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Estimation of the air/sea exchange of ammonia for the North Atlantic Basin

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Abstract. As gas phase atmospheric ammonia reacts with acidic aerosol particles it affects the chemical, physical, and optical properties of the particles. A knowledge of the source strengths of NH_3 is useful in determining the effect of NH_3 on aerosol properties on a regional basis. Here, an attempt is made to determine the direction and magnitude of the air/sea flux of ammonia for the North Atlantic Basin from both measured and modeled seawater and atmospheric ammonia concentrations. Previously reported measured seawater concentrations range from less than 30 to 4600 nM with the highest concentrations reported for the Caribbean Sea, the North Sea, and the Belgium coast. Measured atmospheric ammonia concentrations range from 2 to 500 nmol m^{-3} with the largest values occurring over the Sargasso Sea, the Caribbean Sea, and the North Sea. For comparison to the measurements, seawater ammonia concentrations were calculated by the Hamburg Model of the Ocean Carbon Cycle (HAMOCC3). HAMOCC3 open ocean values agree well with the limited number of reported measured concentrations. Calculated coastal values are lower than those measured, however, due to the coarse resolution of the model. Atmospheric ammonia concentrations were calculated by the Acid Deposition Model of the Meteorological Synthesizing Center (MSC-W) and by the global 3-dimensional model Moguntia. The two models predict similar annually averaged values but are about an order of magnitude lower than the measured concentrations. Over the North Sea and the NE Atlantic, the direction and magnitude of the air/sea ammonia flux calculated from MSC-W and Moguntia agree within the uncertainty of the calculations. Flux estimates derived from measured data are larger in both the positive and negative direction than the model derived values. The discrepancies between the measured and modeled concentrations and fluxes may be a result of sampling artifacts, inadequate chemistry and transport schemes in the models, or the difficulty in comparing point measurements to time-averaged model values. Sensitivity tests were performed which indicate that, over the range of values expected for the North Atlantic, the accuracy of the calculated flux depends strongly on seawater and atmospheric ammonia concentrations. Clearly, simultaneous and accurate measurements of seawater and atmospheric ammonia concentrations are needed to reduce the uncertainty of the flux calculations, validate the model results, and characterize the role of oceanic ammonia emissions in aerosol processing and nitrogen cycling for the North Atlantic.

1. Introduction

In the marine atmosphere, gas phase acidic species that can act as aerosol particle precursors include H_2SO_4, HNO_3 and organic acids. Because gas

phase ammonia, NH_3 (g), is the dominant basic species available to interact with these acidic compounds, it has a unique role in determining the chemical, physical, and optical properties of both marine and continental aerosol. It can have a significant impact on the formation of new particles by lowering the vapor concentration of other gases required for the initiation of nucleation. It also can result in particle growth by reacting with acidic particles and lowering the surface acid vapor pressure thereby enhancing the condensation of gas phase acidic species. In addition, the degree of neutralization of non-seasalt sulfate aerosol by NH_3 (g) will influence the aerosol hygroscopicity and, hence, the growth response of particles to changes in atmospheric relative humidity. As light scattering by aerosol particles is determined, in part, by the size dependent aerosol mass concentration, NH_3 (g) will influence the scattering efficiency of the aerosol by adding particulate mass and by changing its hygroscopic properties.

A knowledge of the sources of NH_3 (g) as well as their magnitude is needed to determine the spatial and temporal variability of the effect of NH_3 (g) on aerosol chemical, physical, and optical properties. Much work has been reported on quantifying the sources of NH_3 (g) in continental regions (e.g., Buijsman et al. 1987; Asman et al. 1988). Comparatively little research has been done, however, in characterizing the direction and magnitude of the ammonia flux in oceanic regions. Hence, the importance of the oceanic source of NH_3 on global and regional scales is unknown as is the impact of continental sources on oceanic regions. The goal of the present work is to determine the direction and magnitude of the air/sea ammonia flux for different regions of the North Atlantic and for continental regions bordering the Atlantic. The deposition of ammonium to the sea surface and its importance in ocean processes is described in a separate article (Prospero et al., this issue).

NH_3 (g) reacts primarily with submicron non-seasalt sulfate aerosol, nss $SO_4^=$ (p), to form ammoniated sulfate salts ranging in composition from NH_4HSO_4 to $(NH_4)_2SO_4$ (Quinn et al. 1987). In remote ocean regions, the major source of atmospheric NH_3 will be the ocean itself (Quinn et al. 1988, 1990). In coastal regions, NH_3 (g) also may be derived from continental sources such as biomass burning, animal wastes, emissions from soil and vegetation, and fertilizer losses (Dentener & Crutzen 1994; Warneck 1988). Both the ocean- and the continentally-derived NH_3 (g) will react with unneutralized sulfate aerosol. The resulting particulate phase ammonium, NH_4^+ (p), may be transported long distances (100's to 1000's of miles depending on prevailing wind speeds and precipitation frequency) before it is removed from the atmosphere through wet and dry deposition.

Ammonia exists in seawater as both ionized ammonium, NH_4^+ (s), and dissolved ammonia, NH_3 (s). NH_3 (s) contributes about 10% to the total

seawater ammonium concentration, NH_x (s), at a pH of 8.2 and temperature of 25 °C. NH_x (s) is produced in the upper ocean from the degradation of organic nitrogen containing compounds and excretion from zooplankton. It also is released from bottom sediments to overlying waters. Loss processes for NH_x (s) include bacterial nitrification, uptake by phytoplankton and bacteria, and emission across the air/sea interface. It is the unionized dissolved form, NH_3 (s), that is exchanged across the ocean surface and serves as a source of atmospheric ammonia. At steady state, an equilibrium is reached between air and seawater concentrations of ammonia so that both NH_3 (s) and NH_3 (g) determine the direction and magnitude of the air/sea flux.

Attempts to estimate the air/sea flux of ammonia for the North Atlantic Basin are hindered by a lack of simultaneous measurements of oceanic and atmospheric concentrations. This lack of measurements can be attributed to the difficulty in determining very low concentrations of NH_3 (g) using currently available techniques and in avoiding sample contamination (Williams et al. 1992). Similarly, NH_x (s) concentrations frequently are below the detection limits (50 to 100 nM) of conventional techniques (D'Elia 1983). The result is that little is known about the magnitude and direction of the air/sea ammonia flux. Only one study from the North Atlantic Basin which took place in the North Sea reports results of simultaneously determined NH_3 (g) and NH_x (s) concentrations (Asman et al. 1994). From these measurements, it was determined that there is a variable net flux of ammonia ranging from -75 to 43 μmol m^{-2} d^{-1} where negative values indicate a flux from the atmosphere to the ocean. The direction of the flux appears to depend on the highly variable atmospheric NH_3 (g) concentrations. This variability is, in turn, a result of the proximity of the measurements to continental source regions.

Simultaneous measurements of NH_3 (g) and NH_3 (s) from the central and NE Pacific Ocean indicate that there is a net flux of ammonia from the ocean to the atmosphere ranging between 1.8 and 16 μmol m^{-2} d^{-1} (Quinn et al. 1988, 1990). Based on observations of an increasing NH_4^+ (p) to nss $SO_4^=$ (p) molar ratio, Clarke & Porter (1993) have inferred a similar efflux of ammonia from the ocean to the atmosphere of about 10 μmol m^{-2} d^{-1} over the equatorial Pacific. These few measurements from the North Sea and the Pacific Ocean indicate that the ocean may serve as a local source of NH_3 in remote regions but that there will be a net deposition to the surface in regions impacted by continental sources.

In this paper, we estimate regional air/sea fluxes of ammonia from reported measurements of NH_3 (g) and NH_x (s). We then compare these measurement-derived fluxes with those estimated from two sets of model calculations. The two models used are the Acid Deposition Model of the Meteorological

Table 1. Notation used for ammonia species in the marine environment.

