrate for January and July in the LLNL model, the predicted depositions for these two months were nearly the same. Apparently the model-predicted rainfall during July was somewhat lower than that predicted for January. The model results appeared to agree well with the measured monthly averaged deposition data for January but was significantly lower than the measured deposition for July. In view of the high month-to-month variability in the data at Mace Head, more information was needed to demonstrate that the model predictions differed significantly from the measurements.

Monthly aerosol concentrations simulated by the MPI model consistently exceeded observed values from Mace Head, probably for two reasons: 1) a 10-degree spatial resolution was inadequate for a station close to but normally upwind of a major source region; 2) in the model, pollution that moved from the east to Mace Head could not be filtered out because monthly average winds were used and wind fluctuations on time scales of less than a month were represented by horizontal diffusion. Of the four comparisons discussed here between observed and MPI-model-simulated nitrogen-containing species at AEROCE sites, this was probably the only significant bias in the simulations. The data had a spring-summer maximum, which the model also clearly showed; however, the late-summer, monthly mean values from the MPI model were as much as ten times greater than the measured values. As mentioned above, this may have been due to the large grids used in the MPI model and the resultant amount of diffusion. The annual average nitrate deposition simulated by the MPI model was roughly about equal to the observed annual average value but the month-to-month variations were clearly much smaller than the month-to-month variations in a single year of data. The model produced a very weak summer maximum but the variabilities in the measured values were so great that we could not find a seasonal trend.

In summary, the model results for nitrate concentrations at Mace Head agreed reasonably well (within a factor of 2-3) with the measured aerosol nitrate concentrations (Table 11). The NO_y concentrations predicted by the GFDL model would have been lower by approximately 25% if the deposition velocities had been similar to those used in the LLNL model. Since the ratio of predicted nitrate to NO_y in the LLNL model was about 1:2, a similar scaling applied to the GFDL model's NO_y results should have brought the LLNL and GFDL models' predictions into closer agreement. No model result was selected on the basis of the modeled wind direction so as to complement the actual aerosol sampling conditions; thus we expected all model results to be high relative to the real aerosol data set. Considering the observed month-to-month variabilities at this site and the likely year-to-year variability, the agreement was reasonable.

Model predictions for wet deposition at Mace Head were in substantial agreement (within 20%) despite the differences in the model-predicted surface air concentrations (Table 11). The agreement may have been fortuitous but, on the other hand, it may have been a consequence of the fact that wet scavenging is a process that works throughout the tropospheric column and not just on surface concentrations. The predicted wet deposition values also depended on the precipitation rates used in the models. The measured concentrations and model results appeared to agree well considering the large month-to-month variations that had been observed.

A comparison of the model and the data variability.

Besides comparing the data with the model-predicted concentrations and deposition amounts, we also examined observed and simulated variabilities. Here we compared the interyear and intrayear variabilities in data and model simulations (Table 11). The amplitude of the annual cycle was measured by the range, r (the maximum monthly value minus the minimum monthly value), and by the standard deviation, δ, of the monthly values about the yearly average, c. Because observed and simulated c may have differed greatly, the most useful measures of intrayear variability were r/c and δ/c.

First we considered the data from Barbados, a region distinguished by its remoteness from major continental sources. Table 6 shows a comparison of the statistics for the nitrate concentrations from Barbados for an average of five years' data and for five individual years. The NO_3^- amplitude, r, and standard deviation statistics were uniformly small for the average data year, i.e., a year produced by averaging the data from all Januarys from 1985 to 1989, all Februarys from 1985 to 1989, etc. For this average year, the measures of annual variability were $r/c = 0.62$ and $\delta/c = 0.19$, both of which were substantially smaller than the same statistics for any individual year. These statistics were also smaller than those calculated by either model.

When we compared the data for the five separate years, we found that, in individual years, the average annual concentrations varied from 6.3 nmol m^{-3} to 10.2 nmol m^{-3}, the ranges varied from 5.8 to 9.3 nmol m^{-3}, and the intermonth standard deviations varied from 1.81 to 2.73. The normalized variability statistics varied much less: r/c went from 0.85 to 1.12 and δ/c from 0.24 to 0.36. The lowest variability was found in 1987 and the highest in 1988. The highest average concentration was in 1989 and the lowest in 1986.

The observed intraannual variabilities displayed a few consistent relationships between different stations and different variables. For example, aerosol NO_3^- concentrations at Mace Head varied more than those at Barbados. For an individual year, the concentration's variability changed by a factor of 5 to 6 between stations but the variability of wet deposition changed by much less. (Again, concentration was observed at a single point in the vertical but wet deposition reflected some more complicated, and also more stable, vertical integral of processes and concentrations in the atmosphere.) At Barbados, the normalized statistics for wet deposition were more variable than those for concentrations; however, at Mace Head, the reverse was true.

Both the MPI and GFDL models simulated climatological distributions, but the GFDL model used daily varying meteorology and the MPI model used monthly average meteorology so that the GFDL model could simulate episodes of a few days' duration and the MPI model could not simulate episodes. Thus, the intraannual variability simulated by the GFDL model was consistently larger than that simulated by the MPI model.

The variabilities of the NO_3^- concentrations simulated by the GFDL model seemed remarkably good because the simulated values were scattered about the observed values: The simulated variabilities were high at Barbados and low at Mace Head relative to the observed variabilities. The r/c simulated by the GFDL model was almost constant at about 1.7-1.9 for wet deposition. On the other hand, the variability simulated by the MPI model was biased low and only exceeded the observed value for aerosol concentration at Barbados. Thus, in summary, the GFDL model seemed to simulate the observed intraannual variability in the data better than did the MPI model.

3.3.3 Conclusions

This case study clearly showed that any comparison between the results for a single year from a climatological model and the measurements from a single year, or even several years, should be interpreted with great care. The comparisons would have been far more informative if either they had taken into account the differences between the meteorology and the precipitation used in the models and the actual meteorology and precipitation for a specific year or they had compared multiple years of simulation with multiple years of observations. Obviously we should strive towards this goal in the future.

The differences among the results of the various models could sometimes be reconciled by considering the differences in model treatments. When doing this, we found reasonable agreement with the measured concentrations given the limitations of the data. However, a time series with a more complete suite of measured NO_y species at these locations would have allowed for a better test of the model physics.

Mace Head was a particularly interesting site for future model and data comparisons because it is at a higher latitude where there were significant seasonal variations in nitrate production as a result of photochemical processes. However, the relatively small fraction of in-sector time was of considerable concern. The appearance, or lack there of, of a seasonal cycle in the data would have tested the model results more completely.

3.4 Nitrogen: Reactive Species

In this case study we compared model results with data from the GCE/WATOX/CASE expedition (Pszenny et al., 1990a). Surface measurements were taken aboard the NOAA R/V Mt. Mitchell as it approached Bermuda from July 22-29, 1988; measurements were also taken at two altitudes from the NOAA King Air aircraft as it flew over the ship. This intercomparison focused on some species important in the atmospheric oxidant cycle, namely O_3, NO_x, NO_y, and nitrate. Some species were also measured aboard an aircraft at different altitudes.

This intercomparison consisted primarily of event measurements being contrasted to results from climatological models. This raised concerns as to the validity of comparing a few measurements to longer term averages generated by the models. There was the potential for these measurements to be significantly different from the monthly means.

The reactive nitrogen case study was the worst equipped to deal with this issue as the measurement data were only for a particular location and time; no spatial or temporal averaging was possible. We examined the available data to establish that the measurement period was at least representative of this area in July. The synoptic-scale flow, the calculated isentropic back trajectories, the precipitation pattern, and both the upper-air and surface maps were typical of the Bermuda area in July; there was no evidence of abnormal airflow into the area. The trajectories indicated that the sampled air had circulated around the Bermuda-Azores high before being sampled and that the residence time over the ocean was at least five days. For the seven-day period, the ^{222}Rn, O_3, NO_y, and NO_3^- concentrations measured from the ship were consistent. The small day-to-day variabilities of the chemical data were consistent with the stable meteorology regime. Thus, we had some confidence that the study event could be realistically compared to the results from the climatological models for the month of July.

3.4.1 The aims and possible results of this case study

Our aim was to test the understanding of the distributions of

1. NO_y near Bermuda, including its altitude dependence. This test was sensitive to the nitrogen source and sink terms in the models but not to the details of the chemistry;
2. Nitrate and NO_x near Bermuda. This test was much more sensitive to the chemistry in the models, particularly of NO_x.

