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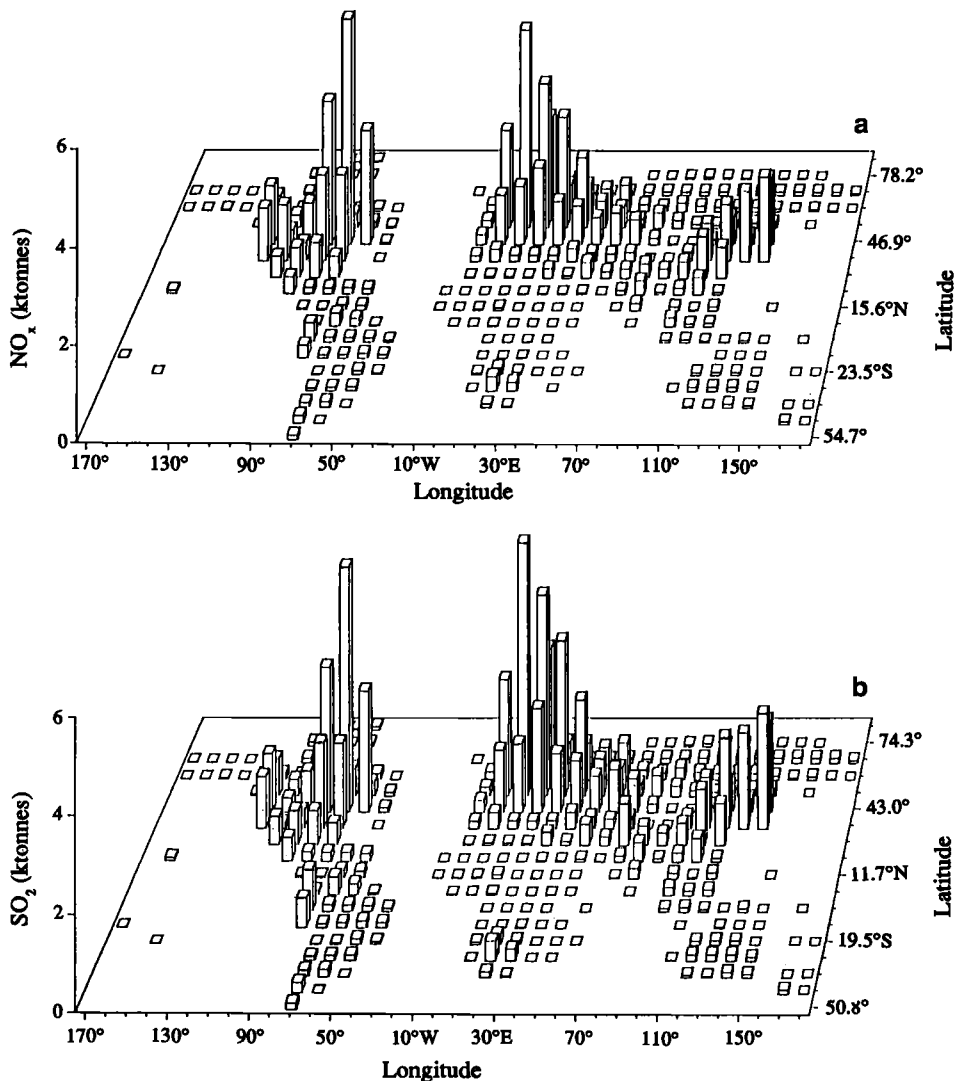
Fig. 1.   Gridded emissions of (a) nitrogen oxides and (b) sulfur to the global atmosphere for 1980 [data from Hameed and Dignon, 1988].