Species	Notation	Concentration notation
Atmospheric gas phase NH_3	NH_3 (g)	$(NH_3)_g$, nmol m^{-3}
Atmospheric particulate phase NH_4^+	NH_4^+ (p)	$(NH_4^+)_p$, nmol m^{-3}
Seawater total NH_3 and NH_4^+	NH_x (s)	$[NH_x]_s$, nM
Seawater dissolved, unionized NH_3	NH_3 (s)	$[NH_3]_s$, nM
NH_3 in equilibrium with dissolved NH_3 in the sea surface	NH_3 (s,eq)	$(NH_3)_{s,eq}$, nmol m^{-3}

Synthesizing Center-West of EMEP (MSC-W) (Tuovinen et al. 1994) and the global atmospheric transport/chemistry model Moguntia (Dentener & Crutzen 1994; and references therein) together with the Hamburg Model of the Ocean Carbon Cycle (HAMOCC3) (Kurz 1993). The sensitivity of the flux calculation to changes in surface seawater temperature, pH, salinity, and NH_x (s) and NH_3 (g) concentrations also is determined.

2. Model descriptions

2a. *Moguntia and HAMOCC3 models*

Moguntia, a global transport model of the troposphere, has a horizontal resolution of 10 by 10 degrees and 10 vertical layers which are spaced every 100 hPa. It uses monthly averaged winds and an eddy-diffusion parameterization based on the standard deviations of the winds together with a parameterization for deep cumulus convection. A complete description of the use of Moguntia to simulate the global atmospheric NH_3 cycle is given by Dentener & Crutzen (1994).

In the model, NH_3 (g) is removed from the atmosphere through wet and dry deposition and reaction with acidic sulfate aerosols and cloud droplets. Moguntia-calculated values of ammonium deposition in the North Atlantic basin are presented by Prospero et al. (this issue). NH_3 (g) is allowed to react with sulfuric acid aerosol until an NH_4^+ (p) to non-seasalt $SO_4^=$ (p) molar ratio of 1.5 is reached. This neutralization limit is motivated by the possibility that the equilibrium vapor pressure over nearly-neutralized sulfate aerosols may be substantial. The formation of particulate phase NH_4NO_3 occurs primarily in continental regions where there are high concentrations of HNO_3 (g) and NH_3 (g). Due to the large spatial scales of Moguntia, the formation of NH_4NO_3 is not included in this work. Omission of NH_4NO_3 may add uncertainty to the calculated flux of NH_3 to the ocean surface. This uncertainty is assumed to be negligible, however, as calculations with the

more detailed MSC-W of EMEP model (see Section 2b) indicate that only a small fraction of the aerosol exists as NH_4NO_3. The air/sea flux of NH_3 is calculated using NH_x (s) concentrations estimated by HAMOCC3 and the method described in Section 5a. In the previous work of Dentener & Crutzen (1994), NH_3 fluxes were scaled to those of DMS. In this work, however, calculated oceanic NH_3 concentrations and piston velocities are used.

The global ocean circulation model HAMOCC3 has a horizontal resolution of 3.5 by 3.5 degrees and 15 vertical layers with a finer resolution in the upper 350 m (Maier-Reimer et al. 1993). The model operates on a monthly time step. It originally was designed to simulate the global marine carbon cycle and has been modified to include a simplified plankton model (Kurz 1993). Processes taken into account include the uptake of NH_x (s) by phytoplankton, regeneration of NH_x (s) by grazers, and bacterial utilization of NH_x (s). Monthly averaged exchange velocities are calculated from 6 hour ECMWF windfields following the method of Duce et al. (1991). A complete description of the use of HAMOCC3 to model the air/sea exchange of NH_3 is given by Kurz & Dentener (1994).

Both global models, Moguntia and HAMOCC3, are not designed to resolve processes within the subgrid coastal regions. Therefore, comparison with measurements is most appropriate in and above the open ocean.

2b. *MSC-W of EMEP model*

The MSC-W model provides estimates of NH_3 (g) and NH_4^+ (p) concentrations and depositions arising from emissions in each European country as well as fluxes between each country and to the sea (Tuovinen et al. 1994). The region covered by the model includes the northeast Atlantic, the European Arctic Ocean, and the North, Norwegian, Baltic, Black, and Mediterranean Seas. The model has a single layer Lagrangian formulation representing transport in the European boundary layer. It has a resolution of 150 km at 60° N and calculates mass-balance changes in air parcels traveling on 4-day trajectories to defined receptor points. The model uses actual meteorology which is updated every 6 hours. Wet and dry deposition rates are determined at this frequency. With a resolution of 150 km, the model can not resolve processes in the coastal transition zone but can describe regional sea sub-basins as well as wider oceanic regions.

Nitrogen and sulfur chemistry routines are combined such that ammonia exists as NH_3 (g) and NH_4^+ (p) associated with nitrate or sulfate aerosol. Three NH_3 molecules combine irreversibly with two of $SO_4^=$ to form $(NH_4)_{1.5}SO_4$ (assuming that $(NH_4)_2SO_4$ and NH_4HSO_4 occur equally) until either no ammonia or no sulfate remains. Remaining ammonia then enters into equilibrium with nitric acid. The nitrate equilibrium point is defined according

to $K = NH_{3(eq)}HNO_{3(eq)}$ with (eq) indicating equilibrium concentrations. If the product of non-equilibrium concentrations is larger than K, NH_4NO_3 is formed. If the product is smaller, NH_4NO_3 dissociates to form its precursor gases. In remote oceanic regions with abundant sulfur present, NH_4NO_3 may be of little consequence. Where NH_3 (g) emissions exceed the sulfur capacity of the aerosol, as with the southern North Sea, 20% of NH_4^+ (p) may exist as NH_4NO_3. This compares to 4.5% for the entire model domain for this time period.

The model has been modified for this study to estimate the upper limit of the sea-to-land flux of ammonia for European sea areas that border the North Atlantic Ocean by incorporating emissions from the ocean. An air/sea equilibrium between NH_x (s) and NH_3 (g) has been added to the model and is described by Henry's law as given in Section 5a.

3. Measured and modeled seawater NH_x (s) concentrations

3a. *Measured values*

A representative selection of seawater NH_x (s) concentrations is listed in Table 2. The colorimetric Berthelot method was used to determine the NH_x (s) concentrations in all cases except those reported by Brzezinski (1988) and Lipschultz (this work). Brzezinski (1988) used the Berthelot method followed by solid phase extraction to concentrate the indophenol dye and lower the detection limit. The method used by Lipschultz involves the derivatization of NH_x (s) to form a highly fluorescent compound (Jones 1991).

The measurement of NH_x (s) is difficult due to contamination during sampling, storage, and analysis (D'Elia 1983). These analytical difficulties become critical at the nanomolar levels of NH_x (s) present in most of the world's oceans. The development of new techniques (Brzezinski 1988; Jones 1991) has made a more precise analysis (± 2 nM) with a lower detection limit (<10 nM) possible but an intercomparison of these methods is needed to determine their accuracy. The wide range of values reported for the Sargasso Sea near Bermuda illustrates these analytical difficulties. Concentrations near the detection limit of the colorimetric method, 30 to 50 nM, have been reported for this region (Glibert & McCarthy 1984; Glibert et al. 1988) as well as values as high as 2720 nM (Carpenter 1973). Measurements made with methods which have lower detection limits reveal surface concentrations in the 10 nM range (Brzezinski 1988; Lipschultz, this work). As shown in Figure 1, the only seasonal measurements for this region suggest that values do not exceed 200 nM (Lipschultz, this work) indicating that an average concentration near 50 nM or less is appropriate.

Table 2. Measured $[NH_x]_s$ for the North Atlantic.