One possible result of this case study would be that comparisons could provide diagnostic information for further model development since the model-predicted speciations responded to changes in deposition sources and chemistry. The comparisons could also suggest measurements that might be needed for future comparisons with models; such results could assist in developing future measurement strategies.

3.4.2 The data for the comparisons

The measurements for the comparisons were the mean concentrations reported by Hastie et al. (1990), Piotrowicz et al. (1990), and Ray et al. (1990a) as listed in Table 12. The surface measurements were made from the NOAA R/V Mt. Mitchell; the marine boundary-layer measurements, from constant altitude aircraft flights at 150 m above sea level; and the free troposphere measurements, similarly at 2600 m. Aircraft NO_y was measured with a molybdenum converter chemiluminescent analyzer combination (Dickerson et al., 1984). On the ship, NO_y was converted to NO using a gold converter (Fahey et al., 1985) and the NO measured by a luminol-based NO_2 analyzer with a CrO_3 converter (Drummond et al., 1989). Bypassing the gold converter gave NO_x measurements. One known interference to this measurement was PAN, which was measured as NO_2 with an efficiency of 25% in continental areas. A PAN correction was not made to the data as PAN was not measured during this part of the expedition but previous measurements over the North Atlantic Ocean show that its concentration is below 20 pptv (9 nmol m^{-3}) (Bottenheim and Gallant, 1987; Rudolph et al., 1987; Gallagher et al., 1990).

Table 12.--Measured values versus model estimates for nitrogen species (nmol m^{-3}) and ozone (ppb)

	Measured concentration*	Model concentration			
		LLNL	MPI	GFDL	Harvard
		NO_y			
Surface	46 (±17)	20.1	54	17	
Marine boundary layer	45 (±13)	...	73	25	
Free troposphere	31 (±22)	31.7	94	29	
		NO_x			
Surface	29 (±9)*	4.0	3.4		2.2 (22)**
Free troposphere		3.8	6.4		0.9 (24-5)**
		Total nitrate			
Surface	10 (±2.8)	14.5	51		
Marine boundary layer	3.2 (±0.5)		70		
Free troposphere	3.1 (±1.1)	25.0	87		
		Ozone			
Surface	16 ppb		26 ppb		30 ppb
Marine boundary layer	17 (±1.1)				

*Measurement may contain a contribution from PAN.
**Model calculation of (NO_x + PAN).

Note: Numbers in parentheses are ± the standard deviation.
Sources: Measurement data from Hastie et al. (1990), Piotrowicz et al. (1990), and Ray et al. (1990a).

We used outputs from the LLNL model, the MPI model, the GFDL model, and the Harvard model. These models had different input source functions, different grid scales, and different degrees of chemical complexity. The grid point we chose to compare with the measurements was an ocean point at or close to Bermuda. The Harvard data were from a week in June and the other models' data were averages for July. The data were tabulated with the measurements in Table 12.

3.4.3 The NO_y comparisons

The data.

There were NO_y measurements from the ship and from the aircraft. The instruments operated on different principles but intercompared well on three aircraft flybys during the comparison periods (Boatman et al., 1990). The instrument comparisons gave confidence in the entire data set and showed that it was appropriate to obtain altitude variations using the ship and aircraft instruments. The LLNL, MPI, and GFDL models produced NO_y concentrations as functions of altitude that could be directly compared to the measurements.

Comparisons and discussion.

The NO_y from the LLNL and GFDL models agreed reasonably well with the free-tropospheric measurements but both models predicted lower NO_y, by about a factor of 2, at the surface in the marine boundary layer. The MPI model showed a similar altitude dependence to the other models but with higher concentrations so it simulated the surface measurements better than those aloft.

All models predicted an increase in NO_y with altitude. This was due to a combination of causes: The change in wind speed and direction with height that brought air from the source regions into the free troposphere more efficiently than into the marine boundary layer; the upper air sources, such as lightning and transport from the stratosphere; and the deposition loss to the surface. This contrasted with the data, which showed a decrease in NO_y with altitude. More measurements of the altitude dependence of NO_y were needed to confirm the observed decrease. Measurements from higher altitudes were particularly necessary to look for the NO_y from natural sources.

3.4.4 The NO_x comparisons

The data.

NO_x measurements were only available from a single (luminol-based) instrument aboard the NOAA R/V Mitchell. Given the very low PAN concentrations previously measured over the western North Atlantic Ocean, it was assumed that the instrument was measuring almost entirely NO_x. The instrument was zeroed and calibrated daily but not checked against any other instrument on the ship or aircraft.

These measurements presented some major difficulties for any conceptual model of the nitrogen chemistry. The NO_x concentrations were very high for air that had been over the ocean for more than five days. The lifetime with respect to conversion to HNO_3 should have been on the order of one day; after five days, most of the nitrogen should have been in the form of nitrate. However, according to these measurements, 75% of the nitrogen at the surface was in the form of NO_x. Also there should have been vigorous ozone production at these NO_x levels (provided there were hydrocarbons available), but the measured ozone was extremely low. The measurement data for this comparison had, therefore, to be viewed with some caution.

The LLNL, Harvard, and MPI models generated NO_x concentrations for the comparisons; the Harvard model also included PAN chemistry. We included total reactive nitrogen NO_x + PAN in the comparisons against the measured NO_x. This was particularly valid as the NO_x analyzer responded at least partially to PAN.

Comparisons and discussion.

The measured NO_x was very high compared to the results from all three models. The MPI and LLNL models had converted the bulk of the nitrogen to stable nitrate and were unable to maintain concentrations of NO_x similar to those measured. The Harvard model converted a large amount of the NO_x to PAN and the subsidence of air from aloft kept the surface PAN concentrations high. The comparisons of the NO_x + PAN from the model with the NO_x measurements agreed well not only at Bermuda but also at several points along the course from Virginia, suggesting that the instrument may well have been measuring appreciable amounts of PAN. However, this agreement was tempered by two observations: The Harvard model predicted a strong diurnal variation in NO_x + PAN that was not seen in the measurements and the predicted PAN concentrations were much higher than those measured over the western North Atlantic Ocean.

The differences between the measured and the modeled NO_x were large. Even the agreements with the Harvard model took place with very high PAN concentrations. Including the PAN chemistry in the LLNL and MPI models would have helped to bring the models and measurements closer but the exact changes were unlikely to be large enough to explain the discrepancies.

Given the huge differences between the measured and modeled NO_x but the similarities in the NO_y data, a major priority became to improve the measurement data base. Such unusually high NO_x concentrations needed to be checked, preferably using a technique capable of separately determining NO, NO_2, and PAN. Had we used a model with a more comprehensive chemistry (such as an RADM or STEM II), we could have removed some doubt as to whether the discrepancies were only a result of incomplete model chemistry, which would have provided a little more insight into this problem.

3.4.5 The total nitrate comparisons

The data.

There were systems to measure particulate and volatile nitrate on the ship and the aircraft. In view of the sampling problems associated with nitrate in the presence of sea-salt (see Church et al., 1991; Savoie and Prospero, 1982), only total nitrate was determined. In this comparison, we used a single ship-based data set; this data agreed extremely well with data from two other systems on the ship throughout the comparison period. The filter samples from the ship and from the aircraft were analyzed in the same laboratory so there were no systematic differences between the ship's and aircraft's data sets.

We were concerned about the sampling systems. The ship sampler had already been shown to undersample very large sea-salt particles. Since particulate nitrate is found in higher concentrations on large particles, this could have resulted in an underestimate of nitrate. A much more serious concern was the sampling system on the aircraft. Huebert et al. (1990) report that inlet systems similar to the one used on the aircraft can remove substantial amounts of aerosol prior to sampling. Two observations caused us to treat the data cautiously: The nitrate measurements from aloft were of the same order as those of Huebert and Lazrus (1980) over the Pacific Ocean, whereas we expected more over the Atlantic where there is more total odd nitrogen. The comparison of the ship's data to the aircraft measurements at 150 m showed that much smaller concentrations were measured from the aircraft. This might have been caused by the nitrate being on very large particles and thus having a very strong vertical gradient, but it might also have been caused by sampling problems aboard the aircraft.

Ozone

Ozone was measured from the ship by a Dasiki model 1008-AA photometric analyzer (Piotrowicz et al., 1990) and from the aircraft by a thermo Environmental Instrument model 49 photometric analyzer (Ray et al., 1990b). A number of intercomparisons made during the measurement period showed extremely good agreement between these analyzers (Boatman et al., 1990).

