Atmospheric deposition of nutrients to the North Atlantic Basin

J.M. PROSPERO[1], K. BARRETT[2], T. CHURCH[3], F. DENTENER[4],
R.A. DUCE[5], J.N. GALLOWAY[6], H. LEVY II[7], J. MOODY[8] &
P. QUINN[9]

[1]*University of Miami, RSMAS, Miami, FL;* [2]*Norwegian Meteorological Institute, Oslo, Norway;* [3]*University of Delaware, College of Marine Studies, Newark, DE;* [4]*Wageningen University, Department of Air Quality, Wageningen, The Netherlands;* [5]*Texas A&M Univ., College of Geosciences & Maritime Studies, College Station, TX;* [6]*University of Virginia, Dept. of Environmental Sciences, Charlottesville, VA;* [7]*NOAA/GFDL, Princeton University, Princeton, NJ;* [8]*University of Virginia, Dept. of Environmental Sciences, Charlottesville, VA;* [9]*NOAA, Pacific Marine Environmental Laboratory, Seattle, WA*

Abstract. Atmospheric chemical models are used to estimate the deposition rate of various inorganic oxides of nitrogen (NO_y), reduced nitrogen species (NH_x) and mineral dust to the North Atlantic Ocean (NAO). The estimated deposition of NO_y to the NAO (excluding the coastal ocean) and the Caribbean is 360×10^9 Moles-N m^{-2} yr^{-1} (5.0 Tg N); this is equivalent to about 13% of the estimated global emission rate (natural and anthropogenic) and a quarter of the emission rate from sources in North America and Europe. In the case of NH_x, 258 Moles-N m^{-2} yr^{-1} (3.6 Tg N) are deposited to the NAO and the Caribbean; this is about 6% of the global continental emissions. There is relatively little data on the deposition rate of organic nitrogen species; nonetheless, this evidence suggests that concentrations and deposition rates are comparable to those for inorganic nitrogen.

Because of anthropogenic emissions, the present-day deposition rate of NO_y to the NAO is about five times greater than pre-industrial times largely due to emissions from energy production and biomass burning. The present-day emissions of NH_x from continental anthropogenic sources are about four-to-five times greater than natural sources, mostly due to the impact of emissions from animal wastes associated with food production. Indeed, present-day emissions of NH_x from animal waste are estimated to be about 10 times greater than the pre-human era. The deposition rate of mineral dust to the NAO is about 170 Tg yr^{-1}; deposited with the dust (assuming average crustal abundances) is about 6 Tg yr^{-1} of Fe and 0.2 Tg yr^{-1} of P. Dust deposition in the NAO is almost completely attributable to transport from North African sources; a substantial fraction of the dust over the NAO is probably mobilized as a consequence of land use practices in arid regions and, consequently, it should be regarded as a pollutant.

Abbreviations: AEROCE – Atmosphere/Ocean Chemistry Experiment; AOT – aerosol optical thickness; EMEP – Cooperative Program for Monitoring and Evaluation of Long Range; – Transmission of Air Pollution in Europe; GESAMP – A model used by the Group of Experts on the Scientific Aspects of Marine Pollution; GCM – General Circulation Model; GCTM – Global Chemical Transport Model; GFDL – Geophysical Fluid Dynamic Laboratory; MOGUNTIA – Model of the Global Universal Tracer Transport in the Atmosphere; MSC – Meteorological Synthesizing Centre; NAB – North Atlantic Basin; NAO – North Atlantic Ocean; NAS – National Academy of Sciences

Introduction

The atmosphere is an important pathway by which many gas and aerosol species are carried by winds from their sources to the larger world where they are eventually deposited. There is now ample evidence that a substantial fraction of the global cycles of many chemical species, both natural and anthropogenic, involves transport through the atmosphere. Although the fluxes of some species have been characterized for some regional waters and basins, they are not accurately known for the open ocean. Nonetheless, it is clear that some fluxes could be large enough to have a significant impact on the chemical and biological processes in natural waters and soils.

The North Atlantic Ocean (NAO) is a relatively small ocean basin that is closely bounded by four large continental masses. Consequently there is a relatively high probability that continental emissions, whether natural or anthropogenic, will be carried to the NAO by winds. Pollutant emissions are of particular interest because of the high level of human activities in this region. For example, sources of anthropogenic NO and NO_2 (Levy & Moxim 1989; Logan 1983; Hameed & Dignon 1992) are highly concentrated in northeastern North America and western Europe which together emit about half of the global total. Also, large quantities of soil dust are transported out of North Africa all year long, affecting much of the tropical NAO and Caribbean; dust concentrations are probably greater over the NAO than over any other large ocean region. Biomass burning products are also transported out of North Africa and over the NAO especially during the winter and spring. Thus, if wind-transported pollutants and other continental emissions are having an impact on nutrient cycling in the oceans, then the impacts should be most readily observable in the NAO and associated waters (North Sea, Caribbean, etc.).

In this paper we assess the atmospheric transport and deposition fluxes of a number of nitrogen species that could play a role in the nutrient cycle of natural waters. The primary productivity in surface waters of the ocean depends on the availability of nutrients (see for example, Eppley 1980; McCarthy & Carpenter 1983; Levitus et al. 1993), the most important being phosphate and nitrate. Historically, the major sources of nutrients in the photic zone were considered to be: the fixation of nitrogen in surface waters; the upward transport of nutrients from deeper waters; the recycling of nutrients in the surface waters. However, Duce (1986) showed that in some oligotrophic regions the atmospheric input of NO_3^- and Fe could play a significant role in primary production under certain conditions. A number of studies have supported this conclusion although the magnitude and importance of the effect is still debated (Fanning 1989; Michaels et al. 1993; Owens et al. 1992; Willey & Paerl 1993). Certain trace metals such as Fe (Martin & Fitzwater

1988; Donaghay et al. 1991; DiTullio et al. 1993) could also be important because of their role as essential micronutrients. Wind transported dust could be the dominant source of Fe for many ocean regions (Young et al. 1991; Morel et al. 1991; Miller et al. 1991; Duce 1986; Duce & Tindale 1991).

We present estimates of the atmospheric input to the oceans of several classes of nitrogen species that could play a role in the nutrient cycle. One group consists of nitrogen species that fall primarily into two classes: oxidized nitrogen species including aerosol NO_3^- and gas-phase oxides of nitrogen (NO, NO_2, HNO_3 and related species); reduced nitrogen species including aerosol NH_4^- and gaseous NH_3 (and related organic nitrogen species). There is evidence that organic nitrogen species could also play an important role. However, there are relatively little data for organic nitrogen compounds; most efforts has focused on dissolved organic nitrogen species (DON). We will discuss DON deposition but quantitative estimates are precluded.

The second group of nutrient-related species consists of Fe and P. These elements are primarily associated with mineral dust particles and, hence, the assessment of the fluxes of these elements will depend on estimates of dust transport to the oceans. To this end in this paper we discuss dust transport to the NAO and then use the model estimates of dust deposition to estimate the deposition of Fe and P.

The impact of atmospheric deposition to the NAO depends not only on the absolute quantities of material but also on the spatial and temporal variability of the deposition. Obviously, the deposition of nutrients into oligotrophic waters will have a much greater impact than on nutrient-rich waters (e.g., in a region of upwelling). Also we know that atmospheric transport and deposition processes are highly episodic; thus, nutrient species will often be deposited in short periods of time thereby increasing the nutrient enhancement process, albeit for a brief time. Nonetheless, these short bursts of enhanced productivity could have a number of important implications. For this reason, we devote a section of this paper to the discussion of temporal variability on time scales ranging from seasons to those of individual deposition events which typically extend over a period of hours to days.

In our review of the emissions rates of NO_x and NH_x to the atmosphere, we distinguish between the present-day fluxes due to natural and anthropogenic processes; the "natural" component of the present day emission rates serves as an estimate of "pre-industrial" emissions. A longer-term picture of emission trends is obtained from studies of chemical species in ice cores. We also make projections into the future based on population growth estimates and various scenarios for energy use. Although the projections are somewhat uncertain, they serve to demonstrate the magnitude of possible future impacts and changes in spatial deposition patterns.

The subject of long range atmospheric transport to the oceans has been addressed in a number of workshops (NAS 1978; Duce et al. 1991). A number of papers and reports have summarized various aspects of this subject (Hasse 1983; Merrill 1986; Moody & Galloway 1988; Rodhe 1985; Whelpdale & Moody 1990; Levy 1989; Whelpdale & Galloway 1994; Knap 1990; Riley et al. 1989; Merrill 1989; Whelpdale & Kaiser 1996). This current effort differs from the earlier ones in a number of respects, most notably in the use of a wide range of models to estimate transport and deposition to the North Atlantic.

Scientific background

In this section we review some aspects of the chemistry of the subject species and provide an overview of the larger issues regarding fluxes to the atmosphere. In preparing this section we do not attempt to provide an exhaustive literature review; rather we cite only representative papers and we make use of some comprehensive reviews. The source emissions discussed in the following section are summarized in Table 1. The data for NO_x species in Table 1 are taken largely from Galloway et al. (1995, 1996); the data for NH_x species are taken largely from Schlesinger & Hartley (1992). The purpose of this table is to provide the reader with a sense of the magnitude of the emissions to the atmosphere; the fact that we do not cite other literature sources more extensively in Table 1 (although others are cited in the discussion section) is not intended to imply that the values in Table 1 are necessarily the preferred ones. Nonetheless, as indicated in the text below, there is fairly good agreement for many species.

Nitrogen species

The important oxidized nitrogen species from the standpoint of transport and deposition are NO, NO_2 (collectively referred to as NO_x) and NO_3^- (both in the particulate form and as gas phase HNO_3). There are a number of organic nitrates that may play a significant role, in particular peroxyacetyl nitrate (PAN) which is believed to serve as a substantial reservoir for NO_3^- in the upper troposphere; however, PAN is unstable at typical lower troposphere temperatures, where it decomposes to yield HNO_3. The entire ensemble of reactive gas phase N-species is generally referred to as NO_y which is defined as the sum of NO_x, HNO_3, PAN and other related minor (mostly organic) species. The following discussion of sources and budgets is based largely on Galloway et al. 1995, 1996.

The dominant reduced nitrogen species are NH_4^+ and NH_3 (which, as a pair, are typically referred to as NH_x). It is important to note that in the atmosphere,

Table 1. Source emission estimates for NO_x and for NH_x. Estimates are shown for Pre-industrial missions and Present-day emissions; the difference between the two yields the present-day Anthropogenic emission rate. a) Source emissions of NO_y based on data taken largely from Galloway et al. (1995). b) Source emissions for NH_x. Data are largely from Schlesinger & Hartley (1992) except for pre-industrial biomass burning and animal excreta (Dentener & Crutzen 1994) and ocean sources (Quinn et al., this volume).

Source	Pre-industrial	Present day	Anthropogenic
NO_x (Tg N yr^{-1})*			
Lightning	3	3	–
Soils (and crops)	3.6	5.5	1.9
Biomass burning	0.8	8.5	7.7
Stratospheric injection	0.6	0.6	–
Energy production	0	21.3	21.3
Aircraft	0	0.5	0.5
Total	8.0	39.4	31.4
NH_x (Tg N yr^{-1})+			
Ocean	3■–13	3■–13	–
Soils (and fertilizer)	10	20	10
Biomass burning	0.5◊	5	4.5
Animal excretia	2.5◊	32	29.5
Total	16–26	60–70	44

* Levy et al. 1995; Galloway et al. 1995.
+ Schlesinger & Hartley (1992) except: ◊ Dentener & Crutzen 1994;
■ Quinn et al., this volume.

there is relatively little conversion or exchange between the NO_x/NO_y and the NH_x forms of nitrogen; in particular, NH_3 is quite resistant to oxidation under normal circumstances although in tropical regions model results suggest that significant amounts of NH_3 may be oxidized due to high OH and low sulfate concentrations (Dentener & Crutzen 1994). Similarly, N_2O is relatively stable in the troposphere and does not participate to a significant degree in NO_x/NO_y chemistry nor that of NH_x.

