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

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Abstract. In April 1990, forty-two 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 ships' tracks and island stations. These data were compared with estimates produced by several climatological and event models for two case studies: (1) sulfate surface distributions and deposition and (2) nitrate surface distributions and deposition. Highlights of the conclusions of the case studies were that the measured concentrations and model results of nitrate and non-sea-salt sulfate depositions appeared to be in good agreement at some locations but in poor agreement for some months at other locations. The case studies illustrated the need for the measurement and modeling communities to interact not only to compare results but also to cooperate in improving the designs of the models and the field experiments.

1. INTRODUCTION

Anthropogenic emissions of sulfur and nitrogen to the global atmosphere have increased substantially over the past century, especially in North America and Europe. As a result, the North Atlantic Ocean is surrounded by large sulfur and nitrogen sources (Figure 1). There are a number of ways in which these emissions can have an impact on

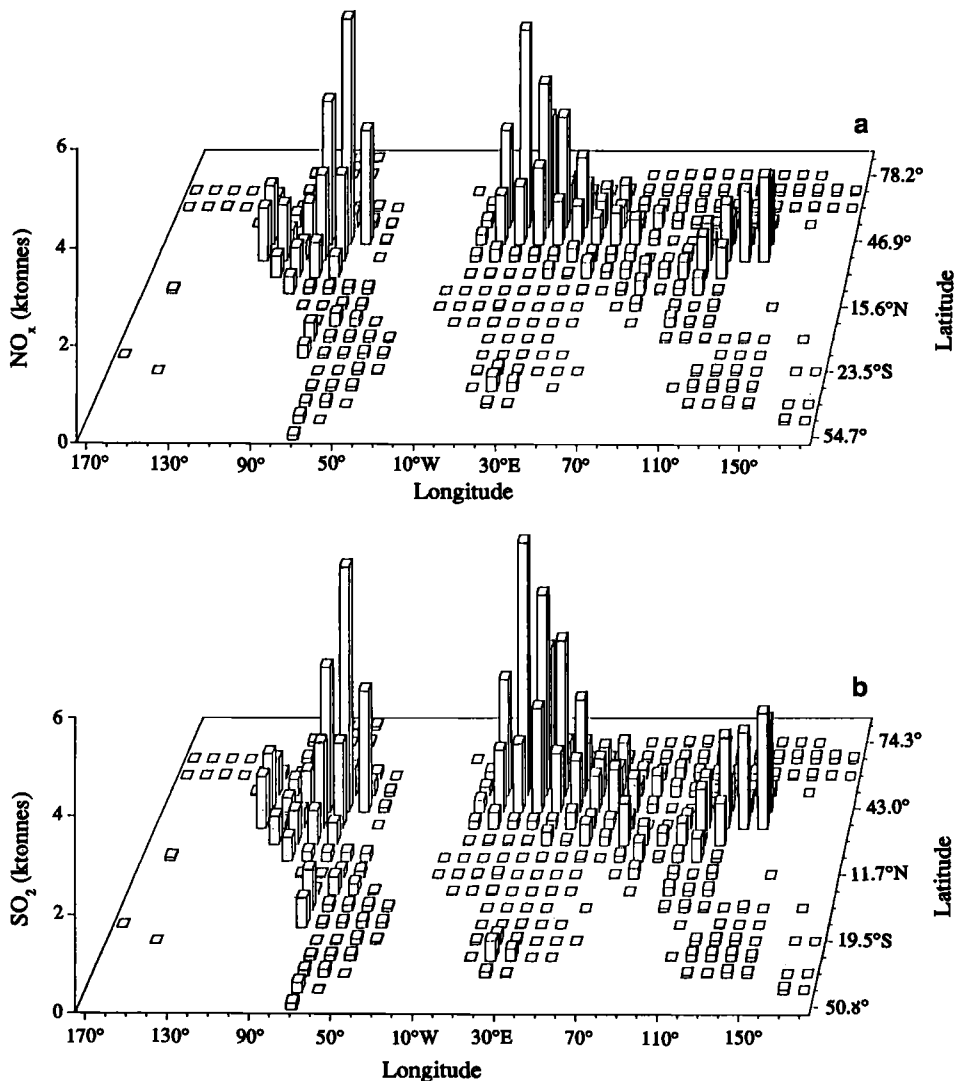


Fig. 1. Gridded emissions of (a) nitrogen oxides and (b) sulfur to the global atmosphere for 1980 [data from Hameed and Dignon, 1988].

the processes in the North Atlantic region. The photochemical reactions involving NO_x influence ozone, a greenhouse gas and a major oxidant. Over some areas of the North Atlantic Ocean, the levels of NO_x are great enough to affect the production of ozone. The concentrations of tropospheric ozone at the northern mid-latitudes have risen by approximately 1% a year over the past few decades [Logan, 1985], and these increases may reflect parallel increases in NO_x emissions. The distribution of NO_x over a relatively remote region, such as the North Atlantic Ocean, is particularly important to the global ozone budget because the ozone produc-

tion efficiency per unit of NO_x increases with the decreasing NO_x concentration [Liu et al., 1987]. Even if the NO_x levels over the North Atlantic Ocean are insufficient to promote vigorous ozone production, increases as low as 10 pptv (parts per trillion by volume) above the natural background may mitigate the potential for ozone photochemical loss.

Because nitrogen can be a limiting nutrient for marine biota, its deposition to the oceans may have implications for the oceanic primary productivity and hence for the oceanic uptake of CO_2 . The studies of the nitrogen budget in the euphotic zone off Bermuda suggest that the annual average atmospheric

deposition of fixed nitrogen is small relative to transport from the aphotic zone. However, the episodic deposition of nitrogen can be a significant source of the nitrogen required for new production [Knap et al., 1986]. For example, algae blooms have been observed following rain events near Bermuda [Glover et al., 1988].

The impact of human emissions on the distribution of sulfur species in the North Atlantic Ocean's atmosphere is interesting because of the possible impact on climate. Sulfate aerosol plays two important roles in the Earth's energy budget: as a light-scattering agent and as a source of cloud condensation nuclei. The perturbations to atmospheric sulfate loadings may modulate the planetary albedos either directly through changes in the aerosol optical depth [Charlson et al., 1990] or indirectly through changes in the microstructures of clouds [Charlson et al., 1987]. The attempts to detect or calculate the climatic signals associated with the anthropogenic sulfur emissions in the northern hemisphere have yielded contradictory results [Schwartz, 1989; Wigley, 1989]. However, more recent data supports the theory that there is a climatic forcing by anthropogenic SO_4^{2-} that is comparable in magnitude but opposite in sign to the greenhouse forcing by enhanced CO_2 [Charlson et al., 1991, 1992]. If there were such a signal, its magnitude would depend critically on the relative contributions of the biogenic and anthropogenic sources to the sulfate budgets over the northern hemisphere's oceans [Galloway and Whelpdale, 1987; Savoie and Prospero, 1989] where the paucity of the aerosols might produce the greatest effects on the cloud microstructures [Charlson et al., 1987]. Understanding the origin of the sulfate over the North Atlantic Ocean is a key issue in evaluating the potential for its climatic effect.