Site	Date	$[NH_x]_s$, nM	Method	Reference
Caribbean 12N, 59W to 17N, 69W	Aug. to Sept., 1977	70–960	Berthelot reaction	Glibert & McCarthy 1984
Caribbean to Bermuda, 23N to 34N, 71W	May	1920–2720	Berthelot reaction	Carpenter 1973
Sargasso Sea	June to July, 1979	<30	Berthelot reaction	Glibert & McCarthy 1984
Sargasso Sea 34N, 73W	May to June, 1982	<30	Berthelot reaction	Glibert et al. 1988
Sargasso Sea 38N, 65W	Sept., 1988	90 ± 65	Berthelot reaction	Longhurst et al. 1989
Sargasso Sea 32N, 62W	June, 1987	10 to 160	Berthelot reaction with solid phase extraction	Brzezinski 1988
Near Bermuda	Sept. to Oct.	60–1070 mean = 460	Berthelot reaction	Carpenter & McCarthy 1975
Bermuda 32N, 64W	Sept. 1992 to April, 1994	10 to 200	OPA derivatization	Lipschultz, this work
SE US Shelf, 32N, 80W	April	300 to 400	Berthelot reaction	Hanson & Robertson 1988
Equator, 0 to 2N, 4W	Various	<50	Berthelot reaction	Le Bouteiller 1986
NW African Coast 31N, 10W to 15N, 18W	March to April, 1971	500 to 1000	Berthelot reaction	Slawyk & MacIsaac 1972
Belgium Coast, 51N, 3E	Spring	600 to 4600	Berthelot reaction	Lancelot et al. 1986

Table 2. Continued.

Site	Date	$[NH_x]_s$, nM	Method	Reference
Scotian Shelf, 43.5N, 62.5W	Various	500 to 1000	Berthelot reaction	Cochlan 1986
W. Canadian Arctic, 67N, 56W	July	240	Berthelot reaction	Harrison 1983
North Atlantic 40N, 47W 45N, 41W	April to May, 1989	80–300	Berthelot reaction	Harrison et al. 1993
North Atlantic 47N, 20W	May	50	Berthelot reaction	Garside & Garside 1993
North Sea	Feb. to Oct., 1989	300 to 4300	Berthelot reaction	Asman et al. 1994 Brockman et al. 1990

Values reported for the equatorial Atlantic near 4° W also are near the detection limit of the colorimetric technique (<50 nM) (Le Bouteiller 1986). In this southern region, NH_x (s) concentrations remain low throughout the year as the water column is permanently stratified and the euphotic zone is isolated from the deep water nitrate reservoir. The northern Atlantic Basin, however, experiences a bloom of phytoplankton in the springtime when the water column restratifies after wintertime convection of deep water brings nitrate to the surface. As the bloom ends, decomposition of the increased biomass can lead to higher levels of NH_x (s) for a short period. This is reflected in the higher concentrations reported for the North Atlantic (up to 300 nM) (Harrison et al. 1993) and the North Sea (up to 4300 nM) (Asman et al. 1994). Reported values also are high in coastal regions including the northwest African coast (500 to 1000 nM) (Slawyk & MacIsaac 1972), the Belgium coast (600 to 4600 nM) (Lancelot et al. 1986), the Scotian Shelf (500 to 1000 nM) (Cochlan 1986), and along the southeastern U.S. (300 to 400 nM) (Hanson & Robertson 1988).

3b. *Modeled values*

Surface NH_x (s) concentrations calculated from the HAMOCC3 model for the North Atlantic are shown in Figures 2a through 2d for the months of October, January, April, and July, respectively. Annual mean concentrations

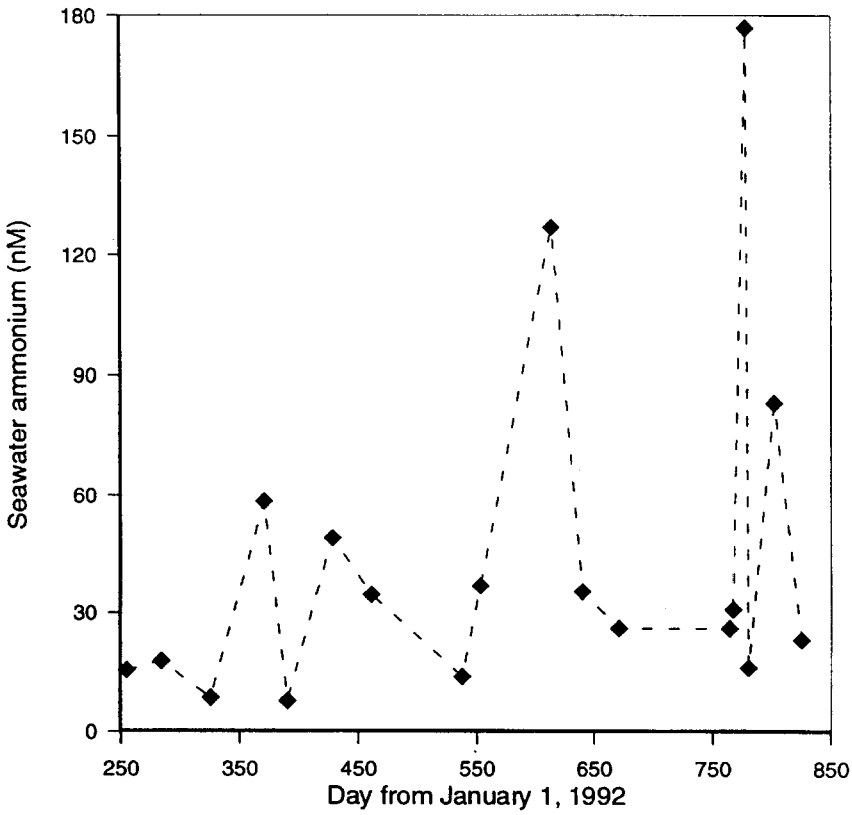


Figure 1. Results of time series measurements of NH_x (s) concentrations made near Bermuda at 31.8° N and 64.1° W with the fluorescence technique of Jones (1991). Concentrations are in units of nM.

range from 10 to 50 nM (Figure 2e) with lower values in the subtropical gyres and higher values at latitudes between 45° and 65° N. Seasonally, the lowest concentrations occur in fall and winter. Highest concentrations are found during and after plankton blooms; values up to 200 nM occur in the mid-Atlantic at 30° N in April and at 45° to 65° N in July. Concentrations higher than 200 nM are not predicted for the North Atlantic at latitudes below 65° N.

The modeled and measured open ocean NH_x (s) concentrations fall within the same range; both are <30 nM for the Sargasso Sea and 10 to 100 nM for Bermuda. The model underestimates coastal values by as much as an order of magnitude, however. For example, off the northwestern African coast, values in the range of 500 to 1000 nM have been observed during March and April (Slawyk & McIsaac 1972) but the model values remain between