Natural sources
The primary natural sources of NO_x are biological fixation and lightning. Lightning is a relatively minor source of NO, about 3 Tg N yr^{-1} (Lawrence et al. 1995; Levy et al. 1995); while there have been much higher estimates in the past, they are no longer tenable based on wide-spread measurements of consistently low values of NO_x and NO_3^- in remote regions.

Pre-industrial biotic N fixation in terrestrial ecosystems is estimated to be about 90–130 Tg N yr^{-1} (Stedman & Shetter 1983); fixed N is converted to

organic N or lost from the organism as reduced inorganic N (NH_4^+). N will remain in reduced form until an element other than N becomes limiting or until there is a reduction of biotic mass (e.g., as a result of fire, seasons with limited growth, widespread vegetation decay, etc.). Of this total, only about 4.4 Tg N yr^{-1} is emitted to the atmosphere as NO_x; 3.6 Tg N yr^{-1} is emitted directly from soils (Yienger & Levy 1995) and 0.8 Tg N yr^{-1} from burning (Galloway et al. 1994). There are no major oceanic sources of NO_x or NO_y. Logan (1983) estimates that less than 1 Tg N yr^{-1} is emitted from the oceans as NO each year. As shown in Table 1, the total pre-industrial emissions of NO_x are about 8 Tg N yr^{-1}.

Major natural sources of NH_x include excreta from wild animals (2.5 Tg N yr^{-1}, Dentener & Crutzen (1994), 4 Tg N yr^{-1}, Warneck (1988)), and emissions from soils and vegetation (5.1 Tg N yr^{-1}, Dentener & Crutzen (1994); 10 Tg N yr^{-1}, Schlesinger & Hartley (1992)). The oceans, especially regions of the Pacific Ocean that are not heavily impacted by anthropogenic activities, are believed to be a source of NH_3 (Quinn et al. 1988, 1990; Quinn et al., this volume). Estimates of a global source strength are highly uncertain, however, due to a lack of confirming atmospheric and seawater measurements. Schlesinger & Hartley (1992) estimate the oceanic source of NH_3 at 13 Tg N yr^{-1}; Dentener & Crutzen (1994) estimate 7 Tg N yr^{-1}. In more recent work (Quinn et al., this volume) an even lower emission rate of about 3 Tg N yr^{-1} has been estimated. Emissions from pre-industrial biomass burning are very difficult to estimate but they are believed to be small (e.g., 0.5 Tg N yr^{-1}; Dentener & Crutzen 1994). The total pre-industrial emissions of NH_x (Table 1) is about 16–26 Tg N yr^{-1}, based largely on the estimates of Schlesinger & Hartley (1992). The lower value reflects the very low emission rate obtained for the oceans by Quinn et al. (this volume). Dentener & Crutzen (1994) also obtain a lower total, 14.6 Tg N yr^{-1}, largely because of their lower estimates for the oceanic source and for emissions from soils and vegetation.

Although inorganic nitrogen has been studied in aerosols and precipitation for some time, only recently has it been recognized that organic nitrogen can be of comparable importance. Organic nitrogen in aerosols and precipitation can result from reactions of gas phase species and by mechanical processes that release particles directly (e.g., plants fragments, sea spray droplets). The protein in pollens or oceanic surface films may degrade in the atmosphere to lower molecular weight organic species such as amino acids or primary amines. Because many different techniques have been used to study organic nitrogen, it is often difficult to make a direct comparison of results. Most research has focused on the DON fraction. The composition, sources and sinks of DON are so poorly characterized that it is impossible to make detailed

model estimates of global budgets as we do for NO_x and NH_x species (see below).

Anthropogenic sources and sinks of NH_x and NO_y
There are three types of anthropogenic activities that are major producers of reactive N: fuel combustion; fertilizers; and the cultivation of certain crops, especially legumes. It is generally agreed that the present day utilization of energy sources (combustion of coal, petroleum products, natural gas) produces about 20 Tg N yr^{-1} as NO_x (Levy & Moxim 1989; Hameed & Dignon 1988, 1992; Benkovitz et al. 1995). This source is growing at a steady rate – from 1960 to 1986, at about 2.7% per year. There is also reasonable agreement that the production of fertilizer converts about 78 Tg N yr^{-1} from N_2 to NH_3 with an annual rate of increase of 5.3% per year (see Galloway et al. 1994). Because of the increased N fixed in soils by crops, there is an additional release of 1.9 Tg N yr^{-1} of NO from soils (Yienger & Levy 1995) and biomass burning produces 7.7 Tg N yr^{-1} (Levy et al. 1991) yielding a total of 9.6 Tg N yr^{-1}.

Large quantities of NH_3 are emitted directly from fields as a result of added fertilizer: 10 Tg N yr^{-1} (Schlesinger & Hartley 1992); 6.4 Tg N yr^{-1} (Dentener & Crutzen 1994). Excreta from domesticated animals yield: 32 Tg N yr^{-1} NH_3 (Schlesinger & Hartley 1992); 22 Tg N yr^{-1} (Dentener & Crutzen 1994). Biomass burning yields: 5 Tg N yr^{-1} (Schlesinger & Hartley 1992); 2 Tg N yr^{-1} (Dentener & Crutzen 1994). Coal combustion is believed to be a negligible source (Dentener & Crutzen 1994); Warneck (1988) estimates less than 2 Tg N yr^{-1}. The present day emissions of NH_x (including both natural and anthropogenic sources) is about 60–70 Tg N yr^{-1} (Table 1), based largely on the estimates of Schlesinger & Hartley (1992); Dentener & Crutzen (1994) obtain a substantially lower value, 45 Tg N yr^{-1}.

Once in the atmosphere, NH_3 can react with acidic non-seasalt sulfate and nitrate aerosol particles to form partially-to-fully neutralized ammoniated salts. Wet deposition is the major removal pathway of this particulate NH_4^+ from the atmosphere. NH_3 also can be dissolved directly into cloud water where, if the cloud does not evaporate, NH_3 will be removed through wet deposition. The lifetime of NH_3 with respect to reaction with sulfate aerosol is very short compared to the lifetime with respect to oxidation by OH (Quinn et al. 1992; DeMore et al. 1992) although in the tropics with high OH and low sulfate concentrations some oxidation of NH_3 may occur (Dentener & Crutzen 1994).

Conclusions
The present day rate of emissions of NO_x and related species is about five times greater than the emissions in pre-industrial times largely due to emis-

sions from energy production and biomass burning. The present day emissions of NH_x are about three times greater mostly due to the impact of emissions from animal wastes associated with food production. Indeed, emissions of NH_x from animal waste have increased by about a factor of 10. From the standpoint of oceanic impacts, the effective increase of NH_x emissions is much greater than the gross numbers would indicate. The oceanic source of NH_x accounts for as much as half of the total pre-industrial emissions. If we compare only the continental components of the NH_x budgets (because these are the only components that could lead to a net increase in oceanic deposition), the present day NH_x emissions are about four-to-five times greater than the pre-industrial rates.

The total present-day emissions for both NO_x and NH_x is about 100–110 Tg N yr^{-1} (Table 1); total pre-industrial emission rates were about 24–34 Tg N yr^{-1}.

A substantial fraction of the continental emissions, whether natural or anthropogenic, are deposited relatively close to the source regions. These deposits may impact processes in watersheds and in coastal waters. However a substantial fraction is carried to the open oceans by winds. In subsequent sections we estimate the total deposition to these various regions. Although we do not attempt to assess the deposition fluxes for anthropogenic and natural sources independently, it can be assumed that the relative deposition rates for these two classes of substances will be approximately the same as those for the gross budgets as shown in Table 1.

Mineral dust

Huge amounts of soil dust are mobilized by winds, mostly in arid regions, and substantial quantities can be carried great distances. The importance of eolian transport to oceanic processes was first suggested by studies of the mineral distributions in pelagic ocean sediments. The concentration patterns of certain minerals (e.g., quartz, kaolinite, illite) in sediments off the coasts of some continents (e.g., the west coast of North Africa and North America, the east coast of Asia) were not related to fluvial sources but rather to the pattern of large scale wind fields (Prospero 1981). The subject of dust mobilization and transport has been extensively studied during the past two decades (for reviews, see for example: Prospero 1981, 1990, 1996; Pye 1987; Middleton 1990; Duce 1995; Goudie & Middleton 1992). A recent issue of Atmospheric Environment is devoted to the results of a large Russian/American field study of dust mobilization in central Asia (Golitsyn & Gillette 1993). Many aspects of dust transport to the ocean are summarized in Duce et al. 1991.

It is difficult to quantitatively estimate dust transport amounts because of the difficulty in defining what is meant by "transport". Vast quantities of soil

material are moved by winds each year especially in regions of sand dunes and in eroding agricultural areas (Pye 1987). However, much of the transported mass in the source regions consists of large particles, that is, particles with diameters greater than about ten microns (d'Almeida and Schütz 1983). Such large particles have a very short residence time in the atmosphere because of their high settling velocity and will not be carried far by winds. For this reason, in assessments of long-range transport it is customary to base flux estimates on that portion of the particle mass that is below about 10–20 μm diameter. Because of the rapid fallout of large particles during transport, the size distribution rapidly shifts to small particles; at distances of about 1000 km or more from the source, the dust attains a relatively stable size distribution with a mass median diameter of several μm (Duce 1995) although some very large particles can be carried great distances (Betzer et al. 1988). Because of these variables, estimates of the source strength of dust are probably the poorest of any major aerosol species and estimates of deposition are also highly uncertain. Nonetheless, on a global scale, dust production rates are estimated to be in the range of about 1000–3000 Tg yr^{-1} (Duce et al. 1991; Duce 1995; Andreae 1995).

North Africa is one of the world's largest sources of dust that can be transported great distances. Large amounts of dust are carried to the north across the Mediterranean to Europe (Bergametti et al. 1989a) and to the west (Bergametti et al. 1989b) across the North Atlantic to the Caribbean, the east coast of North America (Prospero & Nees 1986; Prospero et al. 1987) and to South America (Prospero et al. 1986; Swapp et al. 1992). Satellite imagery of aerosol optical thickness (AOT) (Ignatov et al. 1995; Rao et al. 1989) shows that the highest values of AOT and the largest areal coverage over the oceans is clearly related to dust sources (Prospero 1996). Over the North Atlantic, the pollution plumes (as manifested by AOT distributions) that emerge from the east coast of the US and west coast of Europe are relatively small and weak in comparison to the African dust plume. Furthermore dense African dust plumes are highly visible all year long while the European and North American pollution plumes are prominent only in spring and summer.

The chemical and mineralogical composition of mineral dust over the North Atlantic has been extensively studied (Prospero 1981; Schütz et al. 1990). The elemental composition of the dust is similar to that of average crustal material (Zhuang et al. 1992; Uematsu et al. 1985; Arimoto et al. 1989, 1990, 1992; Prospero 1981; Prospero et al. 1987, 1989; Lepple 1975; Talbot et al. 1986; Graham & Duce 1979; Spokes et al. 1994). Although there have been few studies of the organic composition of the dust, total organic carbon concentrations are on the order of a few percent (Lepple & Brine 1976; Delaney & Zenchelsky 1976; Duce et al. 1983).

Stragety

Introduction

Our strategy is to estimate deposition to the NAO by means of transport/ deposition models and to assess the relative performance of the models by comparing the calculated deposition to the NAO. We also compare the model results with the few deposition measurements that are available. The detailed description of the models and the comparisons of results are found in Prospero et al. (1995). Because the models are very different (they use different "meteorology", source configurations, and parameterizations of the transformation and removal processes), the degree of agreement (or disagreement) will give us some idea of the validity of the computed deposition over the entire NAO. The comparison showed that the models produced surprisingly concordant results for most regions. Consequently, our estimates of deposition will be based on the means of all available model results for specific regions. In the following sections we describe the models and present the estimated deposition rates for NO_y and NH_x. We then compare the model estimates with the deposition rates measured at a few island and coastal sites. Finally we present the deposition estimates for the North Atlantic Basin (NAB), i.e., the entire NAO and the land areas that drain into it.