Our ability to test the hypotheses that the increased sulfur and nitrogen in the North Atlantic Ocean's atmosphere affect the climate and O_3 depends on an understanding of the temporal and spatial variabilities of the concentrations and deposition fields and the factors that affect them. This understanding has depended primarily on the data bases obtained from the island sampling programs. Unfortunately, because of the

sparsity of islands in the North Atlantic Ocean, they do not give us a good picture of the distributions of these species. Several three-dimensional models have recently been developed. These models enable us to examine the spatial variabilities of the sulfur and nitrogen species in the North Atlantic Ocean's atmosphere; they also allow us to predict future changes in distributions. However, there has been no coordinated effort to reconcile model results with the extensive field data in this region. In this paper we have brought together the available data from land-based and ship studies, and we have compared the model predictions with the measurements.

We have used two case studies in these comparisons: (1) the spatial and temporal variabilities of the SO_2 and SO_4^{2-} at the surface and (2) the spatial and temporal variabilities of the NO_3^- at the surface.

2. SUMMARIES OF THE DATA AND THE MODELS

2.1. The Data Bases

The data bases used in these comparisons were primarily from two programs: the Atmosphere-Ocean Chemistry Experiment (AEROCE) and the Western Atlantic Ocean Experiment (WATOX). The data included the compositions of wet deposition and aerosols.

2.1.1. The sulfur case study. The data used in this case study included the results of the aerosol and wet-deposition samples taken during the AEROCE and WATOX programs. The aerosol samples were collected daily on 20- x 25-cm Whatman 41 filters at rates of approximately $1 \text{ m}^3 \text{ min}^{-1}$ during onshore wind conditions at the AEROCE sites at Ragged Point, Barbados; Tucker Hill, Bermuda; Tenerife, Canary Islands, Spain; and Mace Head, Ireland. The samplers were on coastal sites on the climatologically determined windward shore and 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).

The precipitation samples were collected daily with an automated wet-only collector at each of the AEROCE sites at Mace Head, Ireland, and Ragged Point, Barbados. The altitudes of these collectors were the same as for the aerosol

samplers discussed above. However, unlike the aerosol samplers, the precipitation collectors were not sectored but operated independently of the surface wind directions. At Bermuda, because of the 9-year wet-deposition record provided by the WATOX program, we used the data from event sampling of precipitation at Harbour Radio Tower on the northeastern portion of the island. The details of the 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.

2.1.2. The nitrate case study. The aerosol and precipitation samples were collected as previously described for the sulfate case study. Of special concern for NO_3^- was the adsorption of HNO_3 on the filter. Although cellulose filters, such as the Whatman-41, do not normally adsorb gas-phase HNO_3 , the collection efficiency for HNO_3 can be expected to increase progressively as sea-salt concentration builds up on the filter. Consequently, the NO_3^- data reported for these filters were regarded as maximums for NO_3^- aerosol and as minimums for total NO_3^- (i.e., aerosol NO_3^- 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 NO_3^- appeared to be about 0.3 or less based on recent unpublished data presented at this meeting and some earlier works reported in the literature [Huebert, 1988; Savoie and Prospero, 1982]. Thus the variability of the collection efficiency of HNO_3 by the Whatman-41 filter should not have greatly affected the NO_3^- values we used. The concentrations of NO_3^- were invariably much higher than the blank levels and the analytical sensitivities.

2.2. The Models: General Characteristics

We used five models in our comparisons. An overview of their characteristics appears in Table 1; details are discussed in the following sections.

2.2.1. The MOGUNTIA. The basic model, the MOGUNTIA (Model Of the Global Universal Tracer Transport in the Atmosphere), was developed at the Max Planck

Institute (MPI) for Chemistry in Mainz, Germany; it covered the whole globe with a horizontal resolution of 10° longitude by 10° latitude and it 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].

2.2.2. 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 the mechanism 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 , $\text{CH}_3\text{O}_2\text{H}$, 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 the photochemical, steady-state approximation.

2.2.3. 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 [Langner and Rodhe, 1990]. 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 $\text{SO}_4^{=}$, (3) the oxidation of SO_2 to $\text{SO}_4^{=}$, and (4) the wet and dry depositions of SO_2 and $\text{SO}_4^{=}$. Three species were carried prognostically in the model: DMS, SO_2 , and $\text{SO}_4^{=}$. The main objectives of the modeling were to estimate the distributions of various sulfur species in the troposphere on time scales of months or longer, to estimate the relative importance of the natural and anthropogenic emission processes, and to test the hypotheses regarding the transformation and deposition processes.

TABLE 1. Characteristics of Models Used in the Comparisons With Field Observations

Model	Grid Mesh	Meteoro-logical Fields	Key Species	Chemical Kinetics	Emissions	Maximum Integral Time	Temporal Resolution
<u>Eulerian: Global</u>							
MOGUNTIA Mainz version	10° x 10°, 10 layers	observed climatic winds	NO _x , HNO ₃ , O ₃ , OH	parameterization [†]	natural and anthropogenic	years	1 month
Stockholm version	10° x 10°, 10 layers	observed climatic winds	SO ₂ , SO ₄ , DMS	linear kinetic parameterization	natural and anthropogenic	years	1 month
GFDL	265 x 265 km, 11 layers	GFDL GCM (on line operation)	lumped NO _y		fossil fuel,* biomass burning	1 year	26 min
<u>Eulerian: Northern Hemispheric</u>							
Oslo	300 x 300 km, 10 layers	NMC output	SO ₂ , SO ₄	linear kinetics parameterization	EMEP anthropogenic and natural	1 month	6 hours
<u>Lagrangian: Global</u>							
LLNL	4.5° x 7.5°, 9 layers, 12 layers	CCM output	NO _x , HNO ₃ , DMS, SO ₂ , SO ₄ , O ₃ , OH prescribed	simple gaseous, aqueous oxidation parameterization	fossil fuel,* soil, lighting, biomass burning, DMS	1 month	1 month

CCM, community climate model; EMEP, European Monitoring and Evaluation Programme; GCM, general circulation model; GFDL, Geophysical Fluid Dynamics Laboratory; LLNL, Lawrence Livermore National Laboratory; MOGUNTIA, Model of Global Universal Tracer Transport in the Atmosphere; NMC, National Meteorological Center.

*Hameed and Dignon [1988].

†Crutzen and Gidel [1983].

2.2.4. 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, sulfur dioxide and particulate sulfate, with a linear reaction rate dependent on latitude and season in accordance with the general photochemical activity. This was an Eulerian model that used the scheme of Smolarkiewicz [1983] for horizontal and vertical advections. The dry deposition took into account the aerodynamic resistance in the surface boundary layer. The wet scavenging was formulated through the scavenging ratio and was separated between in-cloud and subcloud scavenging efficiencies. Vertical eddy diffusion was parameterized as a function of static stability and wind shear. The emissions were instantly mixed up to a locally defined mixing-layer height. On the subgrid scale, 15% of the emissions was deposited inside the emission grid square although 5% was converted to particulate sulfate.