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 produc-
tion [Knap et al., 1986]. For example,
algae blooms have been observed follow-
ing 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 condensa-
tion nuclei. The perturbations to atmo-
spheric sulfate loadings may modulate
the planetary albedos either directly
through changes in the aerosol optical
depth [Charlson et al., 1990] or indi-
rectly through changes in the micro-
structures of clouds [Charlson et al.,
1987]. The attempts to detect or calcu-
late 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 $SO_4^=$
that is comparable in magnitude but
opposite in sign to the greenhouse forc-
ing by enhanced CO_2 [Charlson et al.,
1991, 1992]. If there were such a sig-
nal, its magnitude would depend criti-
cally on the relative contributions of
the biogenic and anthropogenic sources
to the sulfate budgets over the northern
hemisphere's oceans [Galloway and Whelp-
dale, 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 spa-
tial 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 pro-
grams. Unfortunately, because of the

sparsity of islands in the North Atlan-
tic Ocean, they do not give us a good
picture of the distributions of these
species. Several three-dimensional mod-
els 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 pre-
dict 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
$SO_4^=$ 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 compar-
isons were primarily from two programs:
the Atmosphere-Ocean Chemistry Experi-
ment (AEROCE) and the Western Atlantic
Ocean Experiment (WATOX). The data
included the compositions of wet deposi-
tion 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 m^3 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 sam-
plers were on coastal sites on the cli-
matologically 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 col-
lected 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 col-
lectors 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, 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 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 $SO_4^=$, (3) the oxidation of SO_2 to $SO_4^=$, and (4) the wet and dry depositions of SO_2 and $SO_4^=$. Three species were carried prognostically in the model: DMS, SO_2, and $SO_4^=$. 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 Resolu- tion
				Eulerian: Global			
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
				Eulerian: Northern Hemispheric			
Oslo	300 x 300 km, 10 layers	NMC output	SO_2, SO_4	linear kinetics parameterization	EMEP anthropo- genic and natural	1 month	6 hours
				Lagrangian: Global			
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, auqueous oxida- tion parameter- ization	fossil fuel,[*] soil, light- ning, 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 sul-
fur. 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 par-
ticulate sulfate, with a linear reaction
rate dependent on latitude and season in
accordance with the general photochemi-
cal activity. This was an Eulerian
model that used the scheme of Smolarkie-
wiez [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 par-
ticulate 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 gra-
dients (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 meteoro-
logical preprocessor calculated all the
additional parameters needed in the dis-
persion calculations and included a com-
plete physical package for precipitation
and diabatic heating.

2.2.5. The Geophysical Fluid
Dynamics Laboratory model. The Geophys-
ical 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 emis-
sions of gaseous and particulate
reactive—nitrogen compounds were trans-
ported 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 trans-
port 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. loca-
tions. Although these parameterizations
were based on observations in North
America, the simulated deposition over
Europe and remote regions of the north-
ern hemisphere agreed well with the
observed values. Simulations had
already been completed for global emis-
sions from fossil—fuel combustion [Levy
and Moxim, 1987, 1989a, b] and for
stratospheric injection [Kasibhatla et
al., 1991].

2.2.6. The Lawrence Livermore Na-
tional 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 precipita-
tion fields from a general circulation
model or interactively in a mode that
allowed alterations of the wind and pre-
cipitation 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 photo-
chemistry 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 O_3 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 N_2O. The treatment of chemistry included the major reactions from cycling 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 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 SO_2. SO_2 was converted to $SO_4^=$ 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 SO_2, 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 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 x 10^{-7} s^{-1} to 4 x 10^{-6} s^{-1}. The LLNL model directly converted SO_2 to $SO_4^=$ via a process that had an e-folding time of 6 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 the concentrations of OH increased from winter to summer, so should the amounts of SO_2 converted to $SO_4^=$ in this process. In the second, SO_2 was incorporated into clouds and then transformed to $SO_4^=$. 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 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 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 SO_2 and $SO_4^=$ occurred in the LLNL model at a vertical level, j, at a rate, r,

$$r = S_i \; x \; P_j$$

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 HNO_3 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 HNO_3 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 CH_4, CO, and NO_x reactive scheme. Since none of the models treated particulate-phase NO_3^- separately, in this comparison we assumed that the predicted HNO_3 could be compared with the concentrations of NO_3^- collected at the measurement sites despite the fact that the latter included a combination of gas- and particulate-phase NO_3^-.