Model descriptions

Five models are used: Global Chemical Transport Model (GCTM) of the NOAA Geophysical Fluid Dynamics Laboratory (GFDL); EMEP (Cooperative Program for Monitoring and Evaluation of Long Range Transmission of Air Pollution in Europe); MOGUNTIA (Model of the Global Universal Tracer Transport In the Atmosphere); and two versions of GESAMP (a model used by the Group of Experts on the Scientific Aspects of Marine Pollution. Duce et al. 1991). These are briefly described here. Three models (GCTM, EMEP and MOGUNTIA) are based on meteorological modules (either generated by the model or based on real meteorological data). Emissions (natural and pollutant) from sources are injected into the models' atmosphere where they are transported according to the meteorological wind fields. The chemical transformation and removal processes are parameterized (in varying degrees of detail, depending on the complexity of the model and the computer resources).

The GFDL/GCTM uses transport fields that are derived from a general circulation model (GCM); the model yields twelve months of 6-hour time-averaged wind, temperature, and precipitation fields (Mahlman & Moxim 1978). In common with all GCMs, the GCTM generates a detailed "meteo-

rology" for an average year. While the model may successfully produce the "meteorology" and "climatology" that one might expect for a typical time period (e.g., a typical day in July or a typical July), there is no correspondence to the weather or climate of any specific period (e.g., 4 July 1994). The GCTM has a horizontal resolution of 265 km ($2.4° \times 2.4°$) (Levy et al. 1982; Kasibhatla et al. 1993).

The MSC (Meteorological Synthesizing Centre) EMEP model is a high resolution 3-D model that covers Europe and adjacent seas including the northeast Atlantic, the European Arctic Ocean and the adjacent seas: North, Norwegian, Baltic, Black and Mediterranean. The model has a resolution of 150 km and incorporates real meteorological data. Because of its high resolution and limited spatial coverage, EMEP does not provide estimates for deposition to the open ocean in the North Atlantic.

MOGUNTIA (Zimmermann 1988) is a low-resolution ($10° \times 10°$) 3-D model based on average winds obtained from meteorological data (Oort 1983). Transport by deep cumulus convection is parameterized according to Feichter & Crutzen (1990). Horizontal transport is described by monthly average winds and an eddy diffusion parameterization based on the standard deviation of the winds from the means. Transport by deep cumulus convection is described through parameterizations.

The GESAMP (Duce et al. 1991) models are low resolution ($10° \times 10°$) 2-D empirical models. Wet deposition is calculated using climatological precipitation fields which are combined with existing atmospheric chemical concentration data. The GESAMP-I model uses gas and aerosol concentration fields over the oceans to calculate wet and dry deposition. GESAMP-II (Whelpdale & Galloway 1994) is basically the same as the GESAMP-I model. However, instead of calculating the wet deposition on the basis of gas and aerosol concentration fields, it uses existing data on precipitation concentrations. These are compiled on the map grid and interpolated using physically reasonable approximations; GESAMP-II deposition rates are obtained using the same rainfall amounts used in GESAMP-I.

The comparison of model performance (Prospero et al. 1995) showed that there was general good agreement amongst the various model estimates for the deposition of NO_y and NH_x to the NAO and to the coastal ocean and continental watershed. Indeed, the agreement was surprisingly good when one considers the very different rationales employed in the models, the different meteorologies upon which they are based and the different data sets that are used for source emissions in the models. For the most part the mid-ocean deposition estimates (using GCTM, MOGUNTIA, GESAMP-I and GESAMP-II) for NO_y agree to within $\pm 50\%$ of the mean. Only two

models (MOGUNTIA and GESAMP-I) yield estimates for NH_x; even here the agreement is remarkably good for the mid-ocean regions.

Only the MOGUNTIA and EMEP provide estimates of NH_x deposition to the coastal ocean and the continental watersheds. Even these models yield surprising agreement in their estimates except for NH_x in the western NAO.

Comparison of model estimates with measured deposition rates

There is very little long-term (a year or longer) deposition data with which to compare the model estimates. In Table 2 we summarize wet deposition data (Galloway, pers. comm.) for NO_3^- and NH_4^+ from five stations in the NAB and compare them with the values obtained with the models. For this comparison, it was not convenient to obtain the modeled wet deposition values separate from the dry deposition amounts; instead we show the total deposition (wet and dry) rates obtained from the models and compare them with the measured values for wet deposition only. However, we would expect that the dry deposition fraction would constitute only a small fraction of the total flux at these sites.

Mace Head, Ireland. The averaged models results are close to the measured values for both NO_3^- and NH_4^+ (four years of data).

Lewes, Delaware. Although there is a considerable spread among the model values for NO_y, the mean is close to the measured values (ten year means) for both NO_3^- and NH_4^+.

Bermuda. The Bermuda comparison is the poorest of the entire set. All models substantially overestimate the deposition rate to this region. Table 2 shows the measured means for two periods: 1981–1988, when the sampling site was located at Harbor Tower, near the eastern end of Bermuda; 1989–1993, when the sampling was carried out at the AEROCE (Atmosphere/Ocean Chemistry Experiment) site at Tudor Hill, at the extreme western end of the island. The deposition rate at the eastern site was markedly higher for both species, 31% greater for NO_3^- and 75% greater for NH_4^+ (Figure 1). The relatively high deposition rate at the eastern site appears to be largely due to differences in rainfall amount; the annual mean precipitation at the western site during 1989–1993 was 100.0 cm while at the eastern site during 1981–1988 the mean was 146.3 cm; i.e., 46% greater. In the case of Bermuda, we must ask which deposition rate is most appropriate for use in the comparison with the models. In this regard, it should be noted that the distance between these two sites is only about 30 km, much less than the resolution of any of the models. The large difference in deposition amounts demonstrates the close

Table 2. Comparison of model estimates of deposition with measured values. (Units: mMoles-N m^{-2} yr^{-1}.)

	NO$_3^-$	NH$_4^+$
Mace Head		
MOG	6.1	3.5
GCTM	4.9	–
GES-I	–	3.9
GES-II	7.1	–
Model avg.	6.0	3.7
Meas. (1990–93)	5.2	4.4
Lewes, DE		
MOG	29.8	16.3
GCTM	52.9	–
GES-I	12.7	8.0
GES-II	21.4	–
Model avg.	29.2	12.1
Meas. (1981–90)	22.5	15.5
Bermuda		
MOG	14.7	7.6
GCTM	14.1	–
GES-I	7.9	7.8
GES-II	14.3	–
Model avg.	12.8	7.7
Meas. (1981–88)	6.4	4.2
(1989–93)	4.9	2.4
Everglades, FL		
MOG	7.6	10.0
GCTM	21.4	–
GES-I	5.4	8.8
GES-II	–	–
Model avg.	12.5	9.4
Meas. (1990)	12.1	9.7
Barbados		
MOG	1.6	1.1
GCTM	1.4	–
GES-I	4.1	1.2
GES-II	6.4	–
Model avg.	3.4	1.1
Meas. (1990–93)	2.0	2.0

Coordinates
Mace Head, Ireland	53.32N 9.85W
Lewes, DE	38.75N 75.14W
Bermuda	32.27N 64.87W
Everglades Park, FL	25.10N 80.53W
Barbados	13.17N 59.43W

linkage between scavenging rates and precipitation and shows how the model deposition rates will depend to a considerable degree on the accuracy of the precipitation modeling. In the case of Bermuda, it could be argued that the increased rainfall at the eastern site is due to topographic effects and that the rainfall amounts at the western end should be more representative of oceanic rainfall amounts.

Thus, the models as a group appear to seriously overestimate the eastward transport of materials from North America. However the overestimate does not appear to extend to the NAO on a broader scale. The average model deposition rates for the grid box immediately to the east of the Bermuda box (6.4 mMoles-N m^{-2} yr^{-1} for NO$_y$, 3.8 mMoles-N m^{-2} yr^{-1} for NH$_x$) are close to the mean values measured on Bermuda; similarly, for the box to the south of Bermuda the average model values are 5.6 mMoles-N m^{-2} yr^{-1} and 3.0 mMoles-N m^{-2} yr^{-1} for NO$_y$ and NH$_x$ respectively. The mismatch between the model results and the measured values may be due in part to the very coarse grid size that is used in this comparison.

Everglades, Florida. There is a considerable spread among the model values for NO$_3^-$ but the mean is essentially identical to the measured value. The modeled NH$_4^+$ values are also quite close to the measured values.

Barbados, West Indies. The model estimate for NH$_4^+$ is about half the measured values. In contrast the model average for NO$_y$ is about 70% greater than the measured value. The model average is shifted strongly to the high side by the results from the two GESAMP models; the MOGUNTIA and GCTM values are quite close to the measured mean (four years). The deposition results for NO$_y$ for the Barbados grid cell are somewhat anomalous in that the agreement amongst the models is much better for the adjacent grid cells on all sides.

In summary, the models do a reasonable job of estimating the deposition at the stations. The model estimates for three stations (Mace Head, Lewes and Everglades) were extremely close to the measured values. The Bermuda results were quite poor but they could be rationalized into better agreement. On the basis of these limited comparisons, it is difficult to estimate the overall reliability of the model estimates. Nonetheless, it should be noted that the poorest estimates were off at most by a factor of about two (allowing for a rationalization of the Bermuda results). Thus, for the NAB as a whole, we would expect the model estimates to be within a factor of two of the true value.

(a)

(b)
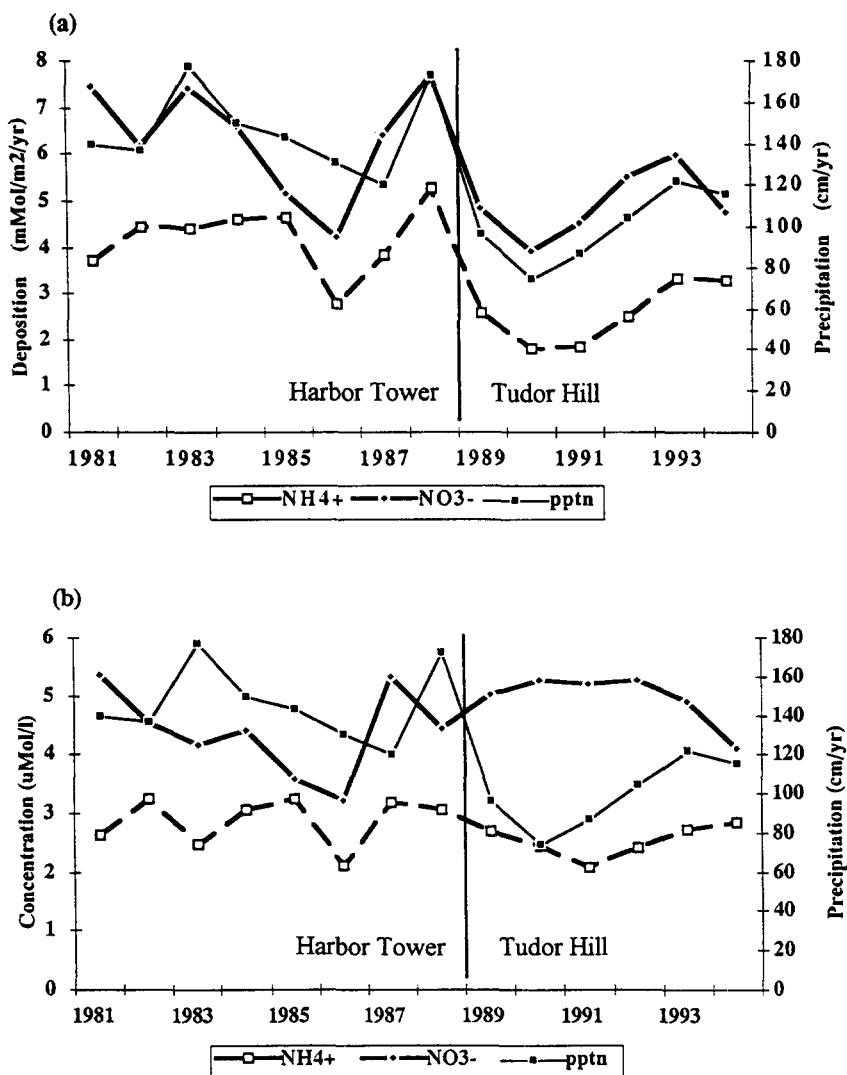
Figure 1. a.) Annual precipitation amounts (cm yr^{-1} and annual volume weighted deposition rates for nitrate-N and ammonium-N (mMoles-N m^{-2} yr^{-1}) for Bermuda for 1981–1993. b.) Annual mean concentration (μMol l^{-1}) for nitrate-N and ammonium-N. The vertical line indicates the change in location of the sampling station from Harbor Tower located near the eastern end of the island to Tudor Hill on the western end (Galloway, pers. comm.).