Comparisons and discussion.

Both the LLNL and MPI models generated nitric acid as their most oxidized nitrogen product. We compared these predictions with measured total nitrate. The LLNL model predicted surface concentrations similar to the measured ones. However, the LLNL model predicted much more nitrate aloft, consistent with the conversion of most nitrogen to NO_3^-. This contrasted sharply with the Pacific Ocean data where the same model agreed to within a factor of two with the nitrate measurements from the aircraft of Huebert and Lazrus (1980) (see Penner et al., 1991a). The MPI model consistently predicted much more nitrate than was observed.

The models predicted increases of NO_3^- with altitude in keeping with their predictions of higher NO_y aloft and the conversion of nitrogen to NO_3^-. They were unable to match either the observed concentrations aloft or any decreases with altitude. Including the PAN chemistry in the model would have lessened these differences but not nearly enough to explain the observations.

Our whole comparison was clouded by concerns regarding the quality of the data on nitrate above the surface. Clearly, more nitrate and PAN measurements were needed aloft, and the question of sampling integrity needed to be addressed.

3.4.6 The ozone comparisons

The data.

Good quality ozone measurements were obtained aboard the aircraft and the ship during this period. The intercomparisons of the instruments on several flybys showed that they were directly comparable.

The concentrations were somewhat unusual in that they were lower than the monthly averages measured on Bermuda and lower than the previous North Atlantic Ocean measurements.

Comparisons and discussion.

Only the MPI and Harvard models computed ozone concentrations. Ray et al. (1990b) show a very strong concentration gradient in O_3 concentration with altitude. Given the limited altitude data and the difficulty in comparing concentrations under such a strong gradient, we tried only a surface comparison. Both model predictions were higher than the shipboard measurements but agreed well with the one-month averages on Bermuda, as expected. This continued to point to problems with the NO_x comparisons. It was difficult to reconcile the large discrepancies between the modeled and the measured NO_x with the close agreement in ozone.

3.4.7 The OH comparisons

The key radical in the oxidation of NO_x to nitrate is the hydroxyl radical, OH. This oxidation can be direct through the production of HNO_3 or indirect through the production of secondary radicals leading to organic nitrates.

The Harvard and LLNL models calculated OH-radical concentrations in very different ways, which led to different concentration fields. We compared calculated OH concentrations from these models (Table 13) to see the extent to which they differed and to see if these differences showed up in NO_x-to-nitrate ratios. The LLNL model prescribed a 2-dimensional field that was zonally averaged and calibrated against the measured distribution of CH_3CCl_3. The Harvard model computed the OH on line using a photochemical mechanism. The OH calculated by the Harvard model agreed well with the LLNL model results and the zonal average concentrations over the continent. The Harvard concentrations decreased by up to a factor of 2 as the grid moved over the ocean. The MPI model also predicted higher OH concentrations over the continent than over the ocean but its concentrations were three to six times greater than those from the Harvard model. Thus, there were significant differences in the model-calculated OH concentrations. The lower NO_x-to-NO_y ratios from the MPI model compared to those from the LLNL model resulted of these differences.

3.4.8 Conclusions and recommendations

The current models generally predicted NO_y concentrations that agreed reasonably well with good quality measurements. However, the models predicted an increase in NO_y concentrations with altitude whereas the measurements indicated a decrease.

There were difficulties with the way in which the nitrogen was partitioned into NO_x and nitrate. The measurements showed NO_x concentrations that were too

Table 13.--Monthly averages of calculated OH concentrations in surface air (10^6 molec cm^{-3})

Latitude °N	LLNL (July)	Harvard (June) 65°W (ocean)	Harvard (June) 85°W (continent)
47	0.95	0.2-0.5	0.2-0.5
42	1.1	0.5-1	1-1.5
38	1.2	0.5-1	1-1.5
33	1.3	0.5-1	1-1.5
29	1.3	0.5-1	1-1.5
24	1.4	0.5-1	1-1.5
20	1.4	0.5-1	1-1.5
16	1.4	1-1.5	1-1.5

high to be maintained by the models; on the other hand, the nitrate measurements aloft were much lower than the models could accommodate. In comparison with the differences between the models and the measurements, the differences between the models were small.

More measurements were required to resolve the discrepancies that arose in this study. We recommended that these be made with multiple redundant techniques and with a good deal of consideration to sampling integrity. The more important measurement would be of NO_x. A full speciation into NO and NO_2 with the accompanying PAN measurements is essential. Measurements of these species must be made at the surface and vertical profiles must be determined. We also needed more NO_y measurements at higher altitudes to ascertain if concentrations do increase, as the models predicted.

The techniques for measuring aerosol NO_3^-/gaseous nitrate measurements from aircraft needed to be improved. Our major concern was the sampling efficiency of the aerosol inlet systems on the aircraft. Until this concern is dealt with, it will be difficult to interpret NO_y partitioning.

3.5 The Advection of Sulfur and Nitrogen from North America

For this case study, we analyzed the results from the regional-scale episodic models (the RADM and the STEM) covering several periods that corresponded to periods of spring storms and summer clear-air conditions. The episodes analyzed by the RADM were in 8/79, 4/81, and 9/83 and those analyzed by the STEM were in 6/84 and 5/85. Although the episodes analyzed by the two models were for different years with no common dates, the simulations covered qualitatively similar periods (i.e., 3 spring storms in 4/81 and 1 in 5/85 and summer clear conditions in 8/79, 9/83, and 6/84).

Table 14 clearly shows strong variations in coastal fluxes for all model calculations from event to event and zone to zone. Under all conditions, much of the flux moved into the North Atlantic Ocean between North Carolina and New Hampshire. This agreed with earlier empirical estimates by Galloway and Whelpdale (1980). Although it is not shown here, these models also indicated that much of this flux was exported from the continent in the upper air, not in the relatively more polluted surface mixed layer.

We also compared total sulfur and nitrogen flux estimates from these two models to other results (Table 15). The ranges in Table 15 are for individual episodes (two for STEM and seven for RADM) and reflect the variabilities of the net exports of nitrogen and sulfur during different meteorological episodes.

These estimates could be compared to those available from the analyses based on observations and the other model studies (Bischoff et al., 1984; Brost et al., 1988; Fay et al., 1986; Galloway and Whelpdale, 1980, 1987; Galloway et al., 1984; and Shannon and Lescht, 1986). Extrapolated fluxes from the episodic models were consistent with these values. (An estimate of the nitrogen flux to the North Atlantic Ocean from the GFDL model [Levy and Moxim, 1987] also appears in Table 15. This value of 1.1 Tg yr^{-1} was consistent with estimates from the episodic models.)

The ranges of total sulfur fluxes overlapped each other well. Except for the STEM cases with only two episodes, all other data showed a deviation from the mean at about 50% of the mean. More thorough and extensive calculations

Table 14.--Sulfur and nitrogen flux estimates into the Atlantic Ocean for the RADM and STEM (g hr^{-1})

Zones	Spring storm events		Summer clear-air conditions	
	RADM	STEM	RADM	STEM
		Nitrogen		
1. Model domain top to Canada/US border	4.0×10^7		2.9×10^7	
2. Canada/US border to New Hampshire	7.8×10^7	3.9×10^7	3.6×10^7	1.2×10^8
3. New Hampshire to Maryland	1.1×10^8	9.0×10^7	3.9×10^7	1.0×10^8
4. Virginia to mid-South Carolina	5.6×10^7		1.2×10^7	1.6×10^7
5. Mid-South Carolina to Florida/Georgia border	4.4×10^7		2.1×10^6	1.4×10^7
		Sulfur		
1. Model domain top to Canada/US border	9.4×10^7		9.8×10^7	
2. Canada/US border to New Hampshire	1.7×10^8	8.0×10^7	1.0×10^8	3.3×10^8
3. New Hampshire to Maryland	2.9×10^8	2.0×10^8	1.2×10^8	1.7×10^8
4. Virginia to mid-South Carolina	1.3×10^8		5.3×10^7	4.8×10^7
5. Mid-South Carolina to Florida/Georgia border	8.1×10^7		1.1×10^7	2.5×10^7

Notes: RADM spring-storm results were averages of three 4/81 storms; STEM results were from one 5/85 storm. RADM summer-clear-air results were averages of two events (8/79 and 9/83); STEM results were from one event in 6/84.

would have been needed to refine these estimates. The GFDL (3-dimensional, global) model estimate of nitrogen flux was on the low side of other estimates but not out of the ranges. This level of agreement was somewhat surprising in view of the diversity of the estimation procedures. Further studies using newer models and more data were certainly needed.