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	
	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

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 Lab-
oratory model; MPI, Max Planck Institute
for Chemistry model; GFDL, Geophysical
Fluid Dynamics Laboratory model. Units
are centimeters per second.

in detail. Because the assumed parti-
tioning for the GFDL model was developed
from the partitioning observed over land
(where NO$_x$ concentrations are larger
than HNO$_3$ concentrations), the deposi-
tion velocities used in this model and
the LLNL and MPI models were expected
to be quite similar over the source
regions. However, the different deposi-
tion velocities we used for HNO$_3$ over
the sea were expected to lead to differ-
ences 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 circula-
tion 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]; how-
ever, we did not compare the wind fields
and precipitation patterns in detail and
expected that there might have been sig-
nificant differences that impacted upon
the predicted concentration and wet-
deposition fields. The data used in
this case study were from the same pro-
jects 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 com-
parison 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 mea-
sured value. In general, the fewer the
measurements, the less representative
they are. These observations were tempo-
rally, and presumably spatially, highly
variable. Measurements from a longer
record of observations would have pro-
vided more information about their
context, e.g., whether they were aver-
age, extreme, etc.

Precipitation measurements from the
official weather station on each island
provided our network observations of
precipitation with climatological con-
texts. We used these climatological
data to extrapolate from the limited
measurements in our comparison of the
modeled with measured non—sea—salt SO$_4^=$
deposition discussed below.

There was also a question about how
representative the aerosol concentra-
tions 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 collec-
tion times to less than 100%. At Barba-
dos 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 repre-
sentative 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 $SO_4^=$ 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
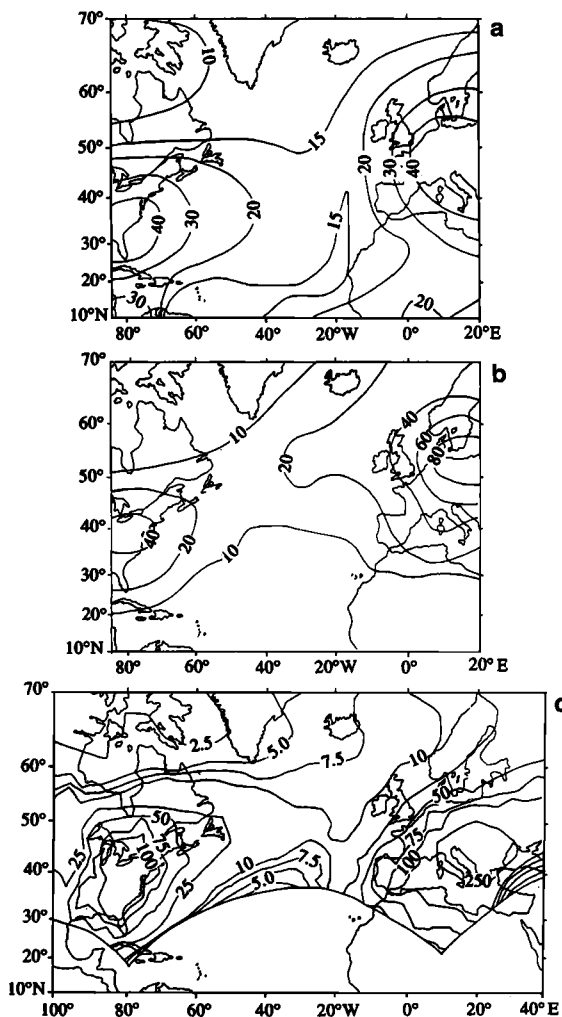

Fig. 2. The predicted sulfate concentrations from (a) the Stockholm model at 250 m (nanomoles per cubic meter), (b) the Lawrence Livermore National Laboratory model at the surface (nanomoles per cubic meter), and (c) the Oslo model at 40 m (micromoles per cubic meter) for January when all sources were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

TABLE 4. Comparisons of the SO_2 and nss $SO_4^=$ 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
			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

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 SO_2 concentrations; the LLNL model predictions for SO_2 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 $SO_4^=$ 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 SO_2, 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 $SO_4^=$ from the stations included in this case study.