Nitrogen species

NO$_y$

The annual mean deposition rates obtained from the four models for the NAO and the Caribbean are shown in Table 3. These rates are computed for a 10° ×

10° grid and they include both the wet and the dry deposition fluxes. Table 3 presents both the deposition rate per unit area (mMoles-N m^{-2} yr^{-1}) and the total annual deposition per grid square (10^9 Moles-N). The table also shows the sums of the total annual deposition in 10° latitude bands.

The model-estimated deposition rates of NO$_y$ and NH$_x$ (mMoles-N m^{-2} yr^{-1}) to continental watersheds and to coastal waters are shown in Table 4. In those areas where the coastal shelves are very narrow (e.g., West Africa, Caribbean Islands, etc.), the model resolution was too coarse to provide an estimate. For the same reason, we do not attempt to assess the total deposition to the watersheds and coastal regions, but provide only the rate per unit area.

Howarth et al. (this volume.) and Nixon et al. (this volume) use the values in Table 4 (deposition rate per unit area) to estimate the total deposition to the shelves and the watersheds.

The impact of continental sources is quite obvious. The deposition rates are much higher in the grid cells adjacent to North America and Europe and they decrease rapidly with distance to the ocean. The NO$_y$ deposition rates along the east coast of North America and the Gulf of Mexico (Table 4) range from about 20 to 40 mMoles-N m^{-2} yr^{-1}; for western European waters, the rates are somewhat lower, about 20 to 25 mMoles-N m^{-2} yr^{-1}. In contrast, the central NAO deposition rates tend to fall in the range of 2 to 4 mMoles-N m^{-2} yr^{-1}, about a factor of ten lower. Looking at the total deposition of NO$_y$ to the NAO as a function of latitude (Table 3), the deposition from 30° N to 60° N is somewhat less than twice as great as that the 10° N to 30° N band. But note that the flux in the band from 0° N to 10° N is comparable to that in the mid-latitudes. Finally, the deposition to the 60°–70° N band is quite low, about a quarter of that in the 30°–60° N band.

NH$_x$

The mean deposition rates of NH$_x$ species to the open NAO are shown in Table 5. Only two models provided NH$_x$ estimates, MOGUNTIA and GESAMP-I; nonetheless, the agreement is quite good. The rates are computed for a 10° × 10° grid and they include both the wet and the dry deposition fluxes. Table 5 presents both the deposition rate per unit area (mMoles-N m^{-2} yr^{-1}) and the total annual deposition per grid square (10^9 Moles-N). The table also shows the sums of the total annual deposition in 10° latitude and longitude bands. The model-estimated deposition rates of NH$_x$ (mMoles-N m^{-2} yr^{-1}) to continental watershed and to coastal waters are shown in Table 4.

As was the case of NO$_y$, the deposition rates are quite high in the coastal waters and decrease rapidly with distance to the oceans. Values along the east coast of North America and the Gulf of Mexico fall in the range of about 10–20 mMoles-N m^{-2} yr^{-1} while those for European coastal waters are in

Table 3. Annual average NO$_y$ deposition to the open ocean. Total (wet plus dry) per 10° square. Also shown are the sums in 10° latitude and longitude bands. The sums do not include deposition to the Caribbean or the Mediterranean.

Lat.	Longitude											Lat. sum
	100–90	90–80	80–70	70–60	60–50	50–40	40–30	30–20	20–10	10–00	00–10	
a: Total NO$_y$ deposition: mMoles N m^{-2} yr^{-1}												
60–70					1.9		2.1	2.7	3.9	6.7	7.1	
50–60					6.4	4.3	3.6	3.8	6.0	50.4		
40–50				17.5	9.5	6.1	4.3	3.3	4.6	13.4		
30–40			29.0	12.8	6.4	4.3	3.1	2.8	4.1			
20–30	18.4	14.9	8.7	5.6	3.5	2.5	2.1	2.6	3.1			
10–20		10.2	6.8	5.6	3.4	2.6	2.4	3.1	8.5			
00–10					7.3	4.4	4.2	5.0	8.1	8.8	12.6	
b: Total NO$_y$ deposition: 10^9 moles N 10°-box^{-1} yr^{-1}												
60–70					1.0		1.1	1.4	2.0	3.5	3.7	12.8
50–60					4.5	3.0	2.6	2.7	4.3	35.6		52.7
40–50				15.2	8.3	5.3	3.8	2.9	4.0	11.6		51.2
30–40			29.2	12.9	6.5	4.3	3.2	2.8	4.1			62.9
20–30	20.6	16.6	9.7	6.3	3.9	2.7	2.3	2.9	3.4			31.3
10–20		12.1	8.1	6.7	4.0	3.1	2.9	3.7	10.1			38.6
00–10					9.0	5.4	5.2	6.1	10.0	10.7	15.4	61.8
										N. Atlantic total		311.2
										Carib. total		49.3

Table 4. NO_y and NH_x Deposition Rates to Continental Watersheds and to Coastal Ocean Regions: Average of Models (mMoles-N m^{-2} yr^{-1}). For total deposition amounts to the watershed and coastal regions, see Howarth et al. (this volume) and Nixon et al. (this volume).

Region	Code	NO_y cont	NO_y coast	NH_x cont	NH_x coast	Ratio: NO_y/NH_x Cont	Coast
North Canadian rivers	NCR	6	5	5	2	1.2	2.0
St. Lawrence Basin	SLB	40	15	19	6	2.1	2.5
North-East USA	NEU	61	38	17	11	3.6	3.5
South-East USA	SEU	66	22	25	10	2.6	2.3
Eastern Gulf of Mexico	EGM	60	20				
Mississippi	MIS	38	30	19	18	2.0	1.6
Western Gulf of Mexico	WGM	20	18	16	14	1.2	1.3
Cent & No. S. Amer. (to Carib)	CNS	19	5	13	7	1.5	0.6
Amazon	AMA	16	5	10	10	1.6	0.5
Mediterranean	MED		16	11	10		1.6
Spain and Portugal	SP	24	22	23	14	1.1	1.6
W. Europe, Grt Brit. (to N. Sea)	WEB	55	25	53	22	1.0	1.2
Baltic	BAL	33	24	40	28	0.8	0.9

the range of 10–30 mMoles-N m^{-2} yr^{-1}. Central ocean values range from about 1–3 mMoles-N m^{-2} yr^{-1}. In the case NH_x high deposition rates are also found in the low latitudes, from 0° N to 20° N; indeed, total deposition in the 0°–10° N band is about twice as high as that in any other latitude band, largely reflecting the impact of sources in North Africa. However, it should be emphasized that our knowledge of NO_y and (especially) NH_x sources in Africa is poor compared to those for Europe and North America.

Organic nitrogen

None of the models provide estimates of organic nitrogen transport and deposition. Because most research has focused on DON and because there is very little data on particulate organic nitrogen (PON), we simply survey the available data on DON. We then use the relative concentrations of DON and dissolved inorganic nitrogen (DIN, largely NO_3^- and NH_4^+) to extrapolate to the entire NAO using the modeled deposition rate of inorganic nitrogen to the region. This estimate assumes that the DON-to-DIN ratio is generally applicable to the region; obviously, this must be regarded as a very rough estimate of DON deposition.

The first reported measurements of DON in rain were made off the coast of California by Williams (1967), (Table 6); values were about 1.7 μmolar or 49 to 65% of the total nitrogen. More recently, in the North Atlantic,

Table 5. Annual average NH$_x$ deposition to the open ocean. Total per 10° square. Also shown are the sums in 10° latitude and longitude bands. The sums do not include deposition to the Caribbean or the Mediterranean.

a: Total NH$_x$ deposition: mMoles N m^{-2} yr^{-1}

Lat.	100–90	90–80	80–70	70–60	60–50	50–40	40–30	30–20	20–10	10–0	0–10	Lat. sum
60–70					2.4		3.6	3.9	3.4	4.4	7.6	
50–60					4.9	3.1	3.1	3.1	3.7	4.8		
40–50				8.5	6.7	3.8	2.0	1.7	2.7	10.3		
30–40			12.1	7.7	3.8	1.8	1.4	1.9	3.0			
20–30	12.5	9.4	7.4	3.0	1.1	0.8	0.7	1.9	1.5			
10–20		13.7	9.1	6.2	1.1	0.9	1.3	3.0	7.1			
00–10					13.1	3.8	2.1	3.2	11.0	13.4	12.6	

b: Total NH$_x$ deposition: 10^9 moles N 10°-box^{-1} yr^{-1}

Lat.	100–90	90–80	80–70	70–60	60–50	50–40	40–30	30–20	20–10	10–0	0–10	Lat. sum
60–70					1.3		1.9	2.0	1.8	2.3	4.0	13.2
50–60					3.5	2.2	2.2	2.2	2.6	3.4		16.0
40–50				7.4	5.8	3.3	1.8	1.5	2.3	9.06		31.1
30–40			12.2	7.8	3.8	1.9	1.4	2.0	3.1			32.1
20–30	14.0	10.5	8.3	3.3	1.3	0.9	0.8	2.1	1.7			18.3
10–20		16.2	10.8	7.4	1.4	1.1	1.6	3.5	8.4			34.2
00–10					16.0	4.7	2.5	4.0	13.5	16.5	15.5	72.7

N. Atlantic total 217.6
Carib. total 40.7

Table 6. Measured concentrations of DON in precipitation.

Site	Rainwater conc. (μMole l^{-1})	Reference
33° N, 117° W	1.73	Williams 1967
6° S, 174° W	1.65	Williams 1967
Bermuda	8	Knap et al. 1986
	16	Cornell et al. 1995
NE Atlantic	9	Jickells et al. 1990
North Sea	6	Rendell et al. 1993
Chesapeake Bay	21	Jordan & Correll 1995
Coastal Delaware	<3 to 30	Scudlark et al., pers. comm.
Coastal Rhode Is.	5 to 10	Nixon et al., pers. comm.
Philadelphia (urban)	15 to 35	Seitzinger, pers. comm.
Texas (rural)	30	Cifuentes, pers. comm.

concentrations have been measured at Bermuda (Knap et al. 1986; Cornell et al. 1995), the northeast Atlantic (Jickells et al. 1990), and the North Sea (Rendell et al. 1993). The measurements yield remarkably similar values, 6 to 16 μmolar. Nearer to the Atlantic coast, reported concentrations are higher (10–25 μmolar) with an average of 16 μmolar (Jordan et al. 1995; Cornell et al. 1995). Extensive measurements of DON and DIN in precipitation from various continental and marine locations including the North Atlantic (Cornell et al. 1995) show that at marine locations the concentration of DON is comparable to, or somewhat greater than, that of DIN.

Concentrations of 3 to 30 μmolar DON have been measured at coastal sites in Delaware (Scudlark et al., pers. comm.), the Carolinas (Paerl et al., pers. comm.), and Rhode Island (Nixon et al., pers. comm.). A similar concentration range has been found for urban Philadelphia (Seitzinger, pers. comm.) and rural Texas (Cifuentes et al., pers. comm.). In addition, there appears to be a distinct seasonality with peak DON precipitation concentrations in late spring or early summer and a correlation between DON and NO$_3^-$ deposition.