The governing equations were written with dry potential temperatures as the vertical coordinates. This choice of coordinates diminished the numerical errors in the horizontal and vertical advection terms because (1) the vertical wind was smaller than when using quasi-horizontal surfaces, (2) the surfaces of constant potential temperatures were tightly packed in layers with large gradients (stratosphere, front, stable atmospheric boundary layer), and (3) the horizontal gradients were much weaker. We applied the model to four specific months (October 1982 and January, March, and July 1983) using data from the U.S. National Meteorological Center (NMC) obtained through the National Center for Atmospheric Research (NCAR). A meteorological preprocessor calculated all the additional parameters needed in the dispersion calculations and included a complete physical package for precipitation and diabatic heating.

2.2.5. The Geophysical Fluid Dynamics Laboratory model. The Geophysical Fluid Dynamics Laboratory (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 min. For transport, the model used 6-hour time-averaged winds and self-consistent precipitation provided by a parent general circulation model with no diurnal cycle; the emissions of gaseous and particulate reactive-nitrogen compounds were transported as a single species, NO_y . In a particular source region those emissions that were not deposited 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 parameterization on the measured yearly wet deposition over North America and the measured partitioning of individual nitrogen species at several U.S. locations. 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, b] and for stratospheric injection [Kasibhatla et al., 1991].

2.2.6. The Lawrence Livermore National Laboratory model. The Lawrence Livermore National Laboratory (LLNL) model (sometimes called GRANTOUR [cf. 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 the wind and precipitation fields consistent with the currently calculated species or aerosol concentrations. This model had been used to study the climatological effects of smoke from a nuclear war [Ghan et al., 1988] and of an asteroid impact [Covey et al., 1990], the cycles of reactive nitrogen [Penner et al., 1991b] and sulfur in the troposphere [Erickson et al., 1991], the effects on cloud reflectivity and climate of smoke from biomass burning [Penner et al., 1991a], the distributions of ^{222}Rn and ^{210}Pb [Dignon et al., 1989], and the photochemistry of O_3 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 mbar x

330 km x 330 km. If the centroid of a parcel came within 50 mbar of the surface, its species concentrations were subject to dry deposition 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 O₃ fields as well as photolysis and reaction-rate coefficients were specified for either a perpetual January or a perpetual July. The nitrogen simulations reported here were run using the 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 nine vertical layers. The model included sources of reactive nitrogen from fossil-fuel burning, soil-microbial activity, biomass burning, lightning, and production in the stratosphere from the oxidation of N₂O. The treatment of chemistry included the major reactions from cycling NO_x (NO + NO₂) to HNO₃. The ratio of NO_x to NO₂ was determined using the photostationary state relation. For the sulfur simulations reported below, we used the 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, the sources from fossil-fuel burning and oceanic DMS emissions were included. The representation of chemistry included the reaction of DMS with OH to form SO₂. SO₂ was converted to SO₄⁼ with a 6-day e-folding lifetime.

2.3. The Case Studies

2.3.1. The sulfate case study. The three models we examined in this case study differed in their treatments of physical and chemical processes. Two of the models, the Stockholm and LLNL models, were climatological; their meteorology represented a statistically typical January or July. Both had global domains. The third model, the Oslo model, used actual meteorological fields analyzed by the NMC and simulated January and July 1983. This model's domain extended over most of the northern hemisphere. Thus the Oslo model results could be compared with specific data

collected during the time simulated although the Stockholm and LLNL models' results were best compared only with the 'average' or 'typical' measurements.

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 for fossil-fuel combustion, 40 Tg S yr⁻¹ for DMS emissions, 12 Tg S yr⁻¹ for volcanoes, 7 Tg S yr⁻¹ for biomass burning, and 5 Tg S yr⁻¹ for biogenic land sources. 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. The emissions of sulfur and the subsequent chemical transformations also differed among the models. The Oslo model assumed that DMS was emitted in the form of SO₂, whereas both the Stockholm and LLNL models assumed that DMS was emitted directly and then reacted with the hydroxyl radical OH. The Stockholm model prescribed three-dimensional monthly mean OH fields calculated using the NO_x-HC chemistry in the MPI model (see the MPI model description, section 2.2.2). In the LLNL model, the monthly mean OH fields were prescribed based on the results from a LLNL two-dimensional model that had been checked against methylchloroform data.

Once the sulfur was emitted, the Oslo model assumed SO₂ was transformed to SO₄⁼ 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 x 10⁻⁷ s⁻¹ to 4 x 10⁻⁶ s⁻¹. The LLNL model directly converted SO₂ to SO₄⁼ via a process that had an e-folding time of 6 days. The Stockholm model converted SO₂ to SO₄⁼ through two different processes: In the first, OH reacted directly with SO₂; thus as the concentrations of OH increased from winter to summer, so should the amounts of SO₂ converted to SO₄⁼ in this process. In the second, SO₂ was incorporated into clouds and then transformed to SO₄⁼. This process, which is a function of height and latitude, was most important in the lower troposphere; it had a minimum e-folding time of 4 days in the tropics and mid-latitudes.

The treatments 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 SO₂ and 0.1 cm s⁻¹, 0.2 cm s⁻¹, and 0.1 cm s⁻¹ for SO₄⁼ 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 subcloud scavenging processes, each of which used a three-dimensional parameterization. The parameterization was based on empirically determined scavenging ratios and was primarily dependent on the temporal and spatial distribution of precipitation. In the Stockholm model, wet deposition was also calculated using empirically determined scavenging ratios together with zonally averaged precipitation fields. Scavenging of SO₂ and SO₄⁼ occurred in the LLNL model at a vertical level, *j*, at a rate, *r*,

$$r = S_i \times P_j$$

where *P_j* was the precipitation rate in centimeters per hour and *S_i* was the species' scavenging coefficient.

2.3.2. The nitrate case study. The three climatological models used in this study were the LLNL model [Penner et al., 1990, 1991b], the MPI model [Feichter and Crutzen, 1990; Zimmermann, 1987; Zimmermann et al., 1989], and the GFDL model [Levy and Moxim, 1989b]. As was

noted before, the models differed in their spatial resolutions and meteorology as well as in their parameterizations of wet and dry removal processes.

The LLNL and MPI models included chemical reaction schemes to partition reactive nitrogen (NO_y) into HNO₃ and NO_x. The GFDL model transported NO_y as a single species and assumed a partitioning of NO_y based on available data to assign dry-deposition velocities over land and over oceans. The reaction scheme in the LLNL model was simplified, allowing only the major reactions between NO_x and HNO₃ to occur, and assumed latitudinally averaged OH concentrations and photolysis rates. The MPI-model chemistry was more complete and calculated concentrations of OH using a CH₄, CO, and NO_x reactive scheme. Since none of the models treated particulate-phase NO₃⁻ separately, in this comparison we assumed that the predicted HNO₃ could be compared with the concentrations of NO₃⁻ collected at the measurement sites despite the fact that the latter included a combination of gas- and particulate-phase NO₃⁻.

The sources of reactive nitrogen and the deposition velocity used in each model are listed in Tables 2 and 3, respectively. The GFDL-model simulations included only sources from fossil-fuel combustion and biomass burning, whereas the LLNL and MPI models also included effects from natural sources. The globally averaged source strength for each source type was approximately the same for these simulations, although the distribution of these sources within each model might have differed somewhat

TABLE 2. Sources of the Reactive Nitrogen Treated in the Models

	LLNL		MPI		GFDL	
	Seasonal Strength	Seasonal Variation	Seasonal Strength	Seasonal Variation	Seasonal 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

LLNL, Lawrence Livermore National Laboratories model; MPI, Max Planck Institute for Chemistry model; GFDL, Geophysical Fluid Dynamics Laboratory model; n/a, not applicable. Units are teragrams N per year.