3.1.2.1. Results for nss $SO_4^=$: Considering the number of months that contributed to the measured averages in Table 5, only Barbados had a nss $SO_4^=$ 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 $SO_4^=$ Concentrations

| | Model Results | | Measurements | | |
	SM	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)

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

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 the increased reaction rates for SO_2 + 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 (SO_2): As is shown in Table 4, the LLNL model predicted SO_2 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 SO_2 were available, none of which were long term. The comparison with measured SO_2 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} SO_2 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 SO_2 was dry deposited and how quickly it was converted to $SO_4^=$. 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 SO_2 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 $SO_4^=$: Figures 3, 4, and 5 compare the results from the Stockholm and LLNL models with the measurements of the wet deposition of nss $SO_4^=$ 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 sta-
tions (Figures 4 and 5) were very ten-
tative because of the short sampling
periods. Because the observations
covered less than 2 years, they may have
differed significantly from the long-
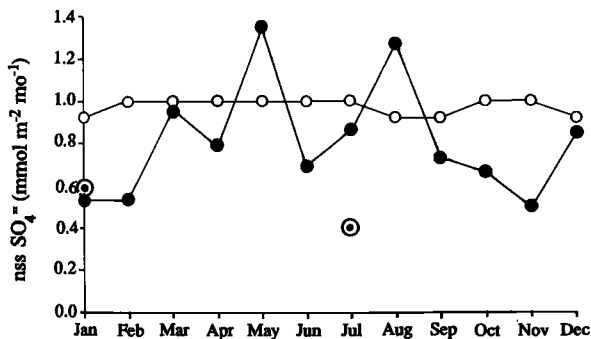term mean. Although at first glance the

Fig. 3. The results from the Stockholm
(open circle) and the Lawrence Livermore
National Laboratory (dot in open circle)
models for the nss $SO_4^=$ wet deposition
by month from Harbour Radio Tower, Ber-
muda, compared with the values from
monthly deposition records based on
storms collected from 1981-1989 (solid
circle).

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 NO_3^- measured on Ber-
muda 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 substan-
tial 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). Like-
wise, if the data in Figure 5 had shown
a similar year—to—year variation, there
could have been a much stronger agree-
ment 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 compar-
ison of the predicted versus the mea-
sured surface distributions and the
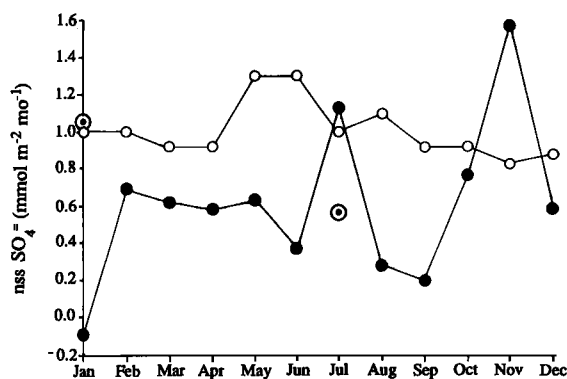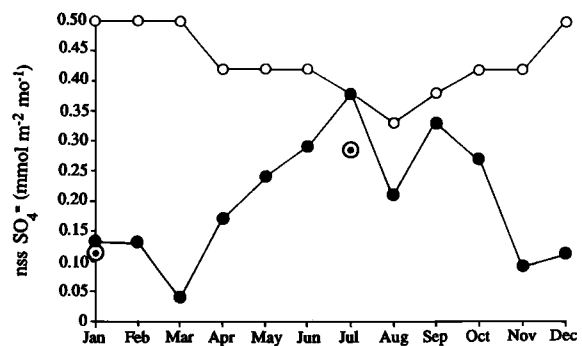deposition fluxes of the reactive nitro-

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 $SO_4^=$ wet deposition by month
(solid circle) from Mace Head, Ireland,
for the period of November 16, 1988, to
July 12, 1990.