Table 15.--Sulfur and nitrogen fluxes into the North Atlantic Ocean's atmosphere from North America (10^{12} g yr^{-1})

	Sulfur	Nitrogen
STEM	2.7-4.9	1.0-2.2
RADM	2.63-8.4	1.1-4.6
GFDL model		1.1
Galloway and Whelpdale, 1987	3 -4	0.8-1.2

4. THE CONCLUSIONS

We compiled data on horizontal and vertical distributions of sulfur and nitrogen species and their rates of deposition in the North Atlantic Ocean region. In five case studies, we compared these data to the estimates produced by climatological and event models: (1) sulfur distributions and deposition, (2) nitrate distributions and deposition, (3) vertical and horizontal distributions of NO_y, (4) spatial and temporal trends in DMS emissions, and (5) advections of sulfur and nitrogen to the North Atlantic Ocean's atmosphere from North America.

From these case studies, we drew several conclusions:

1. The sulfur case study clearly illustrated how the measurement and modeling communities could help each other understand the global sulfur cycle. For example, the SO_2 concentration fields predicted by the Stockholm and Oslo models differed significantly from those predicted by the LLNL model. Our comparisons were handicapped by the dearth of SO_2 data in both the source areas and over the North Atlantic Ocean. Nonetheless, the concentrations predicted by the episodic Oslo model combined with those of the regional models (the STEM and RADM) provided useful information about probable SO_2 fields. In the future, the bridges between the regional and global models and between the climatological and episodic models should be increasingly valuable.

2. The nitrate case study showed that any comparisons between the results for a single year from a climatological model and the measurements from a single year, or even several years, should be interpreted with great care. Our comparisons would have been far more informative if either they had taken into account the differences between the meteorology and the precipitation used in the models and the actual meteorology and precipitation for a specific year or they had compared multiple years of simulation with multiple years of observations. Obviously, we should strive towards this goal in the future.

3. The differences between the results from various models could sometimes be reconciled by considering the differences in the model treatments (i.e., source strengths, deposition velocities, etc.). When these differences were considered, we found, in some cases, a reason-

able agreement with measured concentrations given the limitations of the data. However, a time series with a more complete suite of measured NO_y species would allow for a better test of a model's physics.

4. The current models generally predicted NO_y concentrations that agreed reasonably well with good quality (surface-based) measurements. However, the models also predicted increases in NO_y concentration with altitude whereas the measurements indicated decreases.

5. There were difficulties with the ways in which the nitrogen was partitioned into NO_x and nitrate in both models and measurements. The measurements produced NO_x concentrations that were too high to be maintained by the models; on the other hand, the nitrate measurements aloft were much lower than the models could accommodate. The differences between models were small compared to the differences between the models and the measurements.

From these conclusions, we arrived at the following recommendations:

1. Temporally and spatially distributed measurements should be taken to be used in comparisons with climatological models. Only one site had a long record of $SO_4^=$ concentrations (Barbados) or of deposition (Bermuda). Data from at least three to five stations with long-term sampling records would have greatly assisted our model interpretations. The models predicted 2- to 3-dimensional fields, 2- and 3-dimensional data fields should have been available for comparisons. This would require vertical profiles as well as surface measurements.

2. The number of parameters used in comparisons must be extended. For example, useful comparisons could be made of various statistical properties of flux and precipitation data, not just the averages.

3. Further DMS measurements should be taken so that its seasonal cycle can be characterized. Except for the data of Berresheim et al. (1991), too few data existed to resolve the seasonal variations in the DMS values for the North Atlantic Ocean satisfactorily; the data from the central North Atlantic Ocean were also extremely sparse. Measurements also need to be taken in the central North Atlantic Ocean during several seasons to determine if DMS fluxes there are similar to those from the Pacific to ascertain if the extrapolation of the Pacific data is reasonable.

4. Covariances of oceanic DMS concentrations and piston velocities (i.e., wind speed) should be determined to test the validity of using Equation 3 to calculate mean fluxes from mean Cw multiplied by a Vp determined from climatological wind speed.

5. The techniques for measuring aerosol nitrate from an aircraft should be improved. Our major concern was the sampling efficiency of the aerosol inlet system on the aircraft. Until this concern is dealt with, it will be difficult to interpret the partitioning of NO_y.

5. ACKNOWLEDGMENTS

The authors thank Tamara Gardner for her excellent and highly professional assistance in the organization and operation of the workshop that lead to this paper and the willing help from the always efficient staff of the Bermuda Biological Station for Research, Inc., where the workshop was held. The authors are especially grateful to Mary-Scott Kaiser for her organization of the workshop, her editing of the manuscript, and her never-ending supply of good humor. Our thanks also to Brenda Morris for her incredible patience and willingness to do whatever needed to be done. This manuscript is a contribution to the WATOX program and the GPCP, both funded by NOAA; to AEROCE, funded by the National Science Foundation; and to BBSR. The contributions from Max Planck Institute for Chemistry and Stockholm University were part of the EUROTRAC subproject GLOMAC.

6. REFERENCES

Altabet, M. A., 1989. Time-series study of the vertical structure of nitrogen and particle dynamics in the Sargasso Sea. *Limnol. Oceanogr.* 34:1185-1201.

Andreae, M. O., 1986. The ocean as a source of atmospheric sulphur compounds. In *The Role of Air-Sea Exchange in Geochemical Cycling*. P. Buat-Menard (Ed.), Reidel, Dordrecht, 331-362.

Andreae, M. O., and H. Raemdonck, 1983. Dimethyl sulfide in the surface ocean and the marine atmosphere: A global view. *Science* 221:744-748.

Atherton, C. S., J. E. Penner, and J. J. Walton, 1990. Tropospheric ozone production in a global, three-dimensional chemistry-transport deposition model. Poster paper, International Symposium of the Commission on Atmospheric Chemistry and Global Pollution, September 5-11, 1990. Chamrouse, France.

Atkinson, R., A. Lloyd, and L. Winges, 1982. An updated chemical mechanism for hydrocarbon/NO_x/SO_2 photooxidations suitable for inclusion in atmospheric simulation models. *Atmos. Environ.* 16:1341-1355.

Baker, M. B., and R. J. Charlson, 1990. Bistability of CCN concentrations and thermodynamics in the cloud-topped boundary layer. *Nature* 345:142-145.

Balkanski, Y., D. Jacob, R. Arimoto, and M. Kritz, 1989. General circulation model simulations of ^{222}Rn transport across the North Pacific. *EOS* 70:1024-1030.

Ball, R. J., and G. D. Robinson, 1982. The origin of haze in the central United States and its effect on solar radiation. *J. Appl. Meteorol.* 21:171-188.

Barnard, W. R., M. O. Andreae, W. E. Watkins, H. Bingemer, and H. W. Georgii, 1982. The flux of dimethylsulfide from the ocean to the atmosphere. *J. Geophys. Res.* 87:8787-8793.

Bates, T. S., J. D. Cline, R. H. Gammon, and S. R. Kelly-Hansen, 1987. Regional and seasonal variations in the flux of oceanic dimethylsulfide to the atmosphere. *J. Geophys. Res.* 92:2930-2938.

Berresheim, H., M. O. Andreae, R. L. Iverson, and S. M. Li, 1991. Seasonal variations of dimethylsulfide emissions and atmospheric sulfur and nitrogen species over the western north Atlantic Ocean. *Tellus* 43B:353-372.

Bingemer, H., 1984. Dimethylsulfid in Ozean und mariner Atmosphare: Experimentelle Untersuchung einer natuerlichen Schwefelquelle fuer die Atmosphaere. Ph.D. dissertation, J. W. Goethe University, Frankfurt, 159 pp.

Bischoff, W. D., V. L. Patterson, and F. T. Mackenzie, 1984. Geochemical mass balance for sulfur- and nitrogen-bearing components: Eastern United States. In *Geological Aspects of Acid Deposition, Acid Precipitation Ser.*. O. P. Bricker (Ed.), Butterworth, Boston, 7:1-20.