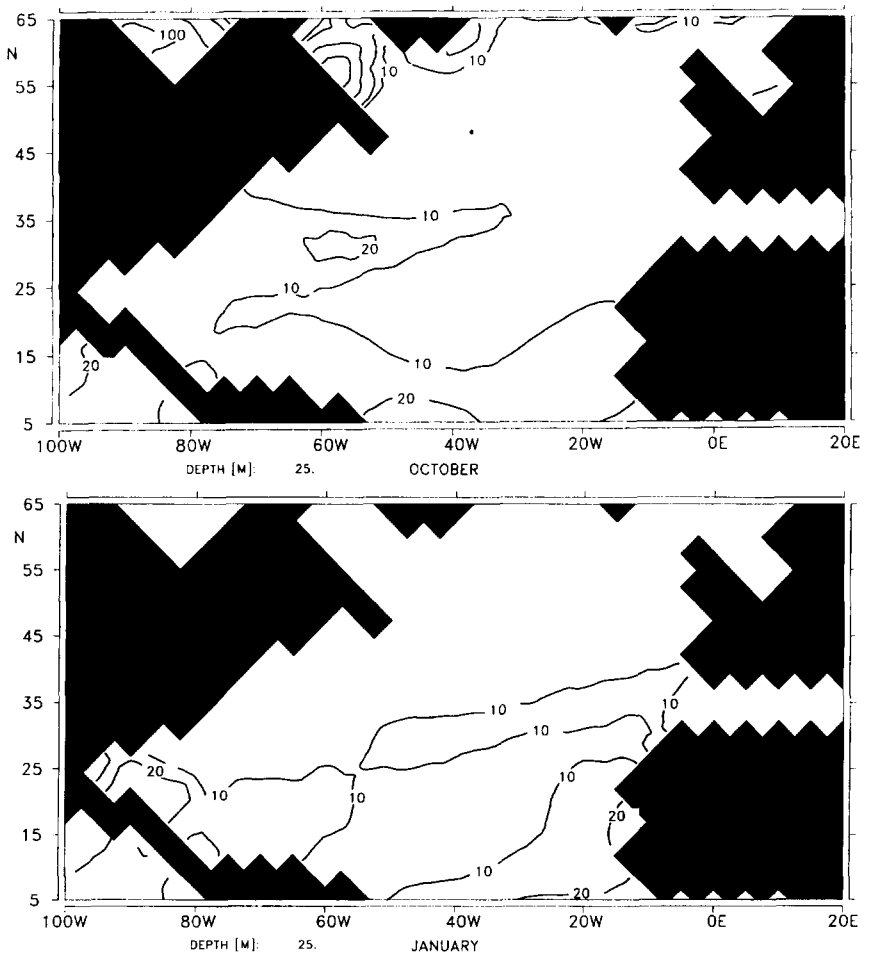


Figure 2. Global distribution of NH_x (s) concentrations calculated by the HAMOCC3 model for a) October, b) January, c) April, and d) July. Annually averaged values are shown in e). Concentrations are in units of nM. Isolines are given in logarithmic scaling: 10, 20, 50, 100, and 200 nM.

10 and 20 nM throughout the year. This discrepancy between measured and modeled results in coastal regions can be explained by the coarse resolution of the model. The complex small scale structure of dynamical and biological processes that exist in coastal areas is not well represented by a global ocean model. In addition, year-to-year variability can not be reproduced accurately by HAMOCC3 as it is based on climatological forcing. Hence, the model results will not reflect the change in the measured concentration from 5 to 40 nM near Bermuda in February, 1993 to 180 nM in February, 1994 (Figure 1). The comparison of point measurements with HAMOCC3 values is most

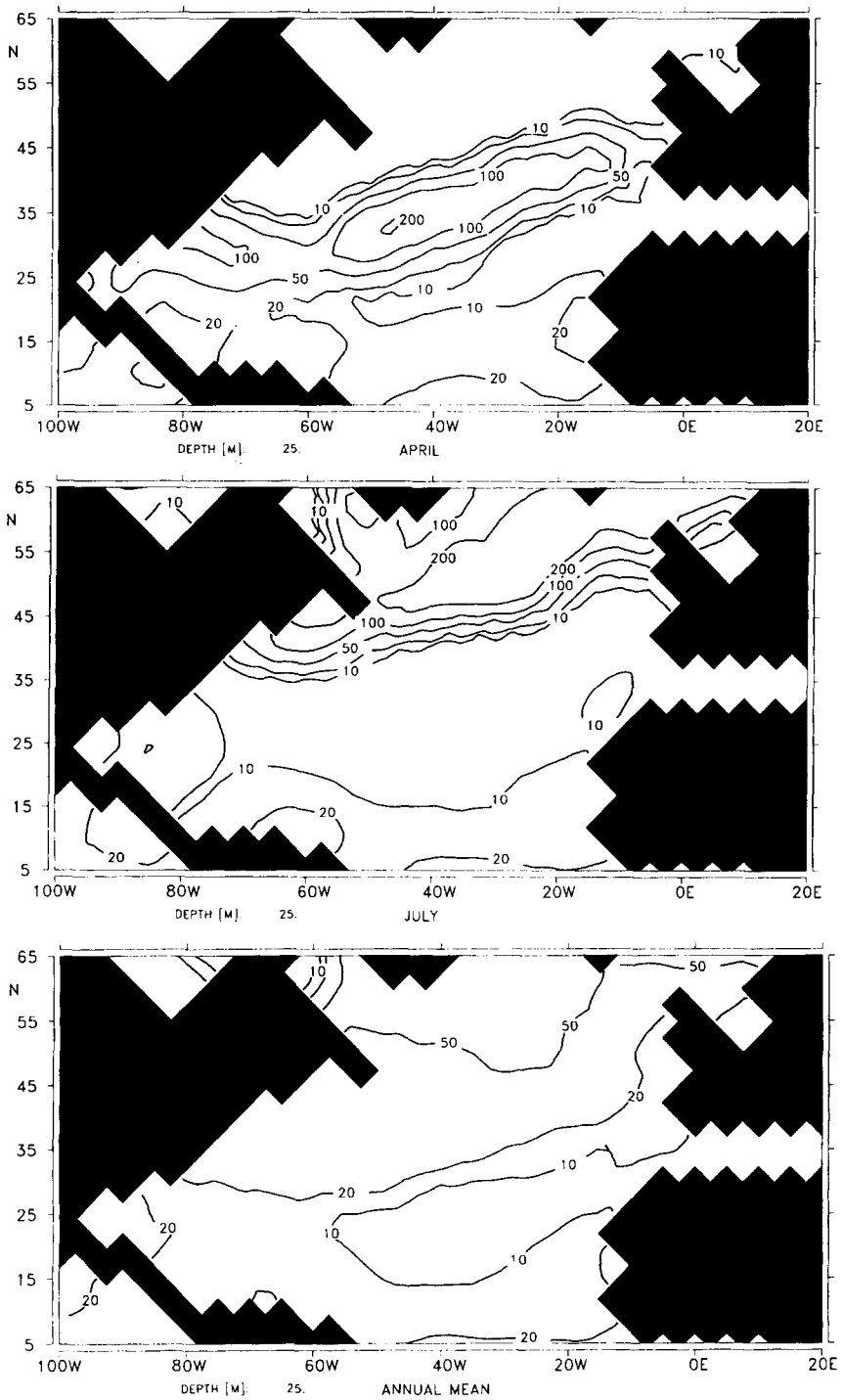


Figure 2. Continued.

appropriate in open ocean regions where spatial and temporal variability is minimized. The agreement within a factor of 2 in large scale structures between observations and HAMOCC3 predictions indicates that the simulated fields can serve as lower ocean boundary conditions for Moguntia.

4. Measured and modeled atmospheric NH_3 (g) concentrations

4a. *Measured values*

Reported values for atmospheric NH_3 (g) concentrations are listed in Table 3. The data are a result of four field experiments in which different measurement methods and, presumably, different protocols to prevent sample contamination were used. Georgii & Gravenhorst (1977) report results from a cruise taken in October of 1973 that traveled between Hamburg, Germany and the Caribbean Sea. No indication is given of the measurement method or precautions taken to avoid sample contamination. High NH_3 (g) concentrations were found near the Azores (50 to 170 nmol m^{-3}) and over the Caribbean (220 nmol m^{-3}) and Sargasso Seas (110 to 500 nmol m^{-3}). Lower concentrations of 11 to 60 nmol m^{-3} were measured over the tropical Atlantic along a transect from 40W to 10W. The high concentrations over the Sargasso Sea prompted the authors to suggest that the ocean was acting as a source of NH_3 in this region. This can not be confirmed, however, without simultaneously measured NH_x (s) concentrations. The high concentrations near the Azores and over the Sargasso Sea contrast with more recent measurements. Zhuang & Huebert (1994) measured concentrations at Santa Maria island in the Azores with annular denuders and found values between 1 and 30 nmol m^{-3} with an average and standard deviation of 9 ± 9.4 nmol m^{-3}. LeBel et al. (1985) measured concentrations at Bermuda of 20 nmol m^{-3} using the WO_x denuder technique. It is unclear if these large discrepancies are a result of sampling artifacts or natural variability.

More recently, Asman et al. (1994) reported concentrations of 2 to 140 nmol m^{-3} for the North Sea using H_3PO_4 impregnated filters. This is the only experiment of the four in which simultaneously measured NH_x (s) concentrations were reported.

4b. *Modeled values*

NH_3 (g) concentrations for the months of October, January, April, and July calculated with the Moguntia model are shown in Figures 3a through 3d, respectively. Annually averaged values are shown in Figure 3e. In the fall and winter, concentrations are low throughout the open ocean of the North

Table 3. Measured atmospheric NH_3 (g) concentrations, $(NH_3)_g$, for the North Atlantic Basin.