TABLE 3.
The Deposition Velocities of
the Reactive Nitrogen Used in the Models

	LLNL	MPI		GFDL	
		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

LLNL, Lawrence Livermore National Laboratory model; MPI, Max Planck Institute for Chemistry model; GFDL, Geophysical Fluid Dynamics Laboratory model. Units are centimeters per second.

in detail. Because the assumed partitioning for the GFDL model was developed from the partitioning observed over land (where NO_x concentrations are larger than HNO₃ concentrations), the deposition velocities used in this model and the LLNL and MPI models were expected to be quite similar over the source regions. However, the different deposition velocities we used for HNO₃ 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], and 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 were from the same projects and sites as those in the sulfate case study.

2.4. The Problems With the Comparisons

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.

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 the limited measurements in our comparison of the modeled with measured non-sea-salt SO₄⁼ deposition discussed below.

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 the winds at tower height were blowing across the island, no aerosol samples were taken. This reduced sample collection times to less than 100%. At Barbados the 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 aerosol signatures that were more representative of aerosol concentrations over the North Atlantic Ocean. Since the models simulated all flow conditions, we had to consider the aerosol observations at Mace Head as biased concentrations that underestimated the real conditions for that site.

3. THE CASE STUDIES

3.1. The Sulfate Comparison Case Study

This case study compared predictions from three models--the Oslo model [Iversen, 1989], the Stockholm model [Langner and Rodhe, 1990], and the LLNL model [Walton et al., 1988; Erickson et al., 1991]--with data collected by the AEROCE and WATOX programs. First, we examined the predictions for the concentrations of sulfur dioxide and particulate sulfate and the wet deposition of sulfur as given by the three models for January and July. Second, we compared the model calculations with the actual measurements of the $\text{SO}_4^{=}$ concentrations in the aerosol samples from four different sites--Mace Head, Ireland; Bermuda; Barbados; and Tenerife, Spain--and the sulfate wet deposition from Barbados, Bermuda, and Mace Head.

3.1.1. Comparisons among the three models. We examined the model results for January and July. The predicted distributions of particulate-sulfate concentrations in the surface level air are shown in Figure 2. There was a fundamental difference in the meteorological representation of these data. The Stockholm and LLNL models (Figures 2a and 2b) represented the distribution of particulate sulfate for a typical (climatological) January weather situation, whereas the Oslo model (Figure 2c) depicted the situation specifically for January 1983.

The three models predicted quite similar sulfate-concentration patterns. The maximum concentrations occurred over continental areas with the low concentration bands over the mid-Atlantic Ocean. The maximum concentrations were larger over Europe than over North America because of the 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 position of the maximum air concentration corresponded to the maximum emission area for the Stockholm model and the Oslo model but was displaced toward the north for the LLNL model. All three models also predicted troughs of roughly 10 to 20 nmol m^{-3} over the mid-Atlantic Ocean.

The climatological models (the Stockholm and LLNL models) showed

smoother gradients than the Oslo model, which, as we have stated, used the actual meteorology for January 1983. Consequently, the Oslo model showed a SW-NE tilt for the North American contours that reflected the particular weather situation of that time.

We compared the model calculations for the surface air concentrations and the wet deposition for three selected areas: over North America, over the

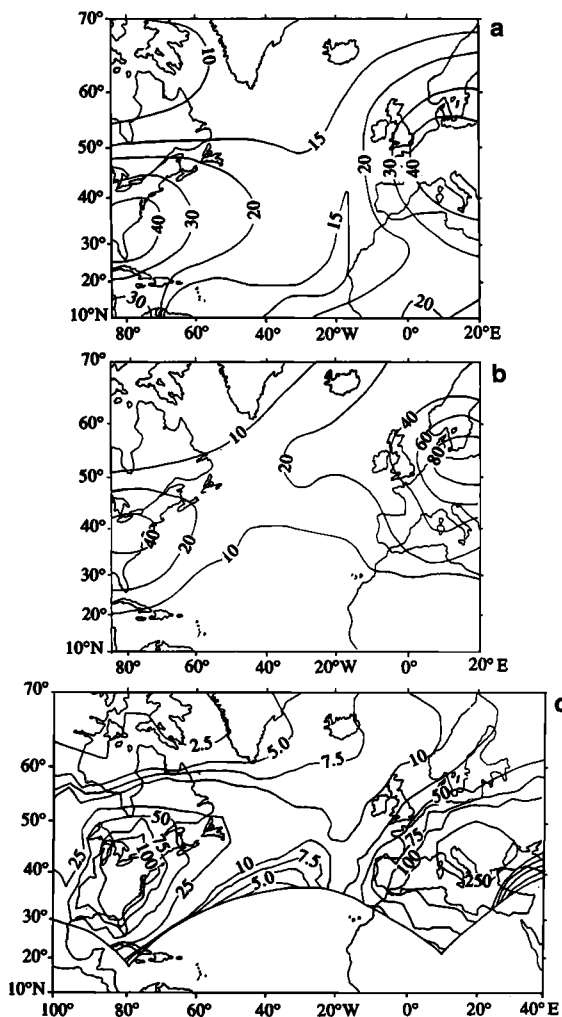


Fig. 2. The predicted sulfate concentrations from (a) the Stockholm model at 250 m (nanomoles per cubic meter), (b) the Lawrence Livermore National Laboratory model at the surface (nanomoles per cubic meter), and (c) the Oslo model at 40 m (micromoles per cubic meter) for January when all sources were considered.

TABLE 4. Comparisons of the SO₂ and nss SO₄⁼ Model Results

	Air Concentrations, nmol S m ⁻³						SO ₄ ⁼ Wet Deposition, μmol S m ⁻² month ⁻¹		
	SO ₂			SO ₄ ⁼			SM	LLNL	OM
	SM	LLNL	OM	SM	LLNL	OM			
	<u>North American Maximum</u>								
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
	<u>Mid-Atlantic Trough</u>								
January	15	2.4	10	15	15	15	700	200	400
July	15	4.0	15	20	10	15	700	100	300
	<u>European Maximum</u>								
January	750	260	500-750	> 60	> 80	250	1800	2970	5000
July	400	320	500	150	>120	250	2700	3200	2800-5000

SM, Stockholm model; LLNL, Lawrence Livermore National Laboratory model; OM, Oslo model.

mid-Atlantic Ocean (50°N, 40°W), and over Europe (Table 4). The selected continental points represented the regions of the maximum predicted concentration. The point over the mid-Atlantic was in the trough region, where the influence of biogenic oceanic sources might have been more evident.

The Oslo and Stockholm models predicted similar SO₂ concentrations; the LLNL model predictions for SO₂ were lower than those from the Oslo or Stockholm models. This might have been partly because the LLNL model predictions were calculated for the surface level while the Stockholm and Oslo models' results were calculated for higher levels (250 m and 40 m, respectively).