Boatman, J. F., W. C. Keene, M. Luria, J. D. Ray, C. A. Bardwell, K. Gorzelska, M. Fennell, D. R. Hastie, A. A. P. Pszenny, and D. Whelpdale, 1990. An intercomparision of the chemical and meteorological data generated from aircraft and shipboard sampling during GCE/CASE/WATOX. NOAA Tech. Memo. ERL ARL-186, NOAA Environmental Research Laboratories, Boulder, Colo, 26 pp.

Bottenheim, J. W., and A. J. Gallant, 1987. The occurrence of peroxyacetyl nitrate over the Atlantic Ocean east of North America during WATOX-86. *Global Biogeochem. Cycles* 1:369-380.

Broecker, W. S., and T.-H. Peng, 1982. *Tracers in the Sea*. Columbia University Press, Palisades, New York, 690 pp.

Brost, R. A., R. B. Chatfield, J. P. Greenberg, P. L. Haagenson, B. G. Heikes, S. Madronich, B. A. Ridley, and P. R. Zimmerman, 1988. Three-dimensional modeling of transport of chemical species from continents to the Atlantic Ocean. *Tellus* 40B:358-379.

Burgermeister, S., R. L. Zimmermann, H.-W. Georgii, H. G. Bingemer, G. O. Kirst, M. Janssen, and W. Ernst, 1990. On the biogenic origin of dimethylsulfide: Relation between chlorophyll, ATP, organismic DMSP, phytoplankton species and DMS distribution in Atlantic surface water and atmosphere. *J. Geophys. Res.* 95:20,607-20,615.

Carmichael, G. R., L. K. Peters, and T. Kitada, 1986. A second generation Eulerian transport/chemistry/removal model. *Atmos. Environ.* 20:173-188.

Carmichael, G., L. Peters, and R. Saylor, 1991. The STEM-II regional scale acid deposition and photochemical oxidant model: Overview of model development and applications. *Atmos. Environ.* 25:2077-2090.

Carpenter, E. J., 1983. Nitrogen fixation by marine *Oscillatoria* (Trichodesmium) in the word's oceans. In *Nitrogen in the Marine Environment*. E. J. Carpenter and D. G. Capone (Eds.), Academic Press, New York, 65-104.

Carpenter, E. J., J. I. Scranton, P. C. Novelli, and A. Michaels, 1987. Validity of N_2 fixation rate measurements in marine *Oscillatoria* (Trichodesmium). *Limnol. Oceanogr.* 9:1047-1056.

Charlson, R. J., and H. Rodhe, 1982. Factors controlling the acidity of natural rainwater, *Nature* 295:683-685.

Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Warren, 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* 326:655-661.

Charlson, R. J., J. Langner, and H. Rodhe, 1990. Sulphate aerosol and climate. *Nature* 348:22.

Charlson, R. J., S. E. Schwartz, J. M. Hales, R. D. Cess, J. A. Conkley, Jr., J. E. Hansen, and D. J. Hofmann, 1992. Climate forcing by anthropogenic aerosols. *Science* 255:423-430.

Church, T. M., J. M. Tramontano, D. M. Whelpdale, M. O. Andreae, J. N. Galloway, W. C. Keene, A. H. Knap, and J. Tokos, Jr., 1991. Atmospheric and precipitation chemistry over the North Atlantic Ocean: Shipboard results from April-May 1984. *J. Geophys. Res.* 96:18,705-18,725.

Covey, C., S. J. Ghan, J. J. Walton, and P. R. Weissman, 1990. Global environmental effects of impact-generated aerosols: Results from a general circulation model. In *An Interdisciplinary Conference on Impacts, Volcanism, and Mass Mortality*. V. L. Sharpton and P. D. Ward (Eds.), Geological Society of America, Boulder, Colo., 263-270.

Crutzen, P. J., and L. T. Gidel, 1983. A two-dimensional photochemical model of the atmosphere. 2: The tropospheric budgets of the anthropogenic chlorocarbons, CO, CH_4, CH_3Cl and the effects of various NO_x sources on tropospheric ozone. *J. Geophys. Res.* 88:6641-6661.

Delmas, R., 1982. On the emission of carbon, nitrogen and sulfur in the atmosphere during brushfires in the intertropical savannah zones. *Geophys. Res. Lett.* 9:761-764.

Dickerson, R. R., A. C. Delany, and A. F. Wartberg, 1984. Further modifications of a commercial NO_x detector for high sensitivity. *Rev. Sci. Instrum.* 55:1995-1998.

Dignon, J., S. Hameed, J. E. Penner, J. J. Walton, and S. J. Ghan, 1989. Global simulation of ^{222}Rn and ^{210}Pb in a 3-dimensional Lagrangian tracer model. *EOS, Trans. Am. Geophys. Union* 70:1025.

Drummond, J. W., D. W. Ehhalt, and A. Volz, 1988. Measurements of nitric oxide between 0-12 km altitude and 67°N to 60°S latitude obtained during STRATOZ III. *J. Geophys. Res.* 93:15,831-15,849.

Drummond, J. W., C. Castledine, J. Green, R. Denno, G. I. Mackay, and H. I. Schiff, 1989. New technologies for use in acid deposition networks. In *Monitoring Methods for Toxics in the Atmosphere*. W. L. Zielinski (Ed.), American Society for Testing and Materials, ASTM STP 1052,Philadelphia, 5-9.

Duce, R. A., 1986. The impact of atmospheric nitrogen, phosphorous and iron species on marine biological productivity. In *The Role of Air-Sea Exchange in Geochemical Cycling*. P. Buat-Menard (Ed.), Reidel, Dordrecht, 497-529.

Dugdale, R. C., and J. J. Goering, 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. *Limnol. Oceanogr.* 12:196-206.

Elliot, W. P., and R. K. Reed, 1984. A climatological estimate of precipitation of the world oceans. *J. Clim. Appl. Meteorol.* 23:434-439.

Eppley, R. W., and B. W. Peterson, 1979. Particulate organic matter flux and planktonic new production in the deep ocean. *Nature* 282:677-680.

Erickson, D. J., III, S. J. Ghan, and J. E. Penner, 1990. Global ocean-to-air dimethyl sulfide flux. *J. Geophys. Res.* 95:7543-7552.

Erickson, D. J., III, J. J. Walton, S. J. Ghan, and J. E. Penner, 1991. Three-dimensional modeling of the global atmospheric sulfur cycle: A first step. *Atmos. Environ.* 25:2513-2520.

Fahey, D. W., C. S. Eubank, G. Huebler, and F. C. Fehsenfeld, 1985. Evaluation of a catalytic reduction technique for the measurement of total reactive odd-nitrogen NO_y in the atmosphere. *J. Atmos. Chem.* 3:435-468.

Fay, J. A., S. Kumar, and D. Golomb, 1986. Annual and semiannual anthropogenic sulfur budget for eastern North America. *Atmos. Environ.* 20:1497-1500.

Feichter, J., and P. J. Crutzen, 1990. Parameterization of vertical tracer transport due to deep cumulus convection in a global transport model and its evaluation with ^{222}radon measurements. *Tellus* 42B:100-117.

Gallagher, M. S., T. P. Carsey, and M. L. Farmer, 1990. Peroxyacetyl nitrate in the North Atlantic marine boundary layer. *Global Biogeochem. Cycles* 4:297-308.

Galloway, J. N., and D. M. Whelpdale, 1980. An atmospheric sulfur budget for eastern North America. *Atmos. Environ.* 14:409-417.

Galloway, J. N., and D. M. Whelpdale, 1987. WATOX-86 overview and western North Atlantic Ocean S and N atmospheric budgets. *Global Biogeochem. Cycles* 1:261-281.

Galloway, J. N., D. M. Whelpdale, and G. T. Wolff, 1984. The flux of S and N eastward from North America. *Atmos. Environ.* 18:2595-2607.

Galloway, J. N., W. C. Keene, R. S. Artz, J. M. Miller, T. M. Church, and A. H. Knap. 1989. Processes controlling the concentrations of $SO_4^=$, NO_3^-, and NH_4^+, H^+, $HCOO_T$, and $CH3COO_t$ in precipitation on Bermuda. *Tellus* 41B:427-443.

Galloway, J. N., W. C. Keene, A. A. P. Pszenny, D. M. Whelpdale, H. Sievering, J. T. Merrill, and J. F. Boatman, 1990. Sulfur in the western North Atlantic Ocean atmosphere: Results from a summer 1988 ship/aircraft experiment. *Global Biogeochem. Cycles* 4:349-365.