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 $SO_4^=$ wet deposition by month
(solid circle) from Ragged Point, Barba-
dos, 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
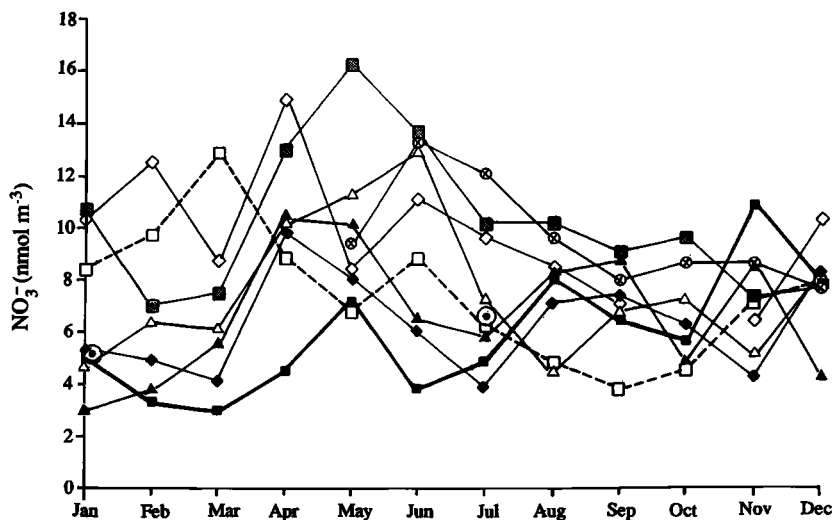

Fig. 6. The mean of the monthly aerosol nitrate concentrations measured at Ragged Point, Barbados, over 6 years (1984, cross in open circle; 1985, open triangle; 1986, solid diamond; 1987, open diamond; 1988, solid triangle; and 1989, stippled square) compared with the nitrate predictions from three 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 con-
centrations were slightly higher than
the January values because of both the
larger OH concentrations (which convert-
ed NO_x to HNO_3 in the model) and the
larger sources in the northern hemi-
sphere. (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 con-
centrations should have been close to
those measured. The model concentra-
tions 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 indi-
vidual 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 evi-
dent in the real data. Compared with
individual years of data, the model sim-
ulated 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 pre-
dicted 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 sub-
stantial disagreements (Figure 6) that
pointed to the need for a more detailed
analysis. In particular it would have
been desirable to compare the meteorol-
ogy used for the predictions with that
associated with any particular year's
data to assess the factors that contrib-
uted to any agreement or to the lack
thereof.

3.2.2. Bermuda: Nitrate wet deposi-
tion 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,
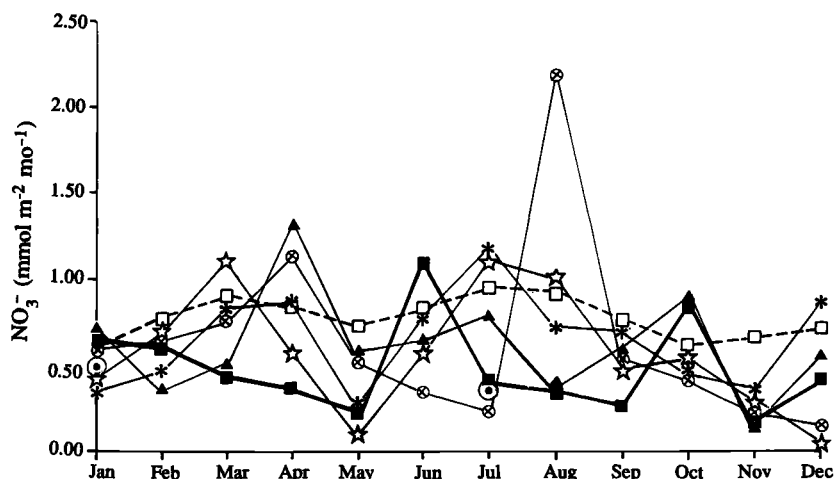and LLNL models (Figure 7). The wet-