The three models showed better agreement for the SO₄⁼ in the air (Table 4), particularly these concentrations over the mid-Atlantic Ocean. The concentrations over the Atlantic Ocean 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 contributions of anthropogenic sources relative to those of biogenic sources were estimated at 50%.

The wet-deposition values depended strongly on the precipitation fields. The Stockholm and LLNL models considered climatological precipitation whereas the Oslo model calculated its own precipitation from actual meteorological data. Because of the large spatial and temporal variabilities in precipitation, the

different treatments of precipitation could have accounted for part of the differences in the wet-deposition values shown by the models. (For example, the Oslo model predicted higher deposition values over Europe than did the Stockholm or LLNL model.)

In general the predicted distributions of the sulfur concentrations and deposition over the North Atlantic Ocean from the two climatological models agreed fairly well except for SO₂, which had lower values in the LLNL model (Table 4). Additionally, the predictions from the Oslo model, which used actual meteorology, were within the range defined by the climatological models.

3.1.2. The climatological model results versus the measurements. Table 5 shows the model results and the measurements of aerosol nss SO₄⁼ from the stations included in this case study.

3.1.2.1. Results for nss SO₄⁼: Considering the number of months that contributed to the measured averages in Table 5, only Barbados had a nss SO₄⁼ record long enough for a good comparison with the model results. The predictions from the Stockholm model were quite accurate for January and within a factor of 2 for July. However, the LLNL model results were a factor of 3 to 4 lower than the measurements. A portion of the differences between the model estimates for Barbados could be related to the differences in the magnitude of the natural emissions, which were almost a factor of 3 higher in the Stockholm

TABLE 5. The Climatological Model Results Versus the Measurements of the Aerosol nss SO₄⁼ Concentrations

	Model Results		Measurements		Number of Months
	SM	LLNL	Mean ± s.d.	Range	
<u>Mace Head, Ireland</u>					
January	25	26	40	---	1 (1989)
July	60	19	42	---	1 (1989)
<u>Harbour Radio Tower, Bermuda</u>					
January	34	18	23	---	1 (1989)
July	34	11	31	19-44	2 (1988, 1989)
<u>Barbados</u>					
January	15	3.5	17 ± 5	---	6 (1984-1989)
July	15	5.4	24 ± 12	---	6 (1984-1989)
<u>Tenerife</u>					
January	15	5.4	9	3-15	2 (1988, 1989)
July	20	18.4	19	18-20	2 (1988, 1989)

SM, Stockholm model; LLNL, Lawrence Livermore National Laboratory model. Units are nanomoles per cubic meter.

model. About half of the nss SO₄⁼ 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 the increased reaction rates for SO₂ + OH because of increased OH during 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 2 years.

3.1.2.2. Results for (SO₂): As is shown in Table 4, the LLNL model predicted SO₂ concentrations in source regions that were about a factor of 2 to 4 lower than those from the Stockholm model. Over the North Atlantic Ocean, only limited measurements of SO₂ were available, none of which were long term. The comparison with measured SO₂ concentrations from the literature [Warneck, 1988] showed a range of 1-4 nmol m⁻³ for limited sampling. During the cruise of the NOAA R/V Mt. Mitchell, an average value of 2 nmol m⁻³ SO₂ was measured in the southeastern part of the North Atlantic Ocean [Pszenny et al., 1990]. These limited measurements indicated that the LLNL model results for this region were close to the measured values

and that the Stockholm model results were a factor of 5 or more too high. The differences between the models were possibly related to how efficiently SO₂ was dry deposited and how quickly it was converted to SO₄⁼. The LLNL model appeared to have a more efficient deposition process than did the Stockholm model. Also, the LLNL model concentrations were actually surface-level quantities, and the Stockholm model concentrations were calculated for 250 m. The vertical profiles from the LLNL model showed increases in height for SO₂ from 1000 mbar to 900 mbar. These differences, together with the differences in source strengths, might explain the discrepancies between the two models.

3.1.2.3. The wet deposition of nss SO₄⁼: Figures 3, 4, and 5 compare the results from the Stockholm and LLNL models with the measurements of the wet deposition of nss SO₄⁼ at Harbour Radio Tower, Bermuda; Mace Head, Ireland; and Ragged Point, Barbados; respectively. For Bermuda, both models predicted values that were within a factor of 2 of the mean measured values, although the Stockholm model predicted higher values than the LLNL model. From Figure 3 one can see that the variability in the wet deposition produced in the Stockholm model was clearly much weaker than that

measured at Bermuda. This may have been somewhat related to the fact that zonally averaged precipitation fields were used to calculate the wet deposition.

The comparisons with the other stations (Figures 4 and 5) were very tentative because of the short sampling periods. Because the observations covered less than 2 years, they may have differed significantly from the long-term mean. Although at first glance the

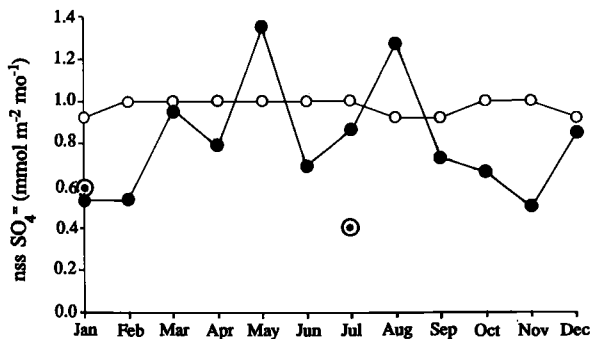


Fig. 3. The results from the Stockholm (open circle) and the Lawrence Livermore National Laboratory (dot in open circle) models for the nss SO₄⁻ wet deposition by month from Harbour Radio Tower, Bermuda, compared with the values from monthly deposition records based on storms collected from 1981-1989 (solid circle).

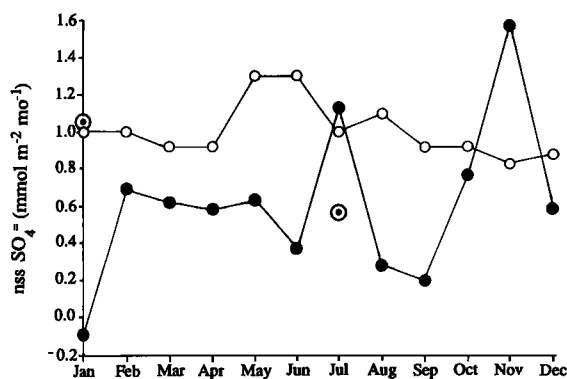


Fig. 4. The results from the Stockholm (open circle) and the Lawrence Livermore National Laboratory (dot in open circle) models compared with the measurements of the nss SO₄⁻ wet deposition by month (solid circle) from Mace Head, Ireland, for the period of November 16, 1988, to July 12, 1990.

agreements between the models and the observations did not seem completely favorable, this may have been caused by the year-to-year variations in the data. As we discuss in a later section, the wet deposition of NO₃⁻ measured 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. This degree of temporal variability may also have existed at Barbados and Mace Head. Figure 4 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 of the months but was similarly high in January. If there had been a substantial year-to-year variation in the data, the agreement between the models and the data could have been further improved (especially for the months with large discrepancies, such as January). Likewise, if the data in Figure 5 had shown a similar year-to-year variation, there could have been a much stronger agreement between the Stockholm model and the observations (the LLNL model had already done fairly well for both January and July).