Galloway, J. N., J. E. Penner, C. S. Atherton, J. M. Prospero, H. Rodhe, R. S. Artz, Y. J. Balkanski, H. G. Bingemer, R. A. Brost, S. Burgermeister, G. R. Carmichael, J. S. Chang, R. J. Charlson, S. Cober, W. G. Ellis, Jr., C. J. Fischer, J. M. Hales, D. R. Hastie, T. Iversen, D. J. Jacob, K. John, J. E. Johnson, P. S. Kasibhatla, J. Langner, J. Lelieveld, H. Levy, II, F. Lipschultz, J. T. Merrill, A. F. Michaels, J. M. Miller, J. L. Moody, J. Pinto, A. A. P. Pszenny, P. A. Spiro, L. Tarrason, S. M. Turner, and D. M. Whelpdale, 1992. Sulfur and nitrogen levels in the North Atlantic Ocean's atmosphere: A synthesis of field and modeling results. *Global Biogeochem. Cycles* 2:77-100.

Ghan, S. J., M. C. MacCracken, and J. J. Walton, 1988. Climatic response to large atmospheric smoke injections: Sensitivity studies with a tropospheric general circulation model. *J. Geophys. Res.* 93:8315-8337.

GESAMP-IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP (Joint Group of Experts on the Scientific Aspects of Marine Pollution), 1989. The atmospheric input of trace species to the world ocean. Rep. and Studies No. 38, 111 pp.

Glibert, P. M., 1982. Regional studies of daily, seasonal and size fraction variability in ammonium remineralization. *Mar. Biol.* 70:209-222.

Glover, H. E., B. B. Prezelin, L. Campbell, M. Wyman, and C. Garside, 1988. A nitrate-dependent Synechococcus bloom in surface Sargasso Sea water. *Nature* 331:161-163.

Grassl, H., 1988. What are the radiative and climatic consequences of the changing concentrations of atmospheric particles? In *The Changing Atmosphere*. F. S. Rowland and I. S. H. Isaksen (Eds.), Wiley, Chichester, 281 pp.

Gust, G., 1989. Understanding sediment trap performance: An evolutionary process. In *Sediment Trap Technology and Sampling*. G. A. Knauer and V. Asper (Eds.), U. S. GOFS Planning Rep. 10, U. S. JGOFS Planning Office, Woods Hole, Mass., 82-83.

Hameed, S., and J. Dignon, 1988. Changes in the geographical distribution of global emissions of NO_X and SO_X from fuel combustion between 1966 and 1980. *Atmos. Environ.* 22:941-950.

Hamelin, B., F. E. Grousett, P. E. Biscaye, A. Zindler, and J. M. Prospero, 1989. Lead isotopes in trade wind aerosols at Barbados: The influence of European emissions over the North Atlantic. *J. Geophys. Res.* 94:16,243-16,250.

Hastie, D. R., H. I. Schiff, D. M. Whelpdale, R. E. Peterson, W. H. Zoller, and D. L. Anderson, 1988. Nitrogen and sulphur over the western North Atlantic Ocean. *Atmos. Environ.* 21:2397-2402.

Hastie, D. R., S. Malle, D. L. Toom, D. M. Whelpdale, W. C. Keene, J. N. Galloway, J. Maben, and A. A. P. Pszenny, 1990. Inorganic nitrogen over the Western North Atlantic Ocean. *Global Biogeochem. Cycles* 4:267-278.

Huebert, B. J., 1988. The partitioning of nitrate between aerosol and vapor in remote marine areas. *EOS, Trans. Am. Geophys. Union* 69:1075.

Huebert, B. J., and A. L. Lazrus, 1980. Tropospheric gas-phase and particulate nitrate measurements. *J. Geophys. Res.* 85:7322-7328.

Huebert, B. J., G. Lee, and W. L. Warren, 1990. Airborne aerosol inlet passing efficiency measurement. *J. Geophys. Res.* 95:16,369-16,381.

Isemer, H.-J. and L. Hasse, 1985. *The Bunker Atlas of the North Atlantic Ocean*. Springer-Verlag, Berlin, 225 pp.

Iversen, T., 1989. Numerical modeling of the long range atmospheric transport of sulphur dioxide and particulate sulphate to the Arctic. *Atmos. Environ.* 23:2571-2595.

Jackson, G. A., 1988. Implications of high dissolved organic matter concentrations for oceanic properties and processes. *Oceanography* 1:28-33.

Jacob, D., E. Gottleib, and M. Prather, 1989. Chemistry of polluted cloudy boundary layer. *J. Geophys. Res.* 94:12,975-13,002.

Jaeger, L., 1983. Monthly and aereal patterns of mean global precipitation. In *Variations in the World Water Budget*. A. Street-Perrott, M. Beran, and R. Ratcliffe (Eds.), Reidel, Dordrecht, 129-140.

Jenkins, W. J., and J. C. Goldman, 1985. Seasonal oxygen cycling and primary production in the Sargasso Sea. *J. Mar. Res.* 43:465-491.

Kasibhatla, P. S., H. Levy, II, W. J. Moxim, and W. L. Chameides, 1991. The relative impact of stratospheric photochemical production of tropospheric NO_y levels: A model study. *J. Geophys. Res.* 96:18,631-18,646.

Keeler, G. J. and P. J. Samson, 1989. Spatial representativeness of trace element ratios. *Environ. Sci. Technol.* 23:1358-1364.

Keeling, C. D., 1973. Industrial production of carbon dioxide for fossil fuels and limestone. *Tellus* 25:174-198.

Knap, A., T. Jickells, A. Pszenny, and J. Galloway, 1986. Significance of atmospheric-derived fixed nitrogen on productivity of the Sargasso Sea. *Nature* 320:158-160.

Knauer, G. A., J. H. Martin, and K. W. Bruland, 1979. Fluxes of particulate carbon, nitrogen and phosphorus in the upper water column of the northeast Pacific. *Deep-Sea Res.* 26:97-108.

Langner, J., and H. Rodhe, 1990. Anthropogenic impact on the global distribution of atmospheric sulphate. In *Global and Regional Environmental Atmospheric Chemistry*. L. Newman, W. Wang, and C. S. Kiang (Eds.), U.S. Dept. of Energy, Washington, D.C., 106-117.

Leck, C., and H. Rodhe, 1991. Emissions of marine biogenic sulfur to the atmosphere of northern Europe, *J. Atmos. Chem.* 12:63-86.

Levy II, H., and W. J. Moxim, 1987. The fate of US and Canadian combustion nitrogen emissions. *Nature* 328:414-416.

Levy II, H., and W. J. Moxim, 1989a. Influence of long-range transport of combustion emissions on the chemical variability of the background atmosphere. *Nature* 338:326-328.

Levy II, H., and W. J. Moxim, 1989b. Simulated global distribution and deposition of reactive nitrogen emitted by fossil fuel combustion. *Tellus* 41B:256-271.

Liss, P. S., and L. Merlivat, 1986. Air-sea gas exchange rates. In *The Role of Air-Sea Exchange in Geochemical Cycling*. P. Buat-Menard (Ed.), Reidel, Dordrecht, 113-127.

Liu, S. C., M. Trainer, F. C. Fehsenfeld, D. D. Parrish, E. J. Williams, D. W. Fahey, G. Hobler, and P. C. Murphy, 1987. Ozone production in the rural troposphere and the implications for regional and global ozone distributions. *J. Geophys. Res.* 92:4191-4197.

Logan, J. A., 1985. Tropospheric ozone: Seasonal behavior trends and anthropogenic influence. *J. Geophys. Res.* 90:10,463-10,482.

Longhurst, A. R., and W. G. Harrison, 1988. Vertical nitrogen flux from the oceanic photic zone by diel migrant zooplankton and nekton. *Deep-Sea Res.* 35:881-889.

Luke, W. T., and R. R. Dickerson, 1987. The flux of reactive nitrogen compounds from eastern North America to the western Atlantic Ocean. *Global Biogeochem. Cycles* 1:329-343.

Luria, M., C. C. Van Valin, J. F. Boatman, D. L. Wellman, and R. F. Pueschel, 1987. Sulfur dioxide flux measurements over the western Atlantic Ocean. *Atmos. Environ.* 21:1631-1636.

Luria, M., C. C. Van Valin, W. C. Keene, D. L. Wellman, J. N. Galloway, and J. F. Boatman, 1988. Eastward sulfur flux from the northeastern United States. *Atmos. Environ.* 22:1847-1854.

Mackey, W. A., 1957. The rainfall of Bermuda. Tech Note 8, Bermuda Meteorological Office, Hamilton, 59 pp.