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 pre-
dictions 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 concen-
trations and the total amount of precip-
itation 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 mmol m^{-2} $month^{-1}$; for
the individual months the variabilities
ranged from a factor of 12 in July (0.2-
2.4 mmol m^{-2} $month^{-1}$) to a factor of 5
in May (0.1-0.5 mmol m^{-2} $month^{-1}$)
(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 expect-
ed 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 depo-
sition 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 depo-
sition 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 some—what surprising because the
LLNL model included lightning and soil-
microbial sources in addition to the
fossil—fuel and biomass sources incorpo-
rated in the GFDL model. In the LLNL-
model simulations, fossil—fuel sources
provided only about 50% of the calcu-
lated 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 fac-
tor 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
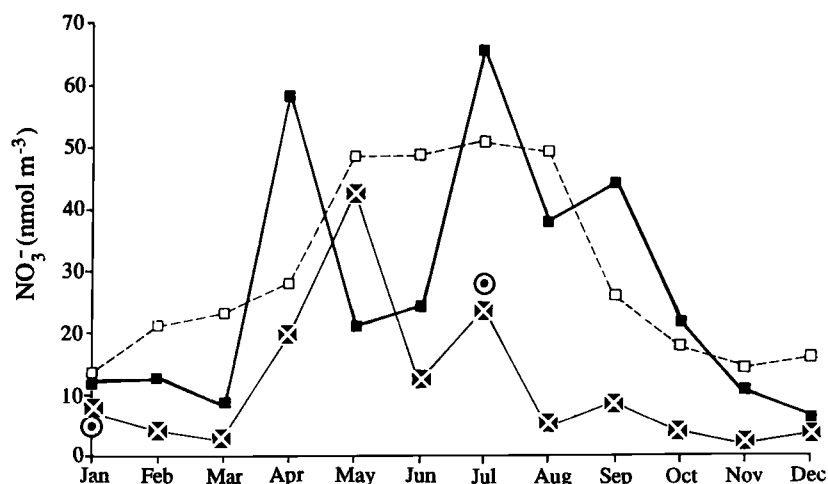model were smoother than in the data,

Fig. 8. The mean of the monthly aerosol nitrate concentrations measured at
Mace Head, Ireland, in 1989 (cross in solid square) compared with the predic-
tions 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 predic-
tions for the deposition of NO_3^- at Ber-
muda were in good agreement. This was
surprising because the predicted concen-
trations 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 deposi-
tion, 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 concentra-
tions may have been caused by a few
intense events (which would be difficult
to reproduce with a large-scale climato-
logical 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. Fig-
ure 8 shows a plot of the observed and

model-predicted, monthly averaged, aero-
sol 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 com-
pared 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. Nonethe-
less, 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, respec-
tively. 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 con-
centrations of pollutants from Europe.
However, as our comparisons showed, this
did not appear to be the case.

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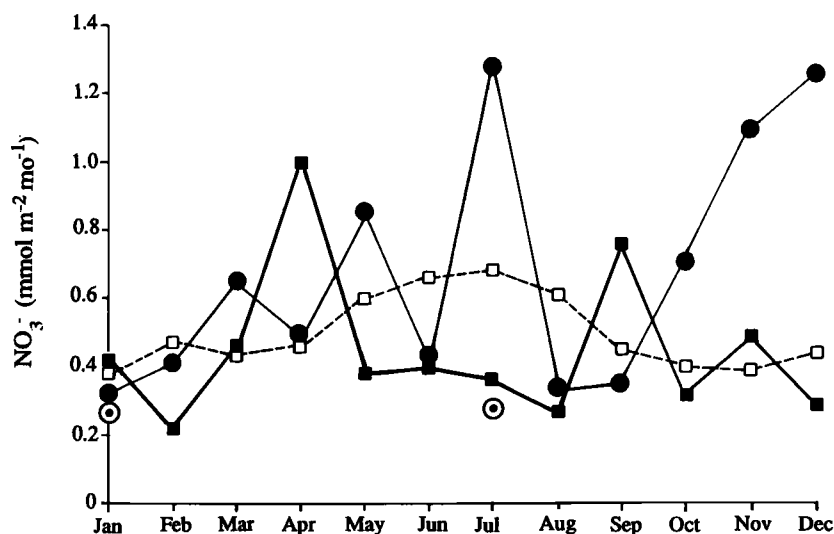during late spring and mid-summer. The