Site	Date	$(NH_3)_g$, nmol m^{-3}	Method	Reference
North Sea South of 56N	March to Sept., 1989	2–140	Impregnated H_3PO_4 filter	Asman et al. 1994
North Sea, English Channel	October, 1973	42–180	Not given	Georgii & Gravenhorst 1977
Azores 30N to 40N	October, 1973	50–170	Not given	Georgii & Gravenhorst 1977
Azores 37N, 25W	June, 1992	1–30	Denuder	Zhuang & Huebert 1994
Tropical Atlantic 40W to 10W	October, 1973	11–60	Not given	Georgii & Gravenhorst 1977
Caribbean 70W	October, 1973	220	Not given	Georgii & Gravenhorst 1977
Sargasso Sea 20N to 30N	October, 1973	110–500	Not given	Georgii & Gravenhorst 1977
Bermuda	1982	20	WO_3 Denuder	LeBel et al. 1985

Atlantic; values are around 1.0 nmol m^{-3} at 30° N and increase to 5 to 10 nmol m^{-3} over the Sargasso Sea and between 5° and 15° N. Concentrations are higher over the Gulf of Mexico (5 to 10 nmol m^{-3}), Caribbean Sea (10 to 20 nmol m^{-3}), and North Sea (2 to 10 nmol m^{-3}). Along the coasts of Ireland, France, and Portugal, concentrations range from 2 to 10 nmol m^{-3}. During the summer, concentrations increase to 5 nmol m^{-3} over the North Atlantic but decrease to 0.5 nmol m^{-3} further south near 25° N. Summer concentrations are similar to those calculated for the winter months over the Gulf of Mexico, the Sargasso Sea and the Caribbean Sea. They are higher, however, over the North Sea and the coasts of Ireland, France, and Portugal reaching values of 20 nmol m^{-3}

Annually averaged NH_3 (g) concentrations calculated with the MSC-W model for the year 1990 are shown in Figure 4. These calculations use a polynomial interpolation between grid squares. The values are based on NH_3 emissions resulting from agricultural and industrial activity and, hence, are of purely anthropogenic origin. Over the open ocean, NH_3 (g) concentrations

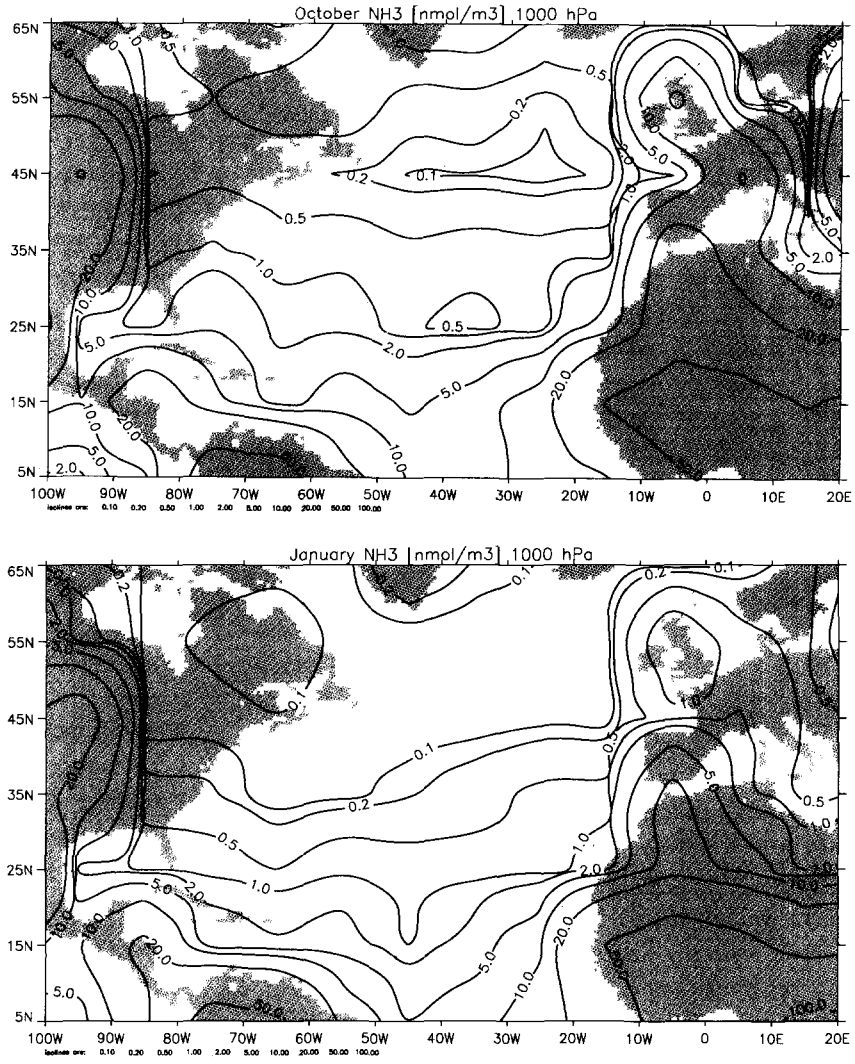
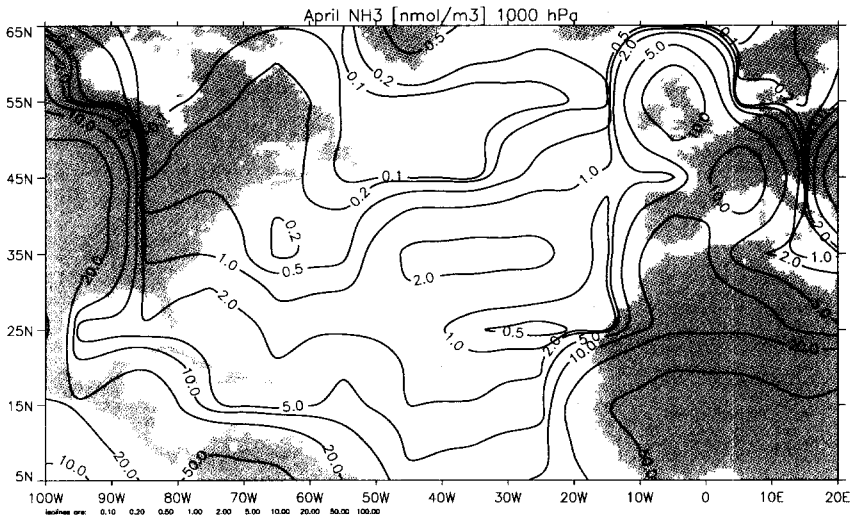
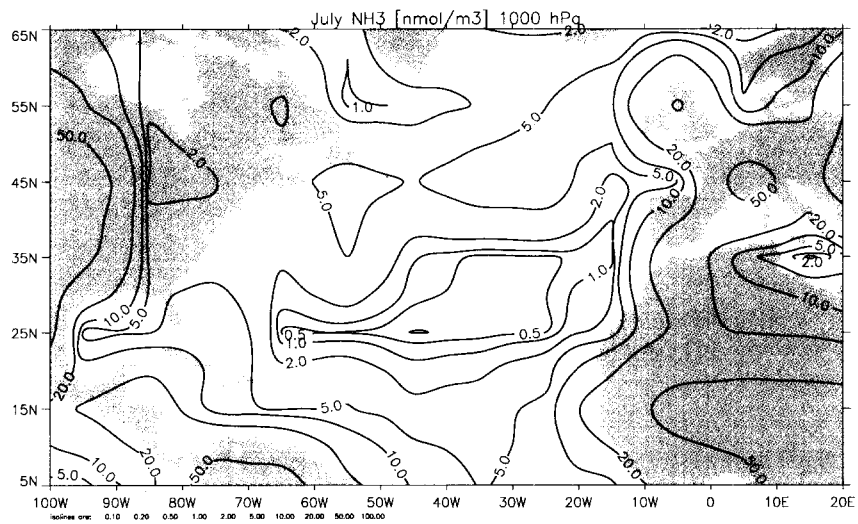
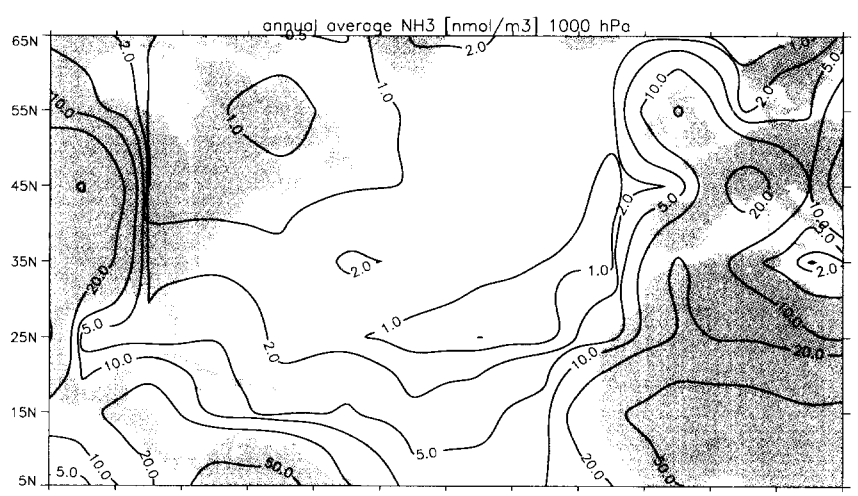