Manabe, S., and J. L. Holloway, Jr., 1975. The seasonal variation of the hydrologic cycle as simulated by a global model of the atmosphere. *J. Geophys. Res.* 80:1617-1649.

Manabe, S., D. G. Hahn, and J. L. Holloway, Jr., 1974. The seasonal variation of the tropical circulation as simulated by a global model of the atmosphere. *J. Atmos. Sci.* 31:43-83.

Martin, J. H., and S. E. Fitzwater, 1988. Iron deficiency limits phytoplankton growth in the northeast Pacific sub-Arctic. *Nature* 331:341-343.

Martinez, L., M. W. Silver, J. M. King, and A. L. Alldredge, 1983. Nitrogen fixation by floating diatom mats: A source of new nitrogen to oligotrophic ocean waters. *Science* 221:152-154.

Maury, M. F., 1857. *The Physical Geography of the Sea.* Harper, New York, 360 pp.

Menzel, D. W., and J. H. Ryther, 1961. Annual variations in primary production of the Sargasso Sea off Bermuda. *Deep-Sea Res.* 7:282-288.

Merrill, J. T. and W. C. Graustein, 1989. Large-scale atmospheric transport patterns over the North Atlantic. Paper, AGU Fall Annual Meeting, San Francisco, Dec. 4-8 (abstract in *EOS* 70:1038).

Merrill, J. T., M. Uematsu, and R. Bleck, 1989. Meteorological analysis of long range transport to the Pacific Ocean. *J. Geophys. Res.* 94:8584-8598.

Meserve, J. M., 1974. *U.S. Navy Marine Climatic Atlas of the World: Vol. 1, North Atlantic Ocean.* NAVAIR 50-IC-528, Naval Air Systems Command, Washington, D. C., 385 pp.

Michaels, A. F., and M. W. Silver, 1988. Primary production, sinking flux and the microbial food web. *Deep-Sea Res.* 35:473-490.

Michaels, A. F., M. W. Silver, M. M. Gowing, and G. A. Knauer, 1990. Cryptic zooplankton "swimmers" in upper ocean sediment traps. *Deep-Sea Res.* 37:1285-1296.

Miller, J. M., 1987. The use of back air trajectories in interpreting atmospheric chemistry data: A review and bibliography. NOAA Tech Memo. ERL/ARL-155, NOAA Environmental Research Laboratories, Silver Spring, Md., 28 pp.

Miller, J. M., and J. Harris, 1985. The flow climatology to Bermuda and its implications for long-range transport. *Atmos. Environ.* 19:409-414.

Moody, J. L., and J. N. Galloway, 1988. Quantifying the relationship between atmospheric transport and the chemical composition of precipitation on Bermuda. *Tellus* 40B:463-479.

Oort, A. H., 1983. Global atmospheric circulation statistics, 1958-1973. NOAA Tech. Rep. 1983-407-474, U.S. Govt. Printing Office, Washington, D.C., 180 pp.

Paerl, H. W., 1985. Enrichment of marine primary production by nitrogen enriched acid rain. *Nature* 315:747-749.

Penner, J. E., C. S. Atherton, J. J. Walton, and S. Hameed, 1990. The global cycle of reactive nitrogen. In *Global and Regional Environmental Atmospheric Chemistry*. L. Newman, W. Wang, and C. S. Kiang (Eds.), U.S. Dept. of Energy, Washington, D.C., 264-279.

Penner, J. E., C. S. Atherton, J. Dignon, S. J. Ghan, J. J. Walton, and S. Hameed, 1991a. Tropospheric nitrogen: A three-dimensional study of sources, distributions, and deposition. *J. Geophys. Res.* 96:959-990.

Penner, J. E., S. J. Ghan, and J. J. Walton, 1991b. The role of biomass burning in the budget and cycle of carbonaceous soot aerosols and their climate impact. In *Global Biomass Burning*. J. Levine (Ed.), MIT Press, Cambridge, Mass., 387-393.

Piotrowicz, S. R., C. J. Fischer, and R. S. Artz, 1990. Ozone and carbon monoxide over the North Atlantic during a boreal summer. *Global Biogeochem. Cycles* 4:215-224.

Pitcher, E. J., R. C. Malone, V. Ramanathan, M. L. Blackmon, K. Puri, and W. Bourke, 1983. January and July simulations with a spectral general circulation model. *J. Atmos. Sci.* 40:580-604.

Poirot, R. L., and P. R. Wishinsky, 1986. Visibility, sulfate and air mass history associated with the summertime aerosol in northern Vermont. *Atmos. Environ.* 20:1457-1469.

Prather, M., M. McElroy, S. Wofsy, G. Russell, and D. Kind, 1987. Chemistry of the global troposphere: Fluorocarbons as tracers of air motion. *J. Geophys. Res.* 92:6579-6613.

Prospero, J. M., 1989. The Atmospheric Ocean Chemistry Experiment (AEROCE): An overview. *EOS, Trans. Am. Geophys. Union* 70:1038.

Prospero, J. M., D. L. Savoie, and R. T. Nees, 1989. Aerosol nitrate and non-sea-salt sulfate concentrations in surface level air over the North Atlantic Ocean. (Abstract) *EOS, Trans. Am. Geophys. Union* 70:1038.

Pszenny, A. A. P., G. R. Harvey, C. J. Brown, R. F. Lang, W. C. Kenne, J. N. Galloway, and J. T. Merrill, 1990. Measurements of dimethyl sulfide oxidation products in the summertime North Atlantic marine boundary layer. *Global Biogeochem. Cycles* 4:367-379.

Pszenny, A. A. P., R. S. Artz, J. F. Boatman, and J. N. Galloway, 1990a. Overview of the 1988 GCE/CASE/ WATOX studies of biogeochemical cycles in the North Atlantic region. *Global Biogeochem. Cycles* 4:121-131.

Ray, J. D., M. Luria, D. R. Hastie, S. Malle, W. C. Keene, and H. Sievering, 1990a. Losses and transport of odd nitrogen species over the Western Atlantic Ocean during CASE/WATOX. *Global Biogeochem. Cycles* 4:267-278.

Ray, J. D., C. C. Van Valin, M. Luria, and J. F. Boatman, 1990b. Oxidants in the marine troposphere: H_2O_2 and O_3 over the Western Atlantic Ocean. *Global Biogeochem. Cycles* 4:201-214.

Reed, R. K., 1980. Comparison of ocean and island rainfall in the tropical North Pacific. *J. Appl. Meteorol.* 19:877-880.

Rudolph, J., B. Vierkorn-Rudolph, and F. X. Meixner, 1987. Large-scale distribution of peroxyacetylnitrate results from the STRATOZ III flights. *J. Geophys. Res.* 92:6653-6661.

Savoie, D. L., and J. M. Prospero, 1982. Particle size distribution of nitrate and sulfate in the marine atmosphere. *Geophys. Res. Lett.* 9:1207-1210.

Savoie, D. L., and J. M. Prospero, 1989. Comparison of oceanic and continental sources of non-sea-salt sulphate over the Pacific Ocean. *Nature* 339:685-687.

Savoie, D. L., J. M. Prospero, and E. S. Saltzman, 1989. Non-sea-salt sulfate and nitrate in trade wind aerosols at Barbados: Evidence for long-range transport. *J. Geophys. Res.* 94:5069-5080.

Schwartz, S. E., 1989. Sulphate aerosols and climate (Scientific Correspondence). *Nature* 340:515-516.

Scranton, M. I., P. C. Novelli, A. F. Michaels, S. Horrigan, and E. J. Carpenter, 1987. Hydrogen production and nitrogen fixation by *Oscillatoria thiebauti* during *in situ* incubations. *Limnol. Oceanogr.* 32:998-1006.

Semb, A., 1985. A circumpolar SO_2 emission survey. NILU OR 69/85. The Norwegian Institute for Air Research, Lillestrøm, Norway, 14 pp.

Shannon, J. D., and M. M. Lescht, 1986. Modelled trends and climatological variability of the net transboundary mass flux of airborne sulfur between the United States and Canada. Paper, Specialty Conference on Meteorology of Acidic Deposition, Air Pollution Control Association, March 18, Albany, New York.

Slutz, R. J., S. J. Lubker, S. D. Woodruff, R. L. Jenne, D. H. Joseph, P. M. Steurer and J. D. Elms, 1985. Comprehensive ocean-atmosphere data set, release 1. NOAA Climate Research Program, USGPO # 1985-579606, U.S. Government Printing Office, Boulder, Colo.