There are only a few measurements of the speciation of DON. Mopper & Zika (1987) measured concentrations of 7 μmolar for disassociated free amino acids and aliphatic amines in the western Atlantic and Gulf of Mexico. Measurements in the North Atlantic have indicated that total amino acids make up only a few percent of the DON (Gorzelska & Galloway 1990; Gorzelska et al. 1995).

From the data discussed above, DON wet deposition fluxes were estimated for a few coastal and mid-Atlantic areas (Table 7). The mid-Atlantic value is near 3 mMoles-N m^{-2} yr^{-1}. Mean values off the northeast and southeast coast of the U.S. are 20 and 8 mMoles-N m^{-2} yr^{-1}, respectively. Fluxes at

Table 7. Wet deposition fluxes of DON (mMoles-N m^{-2} yr^{-1}) in selected regions, estimated from data presented in Table 6.

Site	Wet deposition (mMol N m^{-2} yr^{-1})
Northeast coast of U.S.	mean = 20, winter = 5, summer = 50
Southeast coast of U.S.	6 to 10
Texas (rural)	20
North Sea	4
NE Atlantic	8
N. Atlantic background	3

Bermuda are around 10 mMoles-N m^{-2} yr^{-1} while those in the North Sea and NE Atlantic are 4 and 8 mMoles-N m^{-2} yr^{-1}, respectively.

There are not enough data to make estimates of PON deposition. However, the deposition of pollen alone may be seasonally important in watersheds and coastal areas; the fact that summer-time DON deposition rates are 2.5 times the winter values may be due in part to DON extracted from pollen and other forms of PON brought down in precipitation.

Summary discussion: NO_y, NH_x, DON

Europe and North America appear to have distinctly different emission ratios for NO_y and NH_x. As shown in Table 4, the NO_y/NH_x ratio in deposition along the east coast of North America is about 2–3 whereas for European waters it is close to one. This may reflect the relatively higher concentration of domestic animals in western Europe compared to North America where animals tend to be concentrated in the central and western regions of the continent.

As shown in Table 3, the estimated deposition of NO_y to the NAO (excluding the coastal regions) and the Caribbean is 360×10^9 Moles-N m^{-2} yr^{-1} (5.0 Tg N); this is about 13% of the estimated global emission rate (natural and anthropogenic) for NO_y. We would expect that most of the deposited NO_y in this region is derived from sources in North America and Europe which jointly emit about half of the global total. Our estimated deposition rate comprises about a quarter of the total from these sources. The impact of the continental sources would be greatest in coastal waters. Nixon et al. (this volume) present the total deposition amounts to the continental shelf regions in the NAB. For the western NAO self areas extending to the 200m depth line, the total NO_y deposition is 48.5×10^9 Moles-N yr^{-1} while along the European coast it is 30.1×10^9 Moles-N yr^{-1}; the total, 78.6×10^9 Moles-N yr^{-1}, is about 22% of the total deposited to the open ocean regions of the NAO.

In the case of NH_x, 258 Moles-N m^{-2} yr^{-1} (3.6 Tg N) are deposited to the North Atlantic and the Caribbean (Table 5); this is about 6% of the global continental emissions (Table 1).

Table 8 presents the sum of the NO_y and NH_x depositions to each of the NAO 10° grid cells. Note that the highest deposition occurs in the latitude band 0°–10° N. This is due in part to the relatively high NO_y deposition rates and the very high NH_x deposition rates in this region. The total of NO_y and NH_x is 530 × 10^9 Moles-N yr^{-1} (7.4 Tg N yr^{-1}). This is about 7% of the total global emissions of NO_x and NH_x. Nixon et al. (this volume) obtain total deposition amounts for NO_y and NH_x of 74.9 × 10^9 Moles-N yr^{-1} on shelf areas in the western NAO and 58.2 × 10^9 Moles-N yr^{-1} for the eastern NAO. The total shelf deposition (133.1 × 10^9 Moles-N yr^{-1}) is about 25% of the amount deposited to the open ocean.

Because of the dearth of organic nitrogen data, it is not possible to make an accurate assessment of total nitrogen deposition to the NAO. Nonetheless, it should be noted that the DON concentrations in precipitation at ocean sites are comparable to those of DIN (Cornell et al. 1995). Also the measurements of DON deposition rates for the few sites where there are data (Table 7) are comparable to those estimated for NO_y and NH_x from the models (Table 8). This suggests that the total deposition amounts for all nitrogen species (NO_y, NH_x and DON) may be as much as twice that which we estimate for NO_y and NH_x alone (530 × 10^9 Moles-N, Table 8), yielding a total of about 1 × 10^{12} mMoles-N yr^{-1} for the entire NAO, excluding the coastal ocean regions.

Cornell et al. (1995), assessed the relative importance of DON and DIN in precipitation from various sites around the world. On the basis of various lines of evidence (principally isotopic data and spatial trends in the concentration of DON and DIN), they conclude that a large fraction of the DON is derived from continental sources. However, they could not assess the relative importance of anthropogenic versus natural sources of the DON (or its precursors). Regardless of the source, they conclude that on a global scale the deposition rate of DON is about equal to that of DIN which is consistent with our conclusion for deposition to the NAO.

Mineral dust

The mineral aerosol deposition rates (units 10^9 gm mineral dust) for each 10° grid box are shown in Table 9. For estimating the deposition rates of P and Fe as shown in Table 9, we assume that these elements are present in dust in concentrations that are typical of average crustal material. We use values of upper crustal abundances (Taylor & McLennan 1985): Fe, 3.5%; P, 0.105%. Measurements of P in aerosols often yield P/Al ratios that are higher than that

Table 8. Sum of NO_y and NH_x deposition to 10° squares in the NAO (10^9 mMoles-N yr^{-1}). Also shown are the sums in 10° latitude and longitude bands; these do not include deposition to the Caribbean or the Mediterranean.

Lat.	Longitude											Lat. sum
	100–90	90–80	80–70	70–60	60–50	50–40	40–30	30–20	20–10	10–00	00–10	
60–70					2.2		3.0	3.4	3.8	5.8	7.7	26.0
50–60					8.0	5.2	4.7	4.9	6.9	39.0		68.7
40–50				22.7	14.1	8.6	5.5	4.3	6.4	20.6		82.3
30–40			41.5	20.6	10.3	6.2	4.6	4.7	7.2			95.0
20–30	34.5		18.0	9.6	5.2	3.6	3.1	5.0	5.1			49.6
10–20		27.1	18.9	14.1	5.4	4.2	4.5	7.2	18.5			72.8
00–10		28.4			25.0	10.1	7.7	10.1	23.5	27.2	30.9	134.6

No. Atlantic total 528.9

Carib. total 90.0

of crustal materials but this is believed to the presence of P from sources other than mineral dust (Graham & Duce 1979). In cases where mineral dust is the dominant component in the aerosol (Bergametti et al. 1992), P/Al ratios are close to those of average crustal material. Similarly, Fe/Al ratios are similar to average crustal material (Zhuang et al. 1992).

The GESAMP-I model yields a total mineral dust deposition to the NAO of about 170 Tg yr^{-1}. The equivalent Fe deposition is about 6 Tg yr^{-1} while that for P is about 0.2 Tg yr^{-1}. Dust deposition in the NAO is dominated by transport from African sources. Dust deposition rates in the central and western tropical NAO are relatively high (on the order of several mg m^{-2} yr^{-1}) but they are consistent with the measured accumulation rates of non-biogenic sediment accumulation rates in this regions (Prospero et al. 1987).

There are very few models with which we can compare our data. A mechanistic model of African dust transport (Schütz et al. 1981) based on measured particle size distributions and estimated transport and loss rates yields an annual transport of 260 Tg yr^{-1} about half of which is deposited within the first 500 km of the coast of Africa. This leaves about 130 Tg for transport to the remainder of the NAO, a value that is comparable to our model results.

There have been a number of efforts to model the transport of dust to the oceans using various meteorological models (Joussaume 1990; Tegen & Fung 1994, 1995); however, these models are in their early stages of development and they do not seem to be capable of properly simulating the distribution of dust sources or dust transport – for example, as evidenced by satellite imagery (Tegen & Fung 1995). Another model of Saharan dust transport is based on the inversion of AOT measurements (d'Almeida 1986) and, consequently, it is very sensitive to assumptions about the aerosol size distribution; furthermore, these estimates can not be adequately extended to the open ocean.

The dust deposition measurements (and the corresponding estimates of Fe and P) are subject to a great deal of uncertainty. It is unlikely that we will soon resolve the critical issues that must be addressed to obtain good estimates of dust deposition (more concentration data, better data on size distributions, better understanding of the processes affecting removal from the atmosphere). Nonetheless, it is clear that Africa dust transport is a major phenomenon that affects a large area of the NAO.

An additional factor concerns the biological availability of the Fe and P in the dust to marine organisms. There have been a number of studies of the solubility of P species in aerosols. In some cases solubilities can be quite high. For example, 36% of the total P present in aerosols collected on the U.S. east coast was soluble in water (Graham & Duce 1982); the high solubility is possibly a consequence of anthropogenic effects on aerosol composition, perhaps

Table 9. The mineral aerosol deposition rates (units 10^9 gm mineral dust) for each 10° grid box.

Mineral dust deposition (wet plus dry) to 10° square (10^9 gm yr^{-1})

Lat.	Longitude W90–100	80–90	70–80	60–70	50–60	40–50	30–40	20–30	10–20	10–00	00–10	10–20	20–30E	Lat. sum
60–70					73		28	28	74	72	412			686
50–60					110	43	44	45	110	100	1089			1541
40–50				523	274	137	79	74	119	665				1871
30–40			955	1575	868	262	244	465	1458		3457	6979	14250	5826
20–30	886	1514	2254	1536	912	604	936	1734	17419					25395
10–20		2846	2430	4004	4016	3466	4206	6915	36594					61631
00–10					4681	4840	4882	7765	24727	17764	11083			75742

No. Atlantic total   172693
Medit. total   24685
Carib. total   5246
Grand total   202624

Fe deposition (wet plus dry) to 10° square (10^9 gm yr^{-1})

Lat.	W90–100	80–90	70–80	60–70	50–60	40–50	30–40	20–30	10–20	10–00	00–10	10–20	20–30E	Lat. sum
60–70					3		1	1	3	3	14			24
50–60					4	2	2	2	4	4	38			54
40–50				18	10	5	3	3	4	23				65
30–40			33	55	30	9	9	16	51		121	244	499	204
20–30	31	53	79	54	32	21	33	61	610					889

Table 9. Continued.

| Lat. | Longitude |||||||||||||| Lat. sum |
	W90–100	80–90	70–80	60–70	50–60	40–50	30–40	20–30	10–20	10–00	00–10	10–20	20–30E	
10–20		100	85	140	141	121	147	242	1281					2157
00–10					164	169	171	272	865	622	388			2651

No. Atlantic total 6044
Medit. total 864
Carib. total 184
Grand total 7092

P deposition (wet plus dry) to 10° square (10^9 gm yr^{-1})

Lat.	W90–100	80–90	70–80	60–70	50–60	40–50	30–40	20–30	10–20	10–00	00–10	10–20	20–30E	Lat. sum
60–70					0.1		0.0	0.0	0.1	0.1	0.4			1
50–60					0.1	0.0	0.0	0.0	0.1	0.1	1.1			2
40–50				0.5	0.3	0.1	0.1	0.1	0.1	0.7				2
30–40			1.0	1.7	0.9	0.3	0.3	0.5	1.5		3.6			6
20–30	0.9	1.6	2.4	1.6	1.0	0.6	1.0	1.8	18.3				15.0	27
10–20		3.0	2.6	4.2	4.2	3.6	4.4	7.3	38.4		7.3			65
00–10					4.9	5.1	5.1	8.2	26.0	18.7	11.6			80

No. Atlantic total 181
Medit. total 26
Carib. total 6
Grand total 213

organic materials, although no studies have been made of the speciation. In contrast, in regions dominated by mineral dust, P solubility is considerably lower. Bergametti et al. (1992) find that in precipitation samples collected in the Mediterranean in the presence of high concentrations of Saharan dust, the soluble P is almost totally explainable by the presence of organic P. We would expect that the P in mineral dust would be relatively insoluble; the most abundant mineral form of P is apatite which accounts for 95% of all P in the Earth's crust (Jahnke 1992). Laboratory studies of P solubility in Saharan dust filter samples collected over the North Atlantic indicate that P solubility in aqueous solutions is at most a few percent (J. M. Prospero, unpublished data). Thus, of the estimated 0.2 Tg P yr^{-1} that is deposited in the NAO with African dust, only a small percentage would be readily available to marine organisms. Even if all the P in dust were to be available, it would be unimportant to processes in surface waters compared to other oceanic sources (e.g., nutrient-rich upwelling waters). Duce (1986) estimated that in the Sargasso Sea, atmospheric deposition of P accounted for as much as 5% and as little as 0.2% of the new phosphorus in the photic zone. The relative impact of atmospheric P would be even less in other regions where upwelling sources are stronger.