Figure 3. Global distribution of NH_3 (g) calculated by Moguntia for a) October, b) January, c) April, and d) July. Annually averaged values are shown in e). Concentrations are in units of nmol m^{-3}.

are below 2 nmol m^{-3}. Over the North Sea, concentrations range from 2 to 100 nmol m^{-3} with values decreasing northwards. Along the coast of Ireland, gradients are steep with concentrations on land being over 50 nmol m^{-3} and those 150 km from the coast being below 2 nmol m^{-3}. Adjacent to the coasts of France and Portugal they are over 50 nmol m^{-3}. Throughout this region, concentrations decrease with distance from the shore.


April NH3 [nmol/m3] 1000 hPa
65N
55N
45N
35N
25N
15N
5N
100W
90W
80W
70W
60W
50W
40W
30W
20W
10W
0
10E
20E


July NH3 [nmol/m3] 1000 hPa
65N
55N
45N
35N
25N
15N
5N
100W
90W
80W
70W
60W
50W
40W
30W
20W
10W
0
10E
20E


annual average NH3 [nmol/m3] 1000 hPa
65N
55N
45N
35N
25N
15N
5N

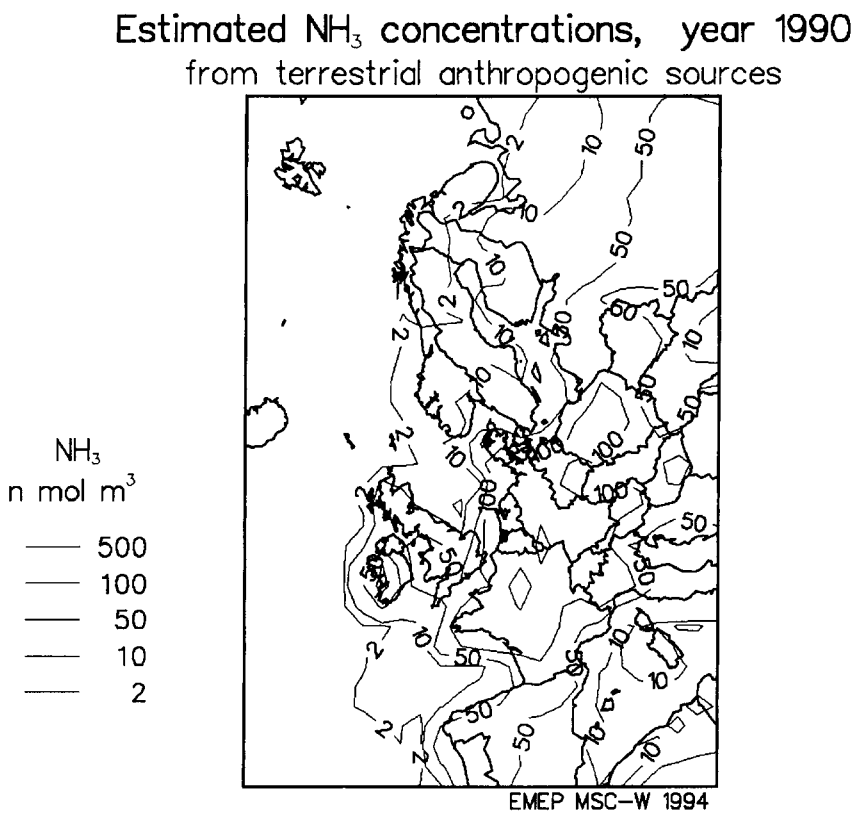


Figure 4. Annually averaged distribution of atmospheric NH_3 (g) for the northeast Atlantic Basin calculated from the MSC-W model for the year 1990. Concentrations are in nmol m^{-3}.

The two models predict similar annually averaged values for the North Sea (Moguntia: 2 to 10 and MSC-W: 2 to over 100 nmol m^{-3}) and the NE Atlantic (Moguntia: 1 to 5 and MSC-W: below 2 nmol m^{-3}). As expected, however, this level of agreement does not extend to regions over land where large point sources can exist. This lack of agreement is due to differences in the model characteristics. MSC-W has a resolution of 150 km. The resolution of Moguntia is 1000 km which leads to a dilution of sources and a lowering of the calculated NH_3 (g) concentrations. Transport schemes also are different as MSC-W uses actual meteorology and Moguntia uses monthly averaged winds. In addition, emissions from MSC-W are more specific in location than those from Moguntia.

In all regions where both measured and modeled concentrations of NH_3 are available, the measured values are about an order of magnitude larger. One exception is over the North Sea where modeled values are within the range

of those that were measured. The systematically higher measured values may be a result of contamination during sample collection and analysis in areas with low concentrations. Additionally, the models could be underestimating the emissions of NH_3 (g) or overestimating the fraction of NH_3 (g) that is converted to NH_4^+ (p). The latter seems unlikely considering the fast reaction rate between NH_3 (g) and sulfate aerosol (Quinn et al. 1992). A final difficulty is that continental modeling at scales in excess of 100 km resolution can not resolve sharp concentration gradients. Hence, for regions with large NH_3 sources, values derived from point measurements are expected to differ from those derived from wider-scale models.

5. Air/sea NH_3 fluxes

5a. *Description of flux calculation*

The following method (Asman et al. 1994) was used to calculate the air/sea NH_3 flux from the measured concentrations of NH_3 (g) and NH_x (s). The same method is used in the MSC-W model and the Moguntia/HAMOCC3 models. The flux of ammonia across the air/sea interface is parameterized as the product of the exchange velocity, V_e, and the difference between the concentration of ammonia in equilibrium with dissolved ammonia in the sea surface, NH_3 (s,eq), and the concentration of atmospheric ammonia, NH_3 (g), such that

$$F = V_e[(NH_3)_{s,eq} - (NH_3)_g] \tag{1}$$

For flux estimates derived from measured concentrations, a constant exchange velocity of 0.8 cm s^{-1} was used. This exchange velocity is based on experimentally determined transfer rates of water at air/water interfaces (Liss & Galloway 1993) recognizing that NH_3 and H_2O have similar molecular structures and behaviors. Values of V_e used in the MSC-W model are determined at 6 hour intervals and vary with wind speed and stability assuming no explicit surface resistance to transfer (Tuovinen et al. 1994). Values of V_e used in the Moguntia/HAMOCC3 models vary with observed wind speeds and range from 0.8 to 2 cm s^{-1}.