Smolarkiewicz, P. K., 1983. A simple positive definite advection scheme with small implicit diffusion. *Mon. Weather Rev.* 111:479-486.

Spitzer, W. S., and W. J. Jenkins, 1989. Rates of vertical mixing, gas exchange and new production: Estimates from seasonal gas cycles in the upper ocean near Bermuda. *J. Mar. Res.* 47:169-196.

Spivakovsky, C. M., R. Yevich, J. A. Logan, S. C. Wofsy, M. B. McElroy, and M. J. Prather, 1990. Tropospheric OH in a three-dimensional chemical tracer model: An assessment based on observations of CH_3CCl_3. *J. Geophys. Res.* 95:18,441-18,471.

Staubes, R., H. W. Georgii, and S. Burgermeister, 1990. Biogenic sulfur compounds in seawater and the marine atmosphere. In *Physico-Chemical Behaviour of Atmospheric Pollutants*. G. Rostelli and G. Angeletti (Eds.), Kluwer, Dordrecht, 686-692.

Stockwell, W. R., 1986. A homogeneous gas phase mechanism for use in a regional acid deposition model. *Atmos. Environ.* 20:1615-1632.

Sugimura, T., and Y. Suzuki, 1988. A high temperature catalytic oxidation method for nonvolatile dissolved organic carbon in seawater by direct injection of liquid samples. *Mar. Chem.* 24:105-131.

Sundquist, E. T., 1985. Geological perspectives on carbon dioxide and the carbon cycle. In *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present*. E. T. Sundquist and W. S. Broecker (Eds.), American Geophysical Union, Washington, D.C., 5-59.

Suzuki, Y., T. Sugimura, and T. Itoh, 1985. A catalytic oxidation method for the determination of total nitrogen dissolved in seawater. *Mar. Chem.* 16:83-97.

Thornton, D. C., A. R. Bandy, and A. R. Driedger, III, 1987. Sulfur dioxide over the western Atlantic Ocean. *Global Biogeochem. Cycles* 1:317-328.

Tucker, G. B., and R. G. Barry, 1984. Chapter 2, Volume Climate of the North Atlantic Ocean. In *World Survey of Climatology*. H. Van Loon (Ed.), Elsevier, Amsterdam, 15:193-262.

Turner, S. M., G. Malin, P. S. Liss, D. S. Harbour, and P. M. Halligan, 1988. The seasonal variation of dimethyl sulfide and dimethylsulfoniopropionate concentrations in nearshore waters. *Limnol. Oceanogr.* 33:364-375.

Walton, J. J., M. C. MacCracken, and S. J. Ghan, 1988. A global-scale Lagrangian trace species model of transport, transformation and removal process. *J. Geophys. Res.* 93:8339-8354.

Warneck, P., 1988. *Chemistry of the Natural Atmosphere*. Academic Press, New York, 753 pp.

Whelpdale, D. M., W. C. Keene, A. D. A. Hansen, and J. Boatman, 1987. Aircraft measurements of sulfur, nitrogen, and carbon species during WATOX-86. *Global Biogeochem. Cycles* 1:357-368.

Whelpdale, D. M., A. Eliassen, J. N. Galloway, H. Dovland, and J. M. Miller, 1988. The trans-Atlantic transfer of sulfur. *Tellus* 40B:1-15.

Wigley, T. M. L., 1989. Possible climate change due to SO_2-derived cloud condensation nuclei. *Nature* 339:365-367.

Zimmermann, P. H., 1987. MOGUNTIA: A handy tracer model. Proceedings of the 16th NATO/CCMS International Technical Meeting on Air Pollution Modeling and Its Application, Lindau, Germany, April 6-10, 1987. H. van Dop (Ed.), Plenum Press, New York, 593-608.

Zimmermann, P. H., J. Feichter, H. K. Rath, P. J. Crutzen, and W. Weiss, 1989. A global three-dimensional source-receptor model investigation using ^{85}Kr. *Atmos. Environ.* 23:25-35.

Appendix: Authors, Affiliations, and Addresses

Dr. Cynthia Atherton
Dr. Joyce E. Penner
Atmospheric/Geophysic Sciences Div.
Lawrence Livermore National Lab.
P. O. Box 808, L-262
Livermore, CA 94550

Dr. Heinz G. Bingemer
Biogeochemistry Department
Max Planck Institute of Chemistry
Post Office Box 3060
D-6500 Mainz (FRG), Germany

Dr. Richard Brost
Dr. Jos Lelieveld
Atmospheric Chemistry Division
Max Planck Institute of Chemistry
Post Office Box 3060
D-6500 Mainz (FRG), Germany

Dr. Stefan Burgermeister
Institute of Meteorology/Geophysics
J. W. Goethe University
Feldbergstrasse 47
6000 Frankfurt (FRG), Germany

Dr. Gregory R. Carmichael
Dr. Kuruvilla John
125B Chemistry Building
Chemical and Biochemical Engineering
University of Iowa
Iowa City, IA 52242

Dr. Julius S. Chang
Atmospheric Science Research Center
State University of New York
100 Fuller Road
Albany, NY 12205

Dr. Robert J. Charlson
Chemistry Department, AK-40
University of Washington
Seattle, WA 98195

Mr. Stewart Cober
Department of Physics, Room 717
60 St. George Street
Toronto, Ontario, M5S 1A7, Canada

Dr. James N. Galloway
Dr. Jennie L. Moody
Department of Environmental Sciences
University of Virginia, Clark Hall
Charlottesville, VA 22903

Dr. Jeremy M. Hales
Battelle Pacific Northwest Lab.
P. O. Box 999, Mail Stop K6-04
Richland, WA 99352

Dr. Donald R. Hastie
Department of Physics
York University
4700 Keele Street
North York, Ontario M3J 1P3, Canada

Dr. Trond Iversen*
Ms. Leonor Tarrason
The Norwegian Meteorology Institute
P. O. Box 43, Blindern
0313 Oslo, Norway

Dr. Daniel J. Jacob
Mr. Yves J. Balkanski
Mr. Peter A. Spiro
Division of Applied Sciences
Pierce Hall, Harvard University
29 Oxford Street
Cambridge, MA 02138

Dr. James E. Johnson
NOAA/PMEL
7600 Sand Point Way
Seattle, WA 98115

Dr. Hiram Levy, II
Dr. Prasad Kasibhatla
NOAA Geophysical Fluid Dynamics Lab
Box 308
Princeton University
Princeton, NJ 08520

---

*Dr. Iversen is now with the Institute of Geophysics, University of Oslo, P. O. Box 1022, Blindern, 0315 Oslo, Norway.

Dr. Frederick Lipschultz
Dr. Anthony Michaels
Bermuda Biological Station
for Research, Inc.
17 Biological Station Lane
Ferry Reach GE01, Bermuda

Dr. John M. Miller*
Dr. Richard Artz
NOAA ARL R/E/AR
SSMCII, Room 9358
1325 East-West Highway
Silver Spring, MD 20910

Dr. John T. Merrill
Mr. William G. Ellis, Jr.
Atmospheric Chemistry Studies Center
Graduate School of Oceanography
University of Rhode Island
Narragansett, RI 02882-1197

Dr. Joseph Pinto
Atmospheric Research/Exposure
Assessment Laboratory
Environmental Protection Agency, MD-80
Research Triangle Park, NC 27711

Dr. Joseph M. Prospero
Rosenstiel School of Marine and
Atmospheric Sciences
4600 Rickenbacker Causeway
Miami, FL 33149-1098

Dr. A. A. P. Pszenny
Mr. Charles J. Fischer
NOAA/AOML/OCD
4301 Rickenbacker Causeway
Miami, FL 33149

Dr. Henning Rodhe
Mr. Joakim Langner
Department of Meteorology
Stockholm University
S-10691 Stockholm, Sweden

Ms. Suzannne Turner
Environmental Sciences School
University of East Anglia
Norwich NR4 7TJ, United Kingdom

Dr. Douglas M. Whelpdale
Atmospheric Environment Service
4905 Dufferin Street
Downsview, Ontario M3H 5T4, Canada

---

*Dr. Miller is now with the World Meteorological Organization, Environment Division, 41 Giuseppe Motta, Case Postale #2300, CH-1211, Geneva 2, Switzerland.

*U.S. GOVERNMENT PRINTING OFFICE:1993-573-013/89050