There have been a number of studies of the solubility of Fe in aerosols (Hardy & Crecelius 1981; Moore et al. 1984; Spokes et al. 1994; Zhuang et al. 1990; Zhu et al. 1992). As much as half of the Fe can be readily extracted from some marine aerosols (Zhuang et al. 1992). However, studies of Fe solubility in Saharan dust collected at Barbados and in laboratory studies (Zhu et al. 1992, 1993; Spokes et al. 1994) show that, in the mean, about 7–8% of the total Fe is soluble in moderately acid saline solutions having a composition similar to that which might be expected to exist on sea-salt-coated mineral dust particles suspended in the marine atmosphere (i.e., 1 M NaCl with the pH adjusted to 1.0 with HCl). We would expect that this Fe fraction (i.e., 7–8%) would be rapidly liberated from the dust particle once it is deposited in the ocean. Other processes in the ocean (including those associated with biological activity) could conceivably mobilize more Fe from the dust matrix (Jickells 1995).

Temporal variability in deposition

Annual budgets are important from the standpoint of understanding the regional fluxes of nitrogen-nutrients throughout the North Atlantic basin. However, from the standpoint of the impact of atmospheric inputs to oceanic productivity, it is necessary to understand the temporal variability of the deposition to the ocean surface. In general, we would expect that the impact of

deposition to be greatest during the season when insolation is greatest and nutrient requirements are highest (i.e., spring and summer, Owens et al. 1991; Michaels et al. 1993). The effects of the nutrient deposition will be enhanced at those times when the ocean surface mixed layer is relatively shallow (i.e., generally in the summer) because the incremental increase in concentration over ambient ocean levels will be greatest (Michaels et al. 1993). The effects will be further enhanced if the deposition takes place primarily in a few large flux events rather than in a large number of low flux events (e.g., Paerl 1985).

The variability in deposition rates depends on a number of factors: the uneven geographical distribution of sources; the seasonal variability of anthropogenic and natural emissions and of the meteorological conditions that transport and deposit the material to the earth's surface. In this section we examine some factors that could affect the temporal variability of precipitation deposition to a few island sampling stations in the North Atlantic basin.

NO_y and NH_x

Seasonal emission patterns for nitrogen species
Some fuel combustion sources have a clear seasonal pattern (e.g., space heating and cooling) while others (e.g., industrial activity or vehicles) do not. For example in Europe (for 1985) the combined industrial and heating sources made up 51% of total anthropogenic nitrogen emissions (Pacyna et al. 1989). European energy generation peaks in winter, with emissions in the maximum month estimated at a factor of two higher than the minimum (OECD 1977). As a measure of the importance of this variability for nitrogen emissions, the peak month would account for around 10% of total yearly emissions, falling only slightly to around 7% in the minimum. Hence the seasonal variability for nitrogen emissions is relatively small.

Reduced nitrogen emissions comprise ~54% of the total anthropogenic nitrogen emissions in Europe (Sandnes 1993). There is a strong spring/summer maximum and an autumn/winter minimum with the emission rates in March/April being 1.4–2.3 times greater than in July, and 3–4 times greater than in late autumn. The seasonal maximum is largely the result of agricultural activities and temperature. Estimates (e.g., Tuovinen et al. 1994) suggest that maximum emissions (35% of annual emissions) occur in March–May, and minimum emissions (approximately 20%) in October–December.

In summary, the combination of the oxidized and reduced nitrogen emissions yield a maximum in March–May, with 30% of the annual total, and a minimum in October to December, with 24%. Thus, from the standpoint of total oxidized and reduced nitrogen emissions, the seasonal variability is quite small compared to other factors discussed below.

Meteorological influences

Given the relative constancy of emissions, the temporal and spatial variability of deposition of nitrogen species will be largely controlled by meteorological factors. The local meteorological conditions in the source regions will determine whether the emissions are confined to a relatively small area (as would be the case during a period of stagnation, typically associated with a stable high pressure system) or whether the emissions are carried to the middle and upper troposphere (as would occur during the passage of a frontal system) where winds could rapidly carry the emissions over great distances.

A second major consideration is the occurrence of clouds and precipitation. Because the secondary oxidized nitrogen products and reduced nitrogen species are generally soluble, clouds scavenge them from the atmosphere with very high efficiency. Over the oceans, precipitation is the dominant removal mechanism for most species. Thus the total deposition rates for many species will be largely determined by the occurrence of precipitation. Hence the deposition to regional seas and the shelf will usually be strongly controlled by mesoscale meteorology. The meteorological factors controlling wet removal rates have been studied in a few field studies; in the western NAO: Galloway et al. (1983); Galloway (1985); Galloway & Whelpdale (1987); Moody & Galloway (1988); Galloway et al. (1989, 1993). Studies in the eastern NAO include: Buijsman et al. (1991); Lacaux et al. (1992); Hanseen et al. (1990); Risbo et al. (1981); Mayewski et al. (1990).

Temporal variability of deposition

In this section we present wet-deposition data for relatively remote ocean stations. For this comparison we use data from three AEROCE stations in the North Atlantic where precipitation data has been gathered for at least several years. These are Bermuda, Barbados and Mace Head, located on the west coast of Ireland. The AEROCE data are collected on a daily schedule using automatic (wet-only) precipitation collectors. For this comparison we use the data for a three year period, 1989 to 1991.

Variability of annual deposition rates

Figure 1a shows the annual (volume weighted) deposition rates for NO_3^- and NH_4^+ (mMoles N m^{-2} yr^{-1}) for Bermuda which has the longest continuous deposition record for an open-ocean NAO site, 1980–1993. As discussed in an earlier section, there was a marked change in deposition rates in 1989 when the sampling site was moved from Harbor Tower to the AEROCE site on the western end of the island, Tudor Hill. There is considerably less rainfall at Tudor Hill compared to Harbor Tower. It is clear that the deposition rates track the precipitation rates across the entire record. This relationship is clearer in Figure 1b which shows the annual mean concentration of NO_3^- and NH_4^+

along with precipitation amount; the concentrations are relatively uniform across the entire record despite the very large changes in rainfall amounts.

Frequency distributions of deposition events and episodicity

At the AEROCE sites, the number of deposition events ranged from about 50 to 100 days depending on site and year. The average for each site for the three years combined (1989–1991) was about 80 events per year. Figure 2a shows for each site the cumulative percentile plots of daily NO_3^- deposition amounts for the years combined, 1989–1991. This figure shows that there can be considerable spatial variability in deposition amounts; note, in particular the large difference between Barbados and sites in the higher latitudes, Bermuda and Mace Head. In contrast, the year-to-year variability of the cumulative frequency distribution is not very great. As an example, Figure 2b shows the cumulative frequency distribution plots for Bermuda for each of the three years, 1989–1991. Note that the number of events per year ranged from 66 to 100.

When we look at the actual number of events that deliver relatively large amounts of deposition, we see that about 30 percent of the daily NO_3^- deposition values measured at Bermuda (23–28 events per year, depending on the year) deposited more than 50 μmoles-N m^{-2}; the deposition rates in individual events ranged from 65 to 450 μmoles-N m^{-2} (see Figure 2a) and accounted for 67% of the total annual NO_3-N deposition. At Mace Head, 15–26 events per year (28% of the total) were greater than 50 μmoles-N m^{-2} during the period 1989–1991; these accounted for 80% of the NO_3-N deposition. In contrast, at Barbados, only 5–9 events per year (10%) yielded nitrate deposition rates greater than 50 μmoles-N m^{-2} and these large events deposited only 37% of the NO_3-N deposition. The lower frequency of high-deposition events at Barbados reflects the lower impact of pollution sources because of the distance from the sources (mainly in Europe and North Africa) and the scavenging that has occurred during transport over the tropical NAO.

Seasonal deposition trends

The average seasonal deposition of NO_3-N measured at three AEROCE sites for a three-year period (1989–1991) is shown in Table 10 along with annual averages. We also show for each season the percentage of the deposition that occurred in events which deposited more than 50 μmoles-N m^{-2} . These values provide an indication of spatial and temporal variation in the episodic N-deposition. At all sites there is a well-defined seasonality in deposition amounts; the ratio of the maximum season to the minimum is about a factor of two for Bermuda and Mace Head and about a factor of four for Barbados. It is also clear that large events (defined here as those depositing more than

(a)

(b)
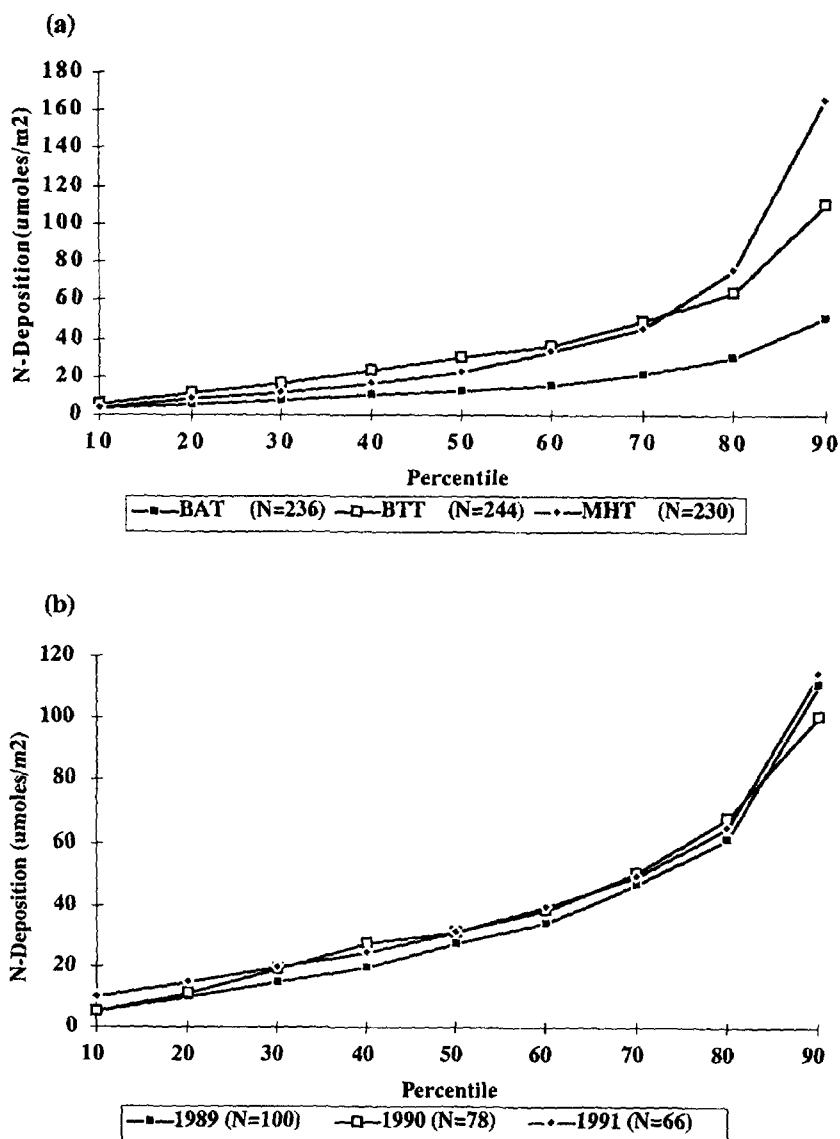
Figure 2. a.) The cumulative frequency distribution of daily nitrate deposition values for each of the AEROCE sites (using data from the years 1989–1991) for Bermuda (BTT), Barbados (BAT) and Mace Head (MHT) (N: number of deposition events for the three year period). b.) The cumulative frequency distribution for nitrate-N deposition at Bermuda for each of the three years, 1989–1991. (N: number of deposition events per year.)