Values of $(NH_3)_{s,eq}$ are derived from

$$(NH_3)_{s,eq} = \frac{M_{NH_3}[NH_x]_s}{RTH_{NH_3}\left(\frac{1}{\alpha} + \frac{10^{-pH}}{\beta K_{NH_4}}\right)} \tag{2}$$

which takes into account the equilibrium in seawater between NH_3 (s) and NH_4^+ (s) and the Henry's law equilibrium between NH_3 (s) and NH_3 (s,eq).

Here, M_{NH_3} is the molecular weight of NH_3 (17 g mol^{-1}), $[NH_x]_s$ is the seawater NH_x concentration in umol l^{-1}, R is the gas constant (8.2075 $\times$ 10^{-5} atm m^3 mol^{-1} K^{-1}), and T is temperature in K. H_{NH_3} is the Henry's law constant for NH_3 in mol l^{-1} atm^{-1} and is given by

$$H_{NH_3} = 56\exp\left(4092\left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \quad (3)$$

(Dasgupta & Dong 1986). α is the activity coefficient of NH_3 (s) and is given by

$$\alpha = 1 + 0.085I \quad (4)$$

(Garrels & Christ 1965) where I is the seawater ionic strength such that

$$I = 0.00147 + 0.01988S + 2.08357 \times 10^{-}5S^2 \quad (5)$$

and S is salinity (Lyman & Fleming 1940). The activity coefficient of NH_4^+ is β where

$$\beta = 10^{\gamma} \quad (6)$$

(Seinfeld 1986) and

$$\gamma = -A_i z(\sqrt{I}/(1 + \sqrt{I}) - 0.2I) \quad (7)$$

Here, $A_i = A + BT + CT^2$, A = 0.4896844, B = -0.0007477, c = 2.729 $\times$ 10^{-6}, and z is the charge on the ion. The dissociation constant of NH_4^+ is in units of mol l^{-1} and is given by

$$K_{NH_4} = 5.67x10^{-10}\exp\left(-6286\left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \quad (8)$$

(Bates & Pinching 1950).

5b. *Flux estimates derived from measured concentrations*

Reported concentrations of atmospheric NH_3 (g) and seawater NH_x (s) were used to calculate fluxes for those regions of the North Atlantic where both atmospheric and seawater data are available. These regions include the Caribbean and Sargasso Seas, Bermuda, and the North Sea. The measurements from the North Sea are the only ones in which the atmospheric and oceanic data were collected simultaneously. For the other regions, the

atmospheric and seawater data were collected at different times by different researchers. Samples for atmospheric NH_3 (g) are collected for longer periods of time than are samples for NH_x (s) and will be representative of a larger region. The seawater samples may be collected at a depth that does not represent the surface layer concentration that determines the flux. As a result, the flux estimates reported here are intended to be a first approximation for the North Atlantic Ocean. As these estimates are derived from discrete measurements, they are "point-in-time" fluxes and are not time averaged net balances of deposition and emission.

Estimated fluxes as well as the input parameters for the calculation are shown in Table 4. A uniform surface seawater pH of 8.1 was assumed and annually averaged sea surface temperatures (Pickard & Emery 1982) and salinities (Taylor & Stevens 1980) were used. For the Caribbean Sea, a fixed atmospheric NH_3 (g) concentration but a varying seawater concentration was used which resulted in flux values ranging from -150 to -110 μmol m^{-2} d^{-1}. The low concentrations of NH_x (s) resulted in a flux from the atmosphere to the ocean.

Two sets of flux calculations were performed for the region of the Sargasso Sea. In the first, measured NH_x (s) and NH_3 (g) concentrations from the wider region of the Sargasso Sea were used so that NH_x (s) ranged between 10 and 160 nM (Brzezinski 1988) and the NH_3 (g) ranged from 110 to 500 nmol m^{-3} (Georgii & Gravenhorst 1977). The large measured concentrations of atmospheric NH_3 led to a consistent flux from the atmosphere to the ocean ranging between -340 and -6 μmol m^{-2} d^{-1}. In the second estimation, data taken near and on Bermuda were used. A range of NH_x (s) concentrations from 10 to 200 nM (Lipschultz, this work) and an average NH_3 (g) concentration of 20 nmol m^{-3} (LeBel 1985) resulted in an estimated flux of -13 to -5.8 μmol m^{-2} d^{-1}. The discrepancy between these two calculated fluxes for the Sargasso Sea results from a large difference in the measured NH_3 (g) concentrations. It is likely that the early measurements of Georgii & Gravenhorst (1977) suffered from artifacts or contamination during sampling that led to artificially high concentrations. This is supported by the factor of ten difference in the concentrations measured in the Azores by Zhuang & Huebert (1994) (1 to 30 nmol m^{-3}) and Georgii & Gravenhorst (1977) (50 to 170 nmol m^{-3}). This assumption of an artifact in the Georgii & Gravenhorst (1977) measurements can not be confirmed, however, as no indication of the technique used or precautions that were taken to prevent contamination is given.

For the North Sea, where seawater and atmospheric concentrations were measured simultaneously (Asman et al. 1994), flux estimates vary from -75 to 43 μmol m^{-2} d^{-1}. The net direction of the flux appears to be determined

Table 4. NH_3 flux estimates based on measured $(NH_3)_g$ and $[NH_x]_s$ and the Moguntia/HAMOCC3 and MSC-W models. $[NH_x]_s$ are in units of nM, $(NH_3)_g$ are in nmol m^{-3}, and fluxes are in μmol m^{-2} d^{-1}.

Region	$[NH_x]_s$ Measured	$[NH_x]_s$ MOG	$[NH_x]_s$ MSC-W	$(NH_3)_g$ Measured	$(NH_3)_g$ MOG	$(NH_3)_g$ MSC-W	Flux Measured	Flux MOG[a]	Flux MSC-W[b]
Caribbean	70–960[1]	20–60		220[5]	3–25		−150 to −110	−4.0 to 1.3	
Sargasso	10–160[2]	10–180		110–500[5]	4–10		−340 to −76		
Bermuda	10–200[3]	10–100		20[6]	2–5		−13 to −5.8	4.0	
North Sea	300–4300[4]	10–270	1000	2–140[4]	1–20	2–100	−75 to 43[4]	−1.3 to 1.3	−69 to 20
NE Atlantic 40N, 12W		10–250	250		1–3	2–50		0 to 1.3	−1.6 to 3.3
NE Atlantic 50N, 20W		10–250	250		5	0.1		1.3 to 2.7	1.3
Coast of Ireland		10–280	250		1–25	2–10		−1.3 to 0	1.4
Coast of France & Portugal		10–140	250		3–25	2–50		0 to 1.3	−1.6 to 3.3

[a] Net monthly average flux, [b] Disaggregated fluxes
[1] Glibert & McCarthy (1984), [2] Brzezinski (1988), [3] This work, [4] Asman et al. (1994), [5] Georgii & Gravenhorst (1977), [6] Lebel et al. (1985)

by the highly variable NH_3 (g) concentration which, in turn, is a result of the proximity of the measurements to continental source regions. Lower NH_3 (g) concentrations in mid-summer yield near zero fluxes while higher values at other times of the year lead to atmosphere-to-ocean fluxes.

5c. *Flux estimates derived from modeled values*

Flux estimates from the Moguntia and MSC-W models are compared to those derived from the measured concentrations in Table 4. Net fluxes were derived from the Moguntia/HAMOCC3 models using HAMOCC3 calculated NH_x (s) concentrations, sea surface temperature, and pH and Moguntia calculated NH_3 (g). Fluxes from gridboxes partly covered by the ocean were scaled using the oceanic areal fraction. Calculated fluxes for the Caribbean Sea ranged from -4.0 to 1.3 μmol m^{-2} d^{-1}. Around Bermuda, the flux consistently was from the ocean to the atmosphere with a value near 4.0 μmol m^{-2} d^{-1}. Over the northeast Atlantic, fluxes were positive and were between 0 and 1.3 μmol m^{-2} d^{-1} at 40° N and 12° W and 1.3 and 2.7 μmol m^{-2} d^{-1} at 50° N and 20° W. Fluxes from the North Sea were both slightly negative and slightly positive such that, on the average, they were near zero. Near the coasts of Ireland and France, fluxes were both negative and positive with values of -1.3 to 0 and 0 to 1.3 μmol m^{-2} d^{-1}, respectively. Over the open ocean, fluxes were on the order of 1 to 2 μmol m^{-2} d^{-1}. These agree well with the lower range of previously reported flux estimates for the central Pacific Ocean (Quinn et al. 1990).