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) com-
pared 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 mmol
m^{-2} 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 dif-
ferent from that observed for the aero-
sols (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 deposi-
tion 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	$\delta/\bar{c}$
	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} month^{-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} month^{-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

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 concen—trations 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 $SO_4^=$ 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.

REFERENCES

Atherton, C. S., J. E. Penner, and J. J.
    Walton, Tropospheric ozone production in
    a global, three-dimensional chemistry-
    transport deposition model, poster paper
    presented at the International Symposium,
    Commission on Atmospheric Chemistry and
    Global Pollution, Chamrousse, France,
    Sept. 5-11, 1990.
Charlson, R. J., J. E. Lovelock, M. O.
    Andreae, and S. G. Warren, Oceanic phy-
    toplankton, atmospheric sulphur, cloud
    albedo, and climate, Nature, 326, 655-
    661, 1987.
Charlson, R. J., J. Langner, and H. Rodhe,
    Sulphate aerosol and climate, Nature,
    348, 22, 1990.
Charlson, R. J., J. Langner, H. Rodhe, C. B.
    Leovy, and S. G. Warren, Perturbation of
    the northern hemispheric radiative bal-
    ance by backscattering from anthropogenic
    sulfate aerosols, Tellus, Ser. AB, 43,
    152-163, 1991.
Charlson, R. J., S. E. Schwartz, J. M. Hales,
    R. D. Cess, J. A. Conkley, Jr., J. E.
    Hansen, and D. J. Hofmann, Climate forc-
    ing by anthropogenic aerosols, Science,
    255, 423-430, 1992.
Covey, C., S. J. Ghan, J. J. Walton, and
    P. R. Weissman, Global environmental
    effects of impact-generated aerosols:
    Results from a general circulation model,
    in An Interdisciplinary Conference on
    Impacts, Volcanism, and Mass Mortality,
    edited by V. L. Sharpton and P. D. Ward,
    pp. 263-270, Geological Society of Ameri-
    ca, Boulder, Colo., 1990.
Crutzen, P. J., and L. T. Gidel, 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. Geo-
    phys. Res., 88, 6641-6661, 1983.
Delmas, R., On the emission of carbon, nitro-
    gen and sulfur in the atmosphere during
    brushfires in the intertropical savanna