50 μmoles-N m^{-2}) account for a large fraction of the deposition, indeed, the major fraction at Bermuda and Mace Head.

Table 10. Seasonal deposition of NO_3^--N to AEROCE sites: a) measurements; b) GFDL GCTM model.

	Bermuda	% events	Barbados	% events	Mace Head	% events
a)						
Jan–Mar	793	48%	280	2%	1211	79%
Apr–Jun	892	63%	589	40%	916	78%
Jul–Sep	1610	77%	649	34%	896	71%
Oct–Dec	1144	72%	699	49%	1953	85%
Annual avg:	3772		1532		4976	
b)						
Jan–Mar	2160	19%	240	0%	733	7%
Apr–Jun	2147	45%	189	0%	1602	42%
Jul–Sep	1146	20%	303	0%	1582	54%
Oct–Dec	1928	40%	481	0%	761	16%
Annual avg:	7650		1212		4679	

a: Seasonal deposition of NO_3^- N (μMoles-N m^{-2}) at AEROCE sites for the period 1989–1991. The "% events" category shows the percentage of the total seasonal deposition that occurred in episodes with amounts ≥ 50 μMoles-N m^{-2}.
b: GFDL GCTM model NO_3^-N (μMoles-N m^{-2}) in the model grid cells of AEROCE precipitation collection sites. The "% events" category shows the percentage of the total seasonal deposition that ccurred in daily episodes with amounts ≥ 50 μMoles-N m^{-2}.

To more explicitly compare the occurrence of significant deposition events, the data were divided into four categories: $50 < NO_3^- < 100$ μmoles-N m^{-2}, $100 < NO_3^- < 150$ μmoles-N m^{-2}, $150 < NO_3^- < 200$ μmoles-N m^{-2}, and $NO_3^- > 200$ μmoles-N m^{-2}). For each site observations were sorted for these deposition intervals and plotted by season (Figure 3).

The measured deposition distributions show clear evidence of seasonality. At Bermuda (Figure 3a) there is a greater frequency of high deposition events in the warm season quarters of the year (April–June and July–September); this is especially noticeable for events in the range $50 < NO_3^- < 100$ μmoles-N m^{-2}. In contrast at Mace Head (Figure 3b), there is a no consistent seasonal difference except for very large deposition events (i.e., those greater than 200 μmoles-N m^{-2}) which are much more frequent in January–March. Also at Mace Head there is a higher frequency of very large deposition events compared to Bermuda and (especially) Barbados (Figure 3c). In the three years of data, at Mace Head there were 19 daily-deposition events with deposition greater than 200 μmoles-N m^{-2}; in contrast, at Bermuda there

(a)

Deposition Categories (umoles/m2)

(b)

■Jan-Mar □Apr-Jun ▨Jul-Sep ▦Oct-Dec

Deposition Categories (umoles/m2)

(c)

■Jan-Mar □Apr-Jun ▨Jul-Sep ▦Oct-Dec

Deposition Categories (umoles/m2)

■Jan-Mar □Apr-Jun ▨Jul-Sep ▦Oct-Dec
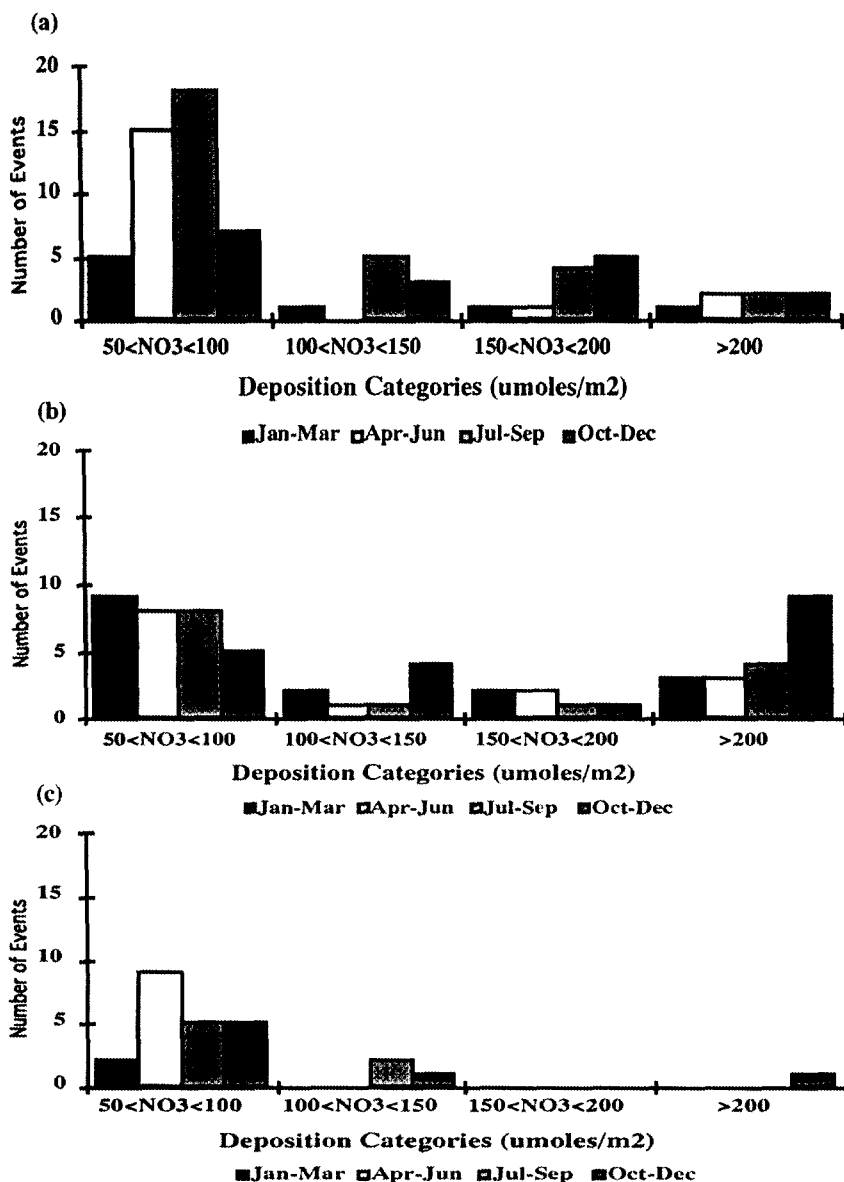
Figure 3. Seasonal distribution of large nitrate-N deposition events. Measured values for the years 1989–1991 at Bermuda (a), Mace Head (b) and Barbados (c).

were 7 events of this magnitude while at Barbados there was only 1 event. Thus of the total of 27 such very large events at the three sites, about 70% of them occurred at Mace Head. At Bermuda, in contrast to Mace Head, there

were many more events with intermediate deposition rates (i.e., in the range 50 to 200 μmoles-N m^{-2}).

As an exercise we have compared the spatial and seasonal variability of the GCTM model with our observations (Table 10). This is the only model for which we could obtain daily values with which to compare our observations. The GCTM model accurately predicts the annual NO3-N deposition at Barbados and Mace Head, but it over predicts the amount at Bermuda by a factor of two. The model does capture some of the variability in deposition; however, it under-predicts large deposition events, producing a large percentage of the deposition in very small events (i.e., in the model the precipitation occurs mainly as drizzle).

While the GCTM accurately predicts the total annual NO3-N deposition amounts for Mace Head and Barbados, it does poorly in predicting the seasonal cycle. The model under-predicts spring and summer deposition at Barbados, and over-predicts spring and summer deposition at Mace Head while under-predicting the fall and winter deposition at Mace Head. These comparisons suggest that this model could not be used to estimate the seasonal variability of deposition.

Conclusions

Field measurements suggest that the temporal and spatial character of NO$_y$ and NH$_x$ deposition episodes is variable over the North Atlantic and that this variability is related to meteorological factors. The data from Mace Head show that the greatest deposition fluxes and the most extreme deposition events occur under conditions of transport of European emissions over the NE North Atlantic during the cold half of the year. During winter the surface waters are well-mixed, the input of atmospheric nitrogen is not likely to be significant. Biological activity is at a maximum during the spring and summer; thus it is during the summer, when the surface waters are highly stratified, that contributions from the atmosphere may play a significant role as a nutrient (Michaels et al. 1993). Bermuda and Barbados both show a seasonal pattern with a maximum atmospheric contribution during the summer, although atmospheric inputs are a factor of two lower at Barbados relative to Bermuda. It may be significant that the deposition of atmospheric nitrogen at Bermuda is highly episodic during the summer, with over three quarters of the total deposition delivered in large events. However, it is clear that at all three sites there is the potential for episodic inputs from the atmosphere to briefly impact the ocean.

Mineral dust and related species

The temporal and spatial variability of dust deposition is expected to be large relative to that for nitrogen aerosols. First of all, the emission rate of dust in the source regions varies strongly with season (Prospero & Nees 1986), much more so than for NO_x, NO_y and NH_x sources. Secondly, the dust particle size distribution is shifted to relatively large sizes compared to that of N-bearing aerosols. Because dust has a mass median diameter of several microns or greater (Duce 1995), sedimentation is an important (often dominant) removal mechanism, especially in coastal regions near the source.

There is relatively little data on the temporal and spatial variability of dust deposition. Nonetheless, it is clear that a large fraction of the annual deposition takes place in a very small fraction of the precipitation events. In a one-year study of Saharan dust deposition in Miami (Prospero et al. 1987), 22% of the annual deposition occurred in once day and 68% in rain events that occurred during two dust episodes spread over a total of four days. In a study at Midway Island (Uematsu et al. 1985), about half of the annual deposition of dust occurred during a two week period. Because of the highly sporadic nature of these events, the concentration of mineral dust in ocean surface waters will be highly variable in time and space. Thus, in ocean regions where there is active dust transport, the mean concentration of dust in the underlying ocean could be relatively high but the concentration distribution could be highly non-uniform, much more so than for the deposition of nitrogen species.

On an annual basis, there is a large seasonal variability in dust concentration which is reflected in the modeled dust deposition rates (Prospero et al. 1995). Over much of the tropical and subtropical NAO, dust concentrations are at a seasonal minimum during the winter; they increase sharply during the spring and attain a maximum during the summer when monthly means concentrations are typically more than an order of magnitude higher than in the winter (Prospero & Nees 1986; Savoie et al. 1992).