3.2. The Nitrate Comparison Case Study

This case study focused on a comparison of the predicted versus the measured surface distributions and the deposition fluxes of the reactive nitro-

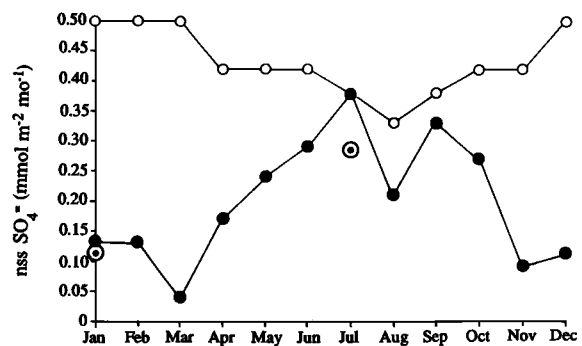


Fig. 5. The results from the Stockholm (open circle) and the Lawrence Livermore National Laboratory (dot in open circle) models compared with the measurements of the nss SO₄⁻ wet deposition by month (solid circle) from Ragged Point, Barbados, for the period of December 18, 1988, to June 20, 1990.

gen compounds (primarily NO_3^-) in the North Atlantic basin. Because multiyear time-series information was available on the wet deposition at Bermuda and on the surface aerosol concentrations at Barbados, we used these data to provide a context within which we compared the predictions from the climatological models. We examined the variations on monthly, seasonal, and annual time scales. We also compared the model results with both the aerosol and the wet-deposition data from Mace Head, Ireland. Although fewer data were available, the results from Mace Head provided a different perspective since it is at a higher latitude and close to the European continent.

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

The data used for this comparison were obtained from daily filter samples collected from 1984 to 1989. The samples were collected during easterly wind conditions; during this time the winds were in sector over 90% of the time.

The measured monthly mean concentrations (Figure 6) ranged from 2.86 nmol m^{-3} to 16.3 nmol m^{-3} . For some months there was considerable variability from year to year. The maximum concentrations were in April, May, and June; the

concentrations tended to be most variable during this time, but those measured in January through March were also quite variable. The concentrations varied the least during August through December, especially August through September.

The previous studies of Savoie et al. [1989] suggest that more than half of the NO_3^- aerosol is derived from anthropogenic sources; the lead isotope studies of Hamelin et al. [1989] indicate that European sources play a significant role in this regard. The ratio of NO_3^- to nss sulfate is very high during the winter and early spring; along with the other evidence, this suggests that biomass burning could serve as a 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 was about 30% less than the yearly average concentration when all observations were considered; this was the upper limit of what the nitrate should have been. Although the simulated seasonal cycle agreed reasonably well with the 1986 and 1988 observations (Figure 6), it underestimated the late spring maximum seen in the

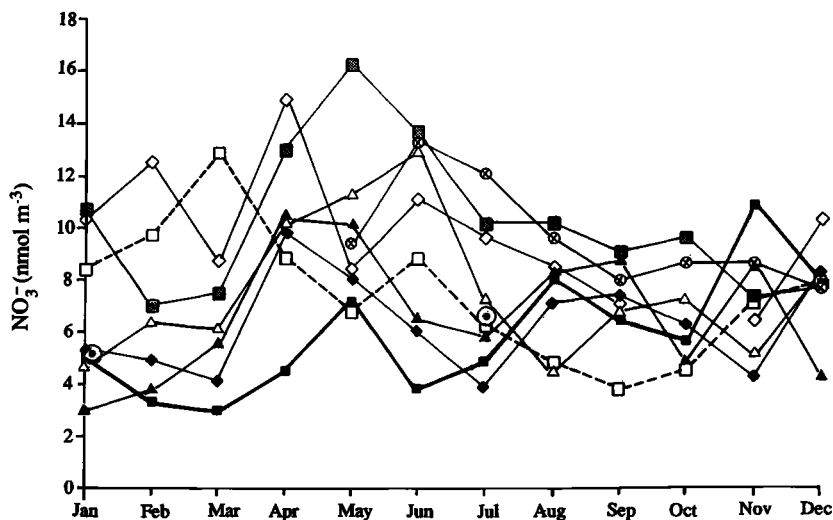


Fig. 6. The mean of the monthly aerosol nitrate concentrations measured at Ragged Point, Barbados, over 6 years (1984, cross in open circle; 1985, open triangle; 1986, solid diamond; 1987, open diamond; 1988, solid triangle; and 1989, stippled square) compared with the nitrate predictions from three models: the Max Planck Institute model (dashed line with open square), the Geophysical Fluid Dynamics Laboratory model (heavy line with solid square), and the Lawrence Livermore National Laboratory model (dot in open circle).

observations and generated an annual maximum in the fall. The differences could be partially due to the GFDL model omission of the lightning sources 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. The July concentrations were slightly higher than the January values because of both the larger OH concentrations (which converted NO_x to HNO_3 in the model) and the larger sources in the northern hemisphere. (The model had both higher lightning and higher soil-microbial sources during this season.) However, the model results fell within the range of measured concentrations. This model attempted to describe all the sources of reactive nitrogen, so 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., 1991b].

The MPI model results were generally in the envelope formed by all the individual years of data. A significant feature of the MPI model simulation was the strong maximum in spring, although the simulated maximum in March was 1 to 3 months before the observed maximum. The MPI model simulation generated a

minimum in September that was not evident in the real data. Compared with 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 results predicted by the models might have been rationalized by the differences in the sources included in each model and the deposition velocities used. The GFDL and MPI model simulations yielded large month-to-month and annual variations that were broadly consistent with the measurements. However, there were substantial disagreements (Figure 6) that pointed to the need for a more detailed analysis. In particular it would have been desirable to compare the meteorology used for the predictions with that associated with any particular year's data to assess the factors that contributed to any agreement or to the lack thereof.

3.2.2. Bermuda: Nitrate wet deposition by year, 1981-1988. The monthly wet-deposition data for NO_3^- at Harbour Radio Tower, Bermuda, were available for May 1980 through August 1989. The data for 1982-1984 and 1988 were compared with the estimates from the MPI, GFDL, and LLNL models (Figure 7). The wet-