zones, Geophys. Res. Lett., 9, 761-764,
    1982.
Dignon, J., S. Hameed, J. E. Penner, J. J.
    Walton, and S. J. Ghan, Global simulation
    of ^{222}Rn and ^{210}Pb in a 3-dimensional
    Lagrangian tracer model, (abstract), Eos
    Trans. AGU, 70, 1025, 1989.
Erickson, D. J., III, J. J. Walton, S. J.
    Ghan, J. E. Penner, Three-dimensional
    modeling of the global atmospheric sulfur
    cycle: A first step, Atmos. Environ.,
    25A, 2513-2520, 1991.
Feichter, J., and P. J. Crutzen, Parameter-
    ization of vertical tracer transport due
    to deep cumulus convection in a global
    transport model and its evaluation with
    $^{222}radon$ measurements, Tellus, Ser. B,
    42, 100-117, 1990.
Galloway, J. N., and D. M. Whelpdale, WATOX-
    86 overview and western North Atlantic
    Ocean S and N atmospheric budgets, Global
    Biogeochem. Cycles, 1, 261-281, 1987.
Galloway, J. N., W. C. Keene, R. S. Artz,
    J. M. Miller, T. M. Church, and A. H.
    Knap, Processes controlling the concen-
    trations of $SO_4=$, NO_3^-, and NH_4^+, H^+,
    $HCOO_T$, and $CH3COO_t$ in precipitation on
    Bermuda, Tellus, Ser. B, 41, 427-443,
    1989.
Ghan, S. J., M. C. MacCracken, and J. J.
    Walton, Climatic response to large atmo-
    spheric smoke injections: Sensitivity
    studies with a tropospheric general cir-
    culation model, J. Geophys. Res., 93,
    8315-8337, 1988.
Glover, H. E., B. B. Prezelin, L. Campbell,
    M. Wyman, and C. Garside, A nitrate-
    dependent Synechococcus bloom in surface
    Sargasso Sea water, Nature, 331, 161-
    163, 1988.
Hameed, S., and J. Dignon, Changes in the
    geographical distribution of global emis-
    sions of NO_x and SO_x from fuel combustion
    between 1966 and 1980, Atmos. Environ.,
    22, 941-950, 1988.
Hamelin, B., F. E. Grousett, P. E. Biscaye,
    A. Zindler, and J. M. Prospero, Lead iso-
    topes in trade wind aerosols at Barbados:
    The influence of European emissions over
    the North Atlantic, J. Geophys. Res., 94,
    16,243-16,250, 1989.
Huebert, B. J., The partitioning of nitrate
    between aerosol and vapor in remote
    marine areas (abstract), Eos Trans. AGU,
    69, 1075, 1988.
Iversen, T., Numerical modeling of the long
    range atmospheric transport of sulphur
    dioxide and particulate sulphate to the
    Arctic, Atmos. Environ., 23, 2571-2595,
    1989.

Jaeger, L., Monthly and aereal patterns of mean global precipitation, in Variations in the World Water Budget, edited by A. Street-Perrott, M. Beran, and R. Ratcliffe, pp. 129-140, D. Reidel, Norwell, Mass., 1983.

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

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

Langner, J., and H. Rodhe, Anthropogenic impact on the global distribution of atmospheric sulphate, in Proceedings of the Conference on Global and Regional Environmental Atmospheric Chemistry, Beijing, China, 3-10 May 1989, edited by L. Newman, W. Wang, and C. S. Kiang, pp. 106-117, U.S. Department of Energy, Washington, D.C., 1990.

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

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

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

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

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

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

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

Oort, A. H., Global atmospheric circulation statistics, 1958-1973, Tech. Rep. 1983-407-474, 180 pp., Natl. Oceanic and Atmos. Admin., Washington, D.C., 1983.

Penner, J. E., C. S. Atherton, J. J. Walton, and S. Hameed, 1990. The global cycle of reactive nitrogen, in Proceedings of Regional/Global Atmospheric Chemistry Conference, Beijing, China, May 3-10, 1989, edited by L. Newman, W. Wang, and C. S. Kiang, pp. 264-279, U.S. Department of Energy, Washington, D.C., 1990.

Penner, J. E., S. J. Ghan, and J. J. Walton, The role of biomass burning in the budget and cycle of carbonaceous soot aerosols and their climate impact, in Global Biomass Burning, edited by J. Levine, pp. 387-393, MIT Press, Cambridge, Mass., 1991a.

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

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

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

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

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

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

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

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

Walton, J. J., M. C. MacCracken, and S. J. Ghan, A global-scale Lagrangian trace species model of transport, transforma-

tion and removal process, J. Geophys. Res., 93, 8339-8354, 1988.

Warneck, P., Chemistry of the Natural Atmosphere, 753 pp., San Diego, Calif., 1988.

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

Zimmermann, P. H., MOGUNTIA: A handy tracer model, in Proceedings 16th NATO/CCMS International Technical Meeting on Air Pollution Modeling and Application, edited by H. van Dop, pp. 593-608, Plenum Press, New York, 1987.

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

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