The emission and transport of soil dust is highly sensitive to climate variables such as rainfall and wind velocity. African dust concentrations in the trade winds have been studied essentially continuously since 1965 at Barbados, West Indies (Prospero & Nees 1986). The mineral dust measurements at Barbados for the period 1965 to 1992 (Figure 4) show that concentrations increased sharply beginning in 1970 when a persistent drought began in the sub-Saharan (Sahel) regions of Africa. Prior to 1970, the annual average dust concentration was 3.9 μg m^{-3} (range 3.2–4.5 μg m^{-3}); from 1970 to 1992, the average was 11.0 μg m^{-3} (5.4–18.7 μg m^{-3}), roughly three times greater than the pre-drought mean. The range of annual means is greater, about a factor of six from the lowest annual mean (in the mid-1960's prior to the drought) to the maximum. The highest dust concentrations at Barbados
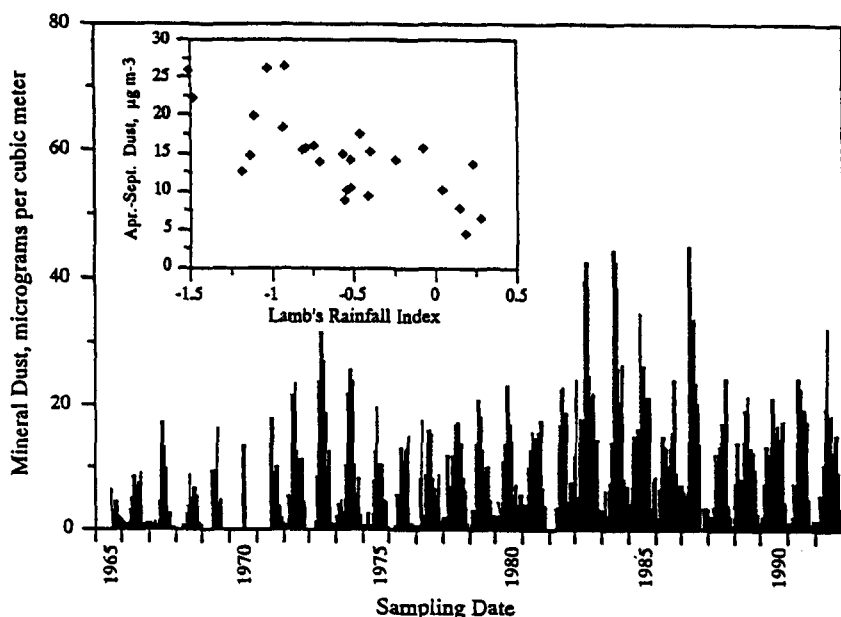
Figure 4. Monthly mean mineral dust concentration (μg m^{-3} at Barbados, 1965–1992. Inset is a scatter plot of the mean annual August–September dust concentration at Barbados vs. the rainfall in the Sahel (see text).

occurred in the mid 1980's when the drought was especially severe; during 1983–87, the June to August average dust concentrations exceeded 25 μg m^{-3}; the maximum June–August mean concentration for the entire 27 year record occurred in 1984, 37.8 μg m^{-3}. It is clear from Figure 4 that there is considerable variability in annual dust transport as measured on the short term (i.e., year-to-year) and over the longer term (i.e., decades).

The dust concentrations at Barbados are inversely related to prior year's rainfall in Africa as indicated by Lamb's rainfall index (inset in Figure 4). This index (P. Lamb, pers. comm.) uses as a reference base the rainfall amounts for 20 sub-Saharan stations from 1941 to 1982; index numbers indicate the standard deviation in annual rainfall from the mean with lower numbers corresponding to drier conditions. Mean summer dust concentrations at Barbados increase by about 10 μg m^{-3} for every standard deviation of rainfall deficit in West Africa. The relationship between dust concentrations and rainfall is less evident during the winter when the transport of dust to Barbados is more sporadic. In the winter and early spring, the large-scale wind systems are displaced to the south, the transport paths move toward more southerly latitudes and dust is transported to South America (Prospero et al. 1986; Swap et al. 1992).

There is a tendency to regard dust emissions as being a "natural" process. However, just as in the case of biomass burning, we can distinguish between the "natural" and "anthropogenic" component of the flux on the basis of the role that humans have played in the process. There is an extensive literature on large scale wind erosion (Middleton 1990; Goudie & Middleton 1992; Pye 1987; Golitsyn & Gillette 1993; Glantz 1994). Clearly, arid and semi arid regions are major sources. However, deserts are not necessarily good dust sources; for example, Australia is a very weak source despite the fact that it is largely arid. High rates of dust emission are generally associated with semi-arid regions where marginal lands are used for agriculture and herding (Middleton 1990; Littmann 1991); during periods of drought, the denuded and broken soil surface is easily carried away. The "dust bowl" in the midwestern United States in the 1930's was a good example of this process. The fact that African dust concentrations in the North Atlantic are correlated with rainfall deficits in the Sahel argues against a Saharan source for the dust. This suggests that much of the increased dust transport over the North Atlantic can be attributed to human actions and thus might be considered to be an anthropogenic pollutant.

Past and future scenarios

Records of past fluxes

Ice cores from permanent glaciers in polar regions can provide a detailed history of changes in atmospheric chemistry (Legrand 1995). Annual cycles can be identified in the core layering and these can be accurately dated thereby permitting the chemical composition to be related to emission histories over the past hundred years or so. The record from Greenland shows that nss-$SO_4^=$ (non-sea-salt $SO_4^=$) concentrations have increased by a factor of two to four since the last century (Mayewski et al. 1990, 1994; Laj et al. 1992); the trend is similar to SO_2 emissions in the United States (Mayewski et al. 1990). Similar increases are noted in the Arctic (Barrie & Bottenheim 1991) and central Greenland (Whitlow et al. 1992) with sources attributed to central Europe and Eurasia. Increases are also seen in the Alps (Wagenbach et al. 1988). In contrast, nss-$SO_4^=$ in Antarctic cores show no such increase. The northern hemisphere records conclusively demonstrate that the long range transport of pollutants has increased deposition levels by a substantial amount over a huge area; however, the time record of deposition is complicated by changes in meteorology so that the interpretation in terms of source/receptor is not always obvious (Mayewski et al. 1994).

Furthermore, there are problems in interpreting the NO_3^- deposition record. There is evidence that NO_3^- can be lost from snows through the volatilization of HNO_3. Nonetheless, on the basis of the nss-$SO_4^=$ record in cores, it is probably safe to assume that the long range transport of NO_3^- to the high latitudes parallels that of $SO_4^=$, following the emission scenario for NO_x.

Ammonium concentrations in Greenland do not show an increase over the past century that could be attributed to anthropogenic emissions. This is surprising in the context of the large increase in nss-$SO_4^=$. The absence of a trend in NH_4^+ over time could be due to losses by volatilization from the snow. Sharp peaks in NH_4^+ concentration are observed in cores; these coincide with peaks in organic acids (formate, acetate, oxalate, etc.) and soot; these peaks are attributed the deposition of products from boreal forest fires (Legrand et al. 1992).

Mineral dust is often an important component in ice cores, especially in the northern hemisphere (Mayewski et al. 1994; Laj et al. 1992; Pfirman et al. 1989) and dust concentrations in cores have been used as a paleoclimate indicator (Hansson 1994). In modern times, substantial amounts of Saharan dust have been detected at Dye 3, Greenland, suggesting that African dust could be a significant contributor to the soil components in high-latitude ice cores (Mosher et al. 1993).

Over the longer term (tens of thousands of years), dust is the most variable of core constituents. In Greenland, dust concentrations were 30–50 times higher during glacial times than today; a similar trend is observed in the Antarctic but absolute concentrations are much lower than in Greenland. The increased dust concentration is related to a number of factors including: increased aridity (which is predicted by a number of climate models and supported by other paleoclimate data); increased availability of fine soil material without vegetative cover in glacial outwash areas and on exposed continental shelves; the presence of more vigorous wind systems and more efficient transport to the high latitudes. However, models have been unable to simulate the transport of dust to the polar regions in glacial times.

Projections of future transport

On a global basis, of the 110 Tg N yr^{-1} created by human processes, about 20 Tg N yr^{-1} are transferred to the oceans by rivers and 16 Tg N yr^{-1} by atmospheric deposition (Galloway 1996). The amount of N transferred to the world's oceans will certainly increase in the future, given the projected increases in fertilizer use and combustion. Galloway (1996) estimates that on a global basis the N fixation rate due to combustion and fertilizer use will increase by about 80 Tg N yr^{-1} in the year 2020. However, most of this

increase (about 70%, 59 Tg N yr^{-1}) will occur in Asia, with much of the remaining increase in Africa (8%) and Central and South America (9%).

In the United States, NO$_x$ emissions increased from about 3 Tg N yr^{-1} in 1950 to about 6 Tg N yr^{-1} in 1970 and then remained relatively constant. Ammonia emissions were in the range of 1.8 to 2.2 Tg N yr^{-1} over the same period. Projections to the year 2020 do not show any substantial increase in either NO$_x$ or NH$_3$ emissions (Galloway et al. 1994, 1995, 1996).

In Europe, nitrogen sources increased after 1960 and reached a maximum in the 1980's. Between 1980 and 1988 (the year of the maximum) the emissions of NO$_x$ from Europe increased by 4%. Since 1988 emissions have declined, partly as a consequence of the NO$_x$ protocol to the Geneva Convention. NH$_x$ emissions during the same period have been essentially unchanged (Tuovinen et al. 1994).

Therefore, we anticipate that over the next few decades, the atmospheric transport and deposition of nutrient-N to the NAO will remain relatively constant. Although some increases in emissions are projected for Africa and Central and South America, these should not contribute substantially to the N cycle of the North Atlantic Ocean.

It is not possible to project the future trend in mineral dust emissions. As stated above, soil erosion is very sensitive to climatic factors coupled with land use practices. Because of the great social and economic changes taking place in North Africa, it is not possible to forecast land-use trends. Climate variability in arid regions is inherently great. These complex factors preclude any assessment of dust transport trends other than they will most likely increase over the longer term (Duce 1995).

Conclusions

Model results suggest that large amounts of aerosol material are being transported by wind to the NAO from the bordering continents. About 13% of the estimated global emissions (natural and anthropogenic) of NO$_y$ are deposited in the NAO and about 6% of the global continental emissions of NH$_x$. We would expect that most of the deposited material is derived from sources in North America and Europe which jointly emit about half of the global total.

Our deposition estimates are based on model estimates that are subject to considerable uncertainty which is difficult to quantify. While agreement amongst the models was quite good, the comparison between the mean model results and the measurements made at various island stations yielded inconsistent results, in some cases excellent and in others poor. There are problems in attempting to "validate" deposition models by comparing results with island measurements. The rainfall amounts on the island can differ greatly

from those over the open ocean because of enhanced convection due to island heating effects. Because deposition rates of chemical species are highly correlated with rainfall amounts, the increased rainfall over the island will result in increased deposition as is evident in the rainfall data from Bermuda. It is not clear how such "validation" comparisons can be easily improved. Nonetheless, at worst the model results are within a factor of two of measured amounts; in general, the results are probably better. Also, the estimated deposition of NO_3^- to the NAO is a "reasonable" fraction of the estimated emissions from the surrounding land masses, for NO_y about a quarter.

There were two classes of materials for which it was particularly difficult to quantify deposition: organic species and mineral dust. Evidence suggests that the deposition rate of organic nitrogen species is quite large, comparable to that of inorganic nitrogen. In order to improve estimates for DON and PON, we will need much more data on their concentration in precipitation over the oceans; this will be difficult to do in a quantitative manner because of the large number of species that are most likely involved. Mineral dust presents a different set of problems. First is the large temporal and spatial variability of dust transport and deposition due to seasonal changes in meteorology. Second, there is a long-term variability that is linked to climate coupled with land-use factors. Third, because of the relatively large size distribution of mineral dust particles, dry deposition (i.e., particle sedimentation) could be an important removal mechanism, especially in ocean regions close to the dust sources; it is much more difficult to measure dry deposition rates than wet deposition.

Because of the huge quantities of mineral dust that are being transported out of North Africa, the NAO is heavily impacted by dust deposition (probably more so than any other region except the Arabian Sea). As shown by Michaels et al. (this volume), the Fe associated with the dust could have a substantial impact on nitrogen cycling in the NAO. Because of the great temporal and spatial variability of dust transport and deposition, the effect on ocean processes should also be highly variable. There is considerable evidence that dust mobilization has been greatly increased because of human activities. If this is true, then the emitted dust must be regarded as a "pollutant" and any resulting effects that this source might have should be thought of as an anthropogenic impact.

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