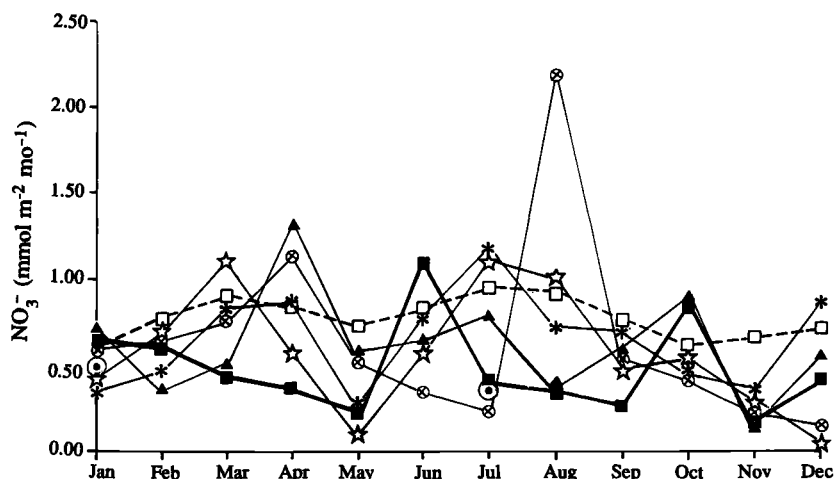


Fig. 7. The mean of the monthly wet deposition of the nitrate measured at Harbour Radio Tower, Bermuda, over 4 years (1982, open star; 1983, asterisk; 1984, cross in open circle; and 1988, solid triangle) compared with the predictions from three models: the Max Planck Institute model (dashed line with open square), the Geophysical Fluid Dynamics Laboratory model (heavy line with solid square), and the Lawrence Livermore National Laboratory model (dot in open circle).

deposition rates of NO_3^- at Harbour Radio Tower were calculated using the monthly volume-weighted average concentrations 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 to 2.4 $\text{mmol m}^{-2} \text{ month}^{-1}$; for the individual months the variabilities ranged from a factor of 12 in July (0.2–2.4 $\text{mmol m}^{-2} \text{ month}^{-1}$) to a factor of 5 in May (0.1–0.5 $\text{mmol m}^{-2} \text{ month}^{-1}$) (Figure 7).

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

The predicted average wet-deposition values for July from the LLNL model were remarkably close to those 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 of the years for which we had data.

Again, the LLNL model predicted little variation between the winter and summer seasons. The similarity between the LLNL and GFDL model predictions of deposition was consistent with the agreement in the predicted surface concentrations of HNO_3 and NO_y in air for these two models, respectively. This agreement was somewhat surprising because the LLNL model included lightning and soil-microbial sources in addition to the fossil-fuel and biomass sources incorporated in the GFDL model. In the LLNL-model simulations, fossil-fuel sources provided only about 50% of the calculated concentration in winter and 70% of the concentration 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 seen in the wet-deposition data. Both in the model simulation and the data, there were maxima in early spring, mid-summer, and December with a corresponding minima between the peaks. However, on a year-to-year basis, the data varied greatly. On the other hand, the modeled concentrations were slightly high, the month-to-month changes in the model were smoother than in the data,

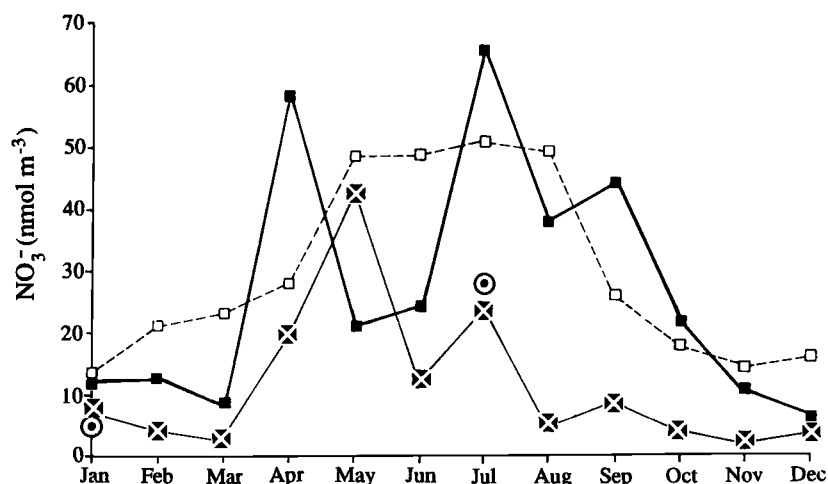


Fig. 8. The mean of the monthly aerosol nitrate concentrations measured at Mace Head, Ireland, in 1989 (cross in solid square) compared with the predictions from three models: the Max Planck Institute model (dashed line with open square), the Geophysical Fluid Dynamics Laboratory model (heavy line with solid square), and the Lawrence Livermore National Laboratory model (dot in open circle).

and the amplitude of the yearly cycle was smaller in the model than that observed in any given year.

In summary the various model predictions for the deposition of NO_3^- at Bermuda were in good agreement. This was surprising because the predicted concentrations in the air at the surface at this site varied by about a factor of 2. This agreement might have been because the predicted wet deposition resulted from a process that occurs throughout the tropospheric column and depended on the predicted precipitation as well as concentration. The model predictions were quite close to the measured deposition, particularly in months where the observed variabilities were low; the predictions in general appeared low in months where the observed variabilities were 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.

3.2.3. Mace Head: A comparison of aerosol nitrate concentrations and wet deposition. Although there was only 1 year of data available from the Mace Head site, we tried a comparison. Figure 8 shows a plot of the observed and

model-predicted, monthly averaged, aerosol NO_3^- concentrations and Figure 9 shows a plot of the wet-deposition values.

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

The monthly mean aerosol NO_3^- concentrations at Mace Head varied over a wide range, 0.165–43 nmol m^{-3} (see Figure 8). The highest concentrations were during late spring and mid-summer. The

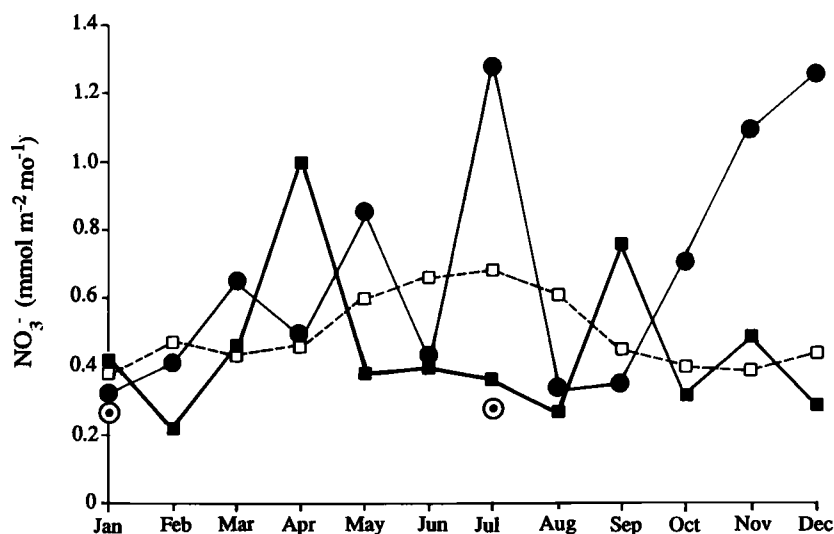


Fig. 9. The mean of the monthly wet deposition of nitrate measured at Mace Head, Ireland, from November 16, 1988, to July 12, 1990, (solid circle) compared with the predictions from three models: the Max Planck Institute model (dashed line with open square), the Geophysical Fluid Dynamics Laboratory model (heavy line with solid square), and the Lawrence Livermore National Laboratory model (dot in open circle).

concentrations were very low during late fall and winter; indeed, during these times, they were lower than those at Bermuda or even Barbados.

At Mace Head, Ireland, the NO_3^- deposition varied from 0.3 to 1.2 $\text{mmol m}^{-2} \text{ month}^{-1}$ with no pronounced seasonal signal (Figure 9). (The climatically weighted data did show a strong signal.) This lack of a seasonal pattern was different from that observed for the aerosols (Figure 8) possibly because of the impact of the seasonal variations of the precipitation amount on the NO_3^- deposition rate and the scavenging of the 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 6). There was a qualitative agreement (within a factor of 2) between the GFDL time series and the observed surface- NO_3^- concentration. The deposition time series from the GFDL model was highly variable and entirely out of phase with the data (Figure 9). 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

TABLE 6. The Variabilities of the NO_3^- Concentrations in the Aerosols and Precipitation at Ragged Point, Barbados, and Mace Head, Ireland

	\bar{c}	r	r/\bar{c}	δ	δ/\bar{c}
<u>Barbados Aerosol Concentrations, nmol m^{-3}</u>					
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
<u>Barbados Wet Deposition, $\mu\text{mol m}^{-2} \text{ month}^{-1}$</u>					
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
<u>Mace Head Aerosol Concentrations, nmol m^{-3}</u>					
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
<u>Mace Head Wet Deposition, $\mu\text{mol m}^{-2} \text{ month}^{-1}$</u>					
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

Symbols are \bar{c} , yearly average; r, range (maximum monthly value minus the minimum monthly value); δ , standard deviation; GFDL, Geophysical Fluid Dynamics Laboratory model; MPI, Max Planck Institute for Chemistry model.

result was still an overestimate since the model concentrations were selected for all wind directions.

The LLNL model results for the aerosol NO_3^- concentrations at Mace Head were significantly higher for July than for January but agreed quite well (within 50%) with the measured values (Figure 8). At this latitude the differences in the prescribed OH concentrations in the model in January and July may have accounted for the predicted seasonal variations.

Despite the differences in the predicted concentrations for aerosol NO_3^- for January and July in the LLNL model, the predicted deposition in these two months was nearly the same. Apparently, the model-predicted rainfall during July was somewhat lower than that for January. The model predictions appeared to agree well with the measured monthly averaged deposition data for January but were significantly lower than the deposition measured in July (Figure 9). 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.

The monthly aerosol concentrations simulated by the MPI model consistently exceeded the observed values from Mace Head, probably for two reasons: (1) a 10-degree spatial resolution is inadequate for a station close to but normally upwind of a major source region, and (2) in the model it was impossible to filter out an episode in which pollution moved from the east to Mace Head because the monthly average winds were used and the wind fluctuations on time scales of less than a month were represented by horizontal diffusion. Of the four comparisons discussed here between the observed and the MPI model-simulated, nitrogen-containing species at the AEROCE sites, this was probably the only significant bias in the simulations. The data had a spring-summer maximum, which the model also showed clearly; however, the late-summer monthly mean values from the MPI model were as much as 10 times greater than the measured values. As was mentioned above, this may have been due to the large grids used in the MPI model and the resultant diffusion. The annual average NO_3^- deposition from the MPI model was roughly 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 weak summer maximum, but the variabilities in the measured values were so great that we could not ascertain any seasonal trends.

In summary, the model results for NO_3^- concentrations at Mace Head agreed reasonably well (within a factor of 2-3) with the measured aerosol concentrations (Table 6). 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. None of the model results was selected on the basis of the modeled wind directions so as to complement the actual aerosol sampling conditions; thus we expected all the 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 variabilities, the agreement was reasonable.

The model predictions for wet deposition at Mace Head agreed substantially (within 20%) despite differences in the model-predicted surface air concentrations (Table 6). This 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 wet deposition also depended on the precipitation rates used in the models. The measured concentrations and the model results appeared to agree well, considering the large month-to-month variations that were observed.

3.2.4. A comparison of model and data variability. Besides comparing the data with the model-predicted concentrations and deposition amounts, we also examined the observed and simulated variabilities. Here we compared the interyear and intrayear variabilities in the data with the model simulations (Table 6). 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 differ 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 NO_3^- concentrations from Barbados for an average of 5 years' data and for 5 individual years. The NO_3^- amplitude (r) and the standard-deviation statistics were uniformly small for the average data year, i.e., a year produced by averaging the data from all Januaries in 1985 to 1989, all Februaries in 1985 to 1989, etc. For this average year, the measures of the annual variabilities 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 for either model.

When we compared the data for the 5 separate years, we found that 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 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, the aerosol NO_3^- concentrations at Mace Head varied more than those at Barbados. For an individual year, the variabilities of the concentrations changed by a factor of 5 to 6 between stations, but the variabilities of the wet deposition changed by much less. (Again, the concentrations were observed at a single point in the vertical, but the 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 the aerosol 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. Thus the intraannual variabilities simulated by the GFDL model were consistently larger than those 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 variabilities simulated by the MPI model were biased low and exceeded the observed values for aerosol concentrations only at Barbados. Thus in summary, the GFDL model seemed to simulate the observed intraannual variabilities in the data better than did the MPI model.

4. SUMMARY AND RECOMMENDATIONS

From these case studies, we drew several conclusions:

1. The SO_4^{2-} case study illustrated how we in the measurement and modeling communities could help each other improve our understanding of 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. To determine which model or models are more realistic, we need an extended data set for SO_2 over both the oceanic and the continental source regions. In the future this bridge between the regional and the global models and between the climatological and the episodic models should be increasingly valuable.

2. The NO_3^- 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. 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 toward this goal in the future.

3. The differences among the results of the 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, in some cases we found reasonable agreement with the measured concentrations given the limitations of the data. However, a time series with a more complete suite of the measured NO_y species would have allowed for a better test of a model's physics.

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

Temporally and spatially representative measurements were critically needed for comparisons with climatological models. As these studies showed, it was quite difficult to compare a climatological monthly model output with a single month of measurements. It would have been a much more valid comparison if we had been able to use data collected for the same month over a 5- to 10-year period. This would have greatly reduced much of the influence that the statistical outliers and extreme events had on the data. The episodic models required measurements that directly coincided with the simulation period; long-term measurements would have helped to assess the representativeness of the simulation period.

A good spatially resolved network of measurements was also necessary. For our case studies, only one site had a long record of concentrations in aerosols (Barbados) or in deposition (Bermuda). At least three to five stations with long-term sampling records would have greatly assisted our model interpretations. When models predict three-dimensional fields, three-dimensional data fields should be used for comparisons. This necessitates data on vertical profiles as well as surface measurements.

Additional information to characterize the situation in which measurements were taken could also help to determine the representativeness of the measurements. This should include information

about the averages and the extremes as well as the pertinent meteorological data (such as the length of an event, the timing of a storm, etc.). If measurements have been taken only during a specific time (for example, only when onshore winds are blowing), the expected bias should be indicated.

We also found that modelers could 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. To determine which model or models are more realistic, SO_2 should have been sampled over both the ocean and continental source regions (both spatially and temporally).

A third 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 10 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., 10 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, measurers and modelers need to provide each other with information about their temporal and spatial resolutions and the representativeness of their measurements or model outputs. In the future, besides averages, useful comparisons could be made as distributions of quantities, such as fluxes and precipitation, by both modelers and measurers.

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