For the flux estimates derived from the MSC-W model, reported seawater concentrations during periods of plankton blooms were used in order to estimate potential maximum fluxes. These concentrations included North Sea values of 1000 to 4000 nM (Brockman et al. 1990; Asman et al. 1994) and North Atlantic values of 250 nM (Harrison et al. 1993). All coastal waters (mixed land/sea grid squares) were given a concentration of 500 nM. Sea surface temperatures were obtained from the Numerical Weather Prediction (NWP) model of the Norwegian Meteorological Institute. Input salinity values for the northeast Atlantic and North Sea were 35 and 34 per mil, respectively (Taylor & Stevens 1980). A surface seawater pH of 8.1 was assumed for all regions. Using these input values, both net fluxes and disaggregated fluxes, i.e, fluxes separated into the upward and downward direction, were estimated for the month of August 1990. The upward flux of oceanic NH_3 is shown in Figure 5a. Emissions ranged from 1.0 to 20 μmol m^{-2} d^{-1} for the North Sea. These are comparable with the summertime values derived from measurements of Asman et al. (1994). For the same month, deposition fluxes between -0.70 and -69 μmol m^{-2} d^{-1} were estimated (Figure 5b). In both cases, the fluxes decrease from the south to the north. The net flux is smaller than the

disaggregated fluxes, ranging between -1.03 to 13 μmol m^{-2} d^{-1}, and is a result of the reversals in direction during the course of the month. Over the northeast Atlantic, both emission and deposition fluxes are much smaller than those over the North Sea. Off the coasts of Ireland and France, emission values were 1.4 and 3.3 μmol m^{-2} d^{-1}, respectively (1.3 and 1.7 μmol m^{-2} d^{-1} net). These are only slightly higher than in the mid North Atlantic at distances of 1000 km from the continent where values range from 1.3 to 2.1 μmol m^{-2} d^{-1} with no deposition flux.

Results from the MSC-W model allow for an assessment of the importance of marine ammonia sources to each European country relative to agricultural and industrial sources. These preliminary calculations, assuming summertime conditions, indicate that marine emissions may be one of the larger external sources of deposited reduced nitrogen for some countries on the western margins of the continent. For Ireland, marine emissions are the second largest source of reduced nitrogen, for the United Kingdom they are the third, for Norway the fifth, and for Finland the sixth. The inclusion of a marine source of reduced nitrogen for the European domain as a whole, however, only increases total emissions by 1.5%. Winter emission fluxes would be much lower due to colder temperatures and smaller seawater NH_x (s) concentrations.

When comparing fluxes from the Moguntia/HAMOCC3 and MSC-W models, net fluxes versus disaggregated fluxes are involved. Yet, in general, the direction of the fluxes predicted by the two models is the same and the magnitudes fall within the same range (Table 4). Flux estimates derived from the measured data are larger in both the negative and positive direction than the model derived values. It is unclear whether this discrepancy is due to inaccurate chemistry and transport schemes in the models, sampling artifacts in the measurements, or factors that make a direct comparison of the measurement- and model-derived results difficult. The measurement-derived fluxes are discrete in time while the model estimates are time averaged. A first step in resolving the disagreement would be to make accurate, simultaneous measurements of $(NH_3)_g$ and $[NH_x]_s$ and then to compare these to the model derived values over equivalent time periods. Such measurements should be made in several regions of the North Atlantic that have different sea surface temperatures and NH_x (s) concentrations as well as atmospheric NH_3 (g) concentrations. Representative regions with large surface areas such as 0 to 20° N or the Sargasso Sea would be most relevant for a basin scale assessment.

5d. *Model geography of oceanic NH_3 (g) emission versus deposition*

To determine the regions of the North Atlantic that serve as a source of atmospheric NH_3, annually averaged net emissions and depositions of NH_3

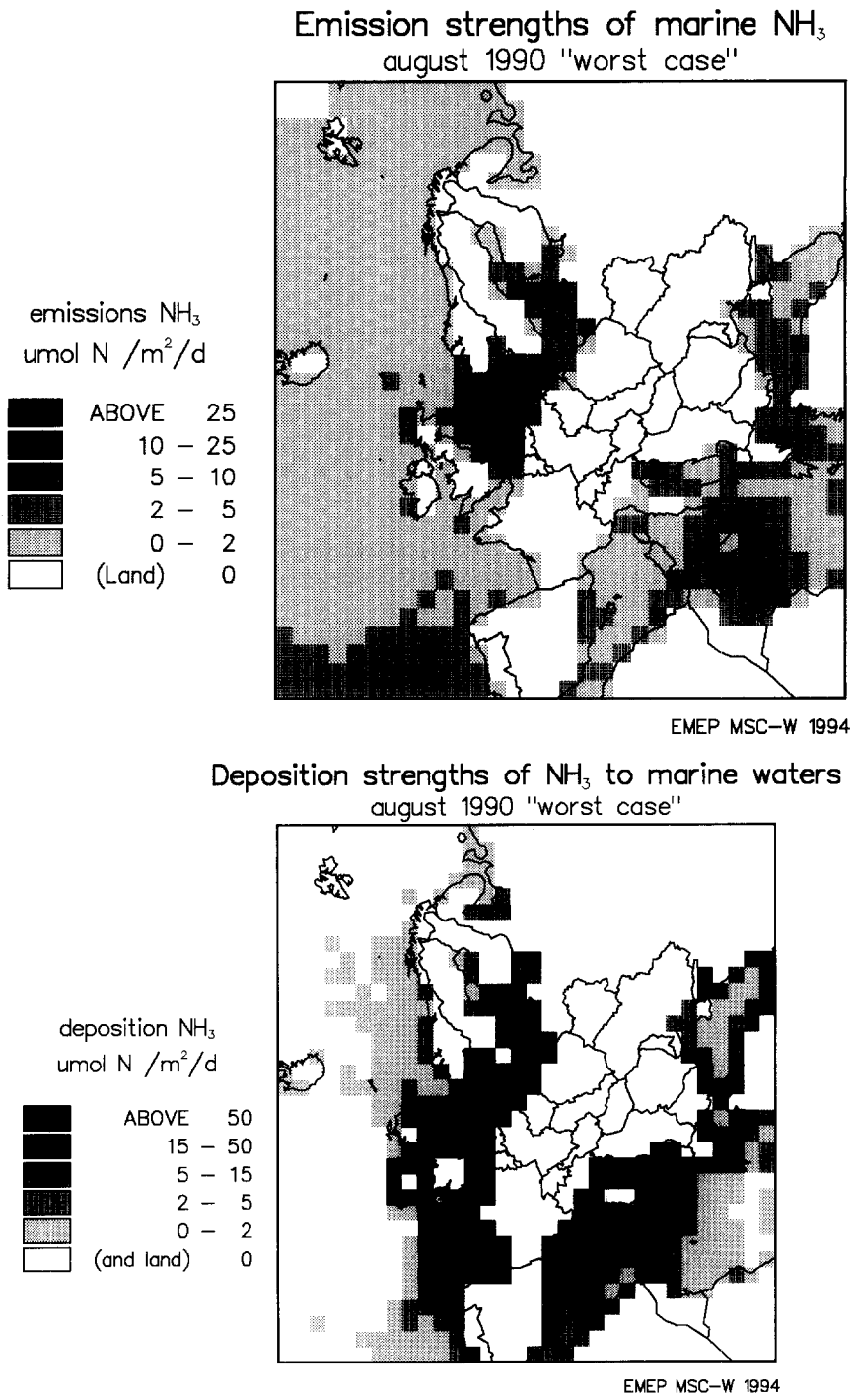


Figure 5. Disaggregated fluxes of ammonia in the a) upward (emission) direction and b) downward (deposition) direction calculated by the MSC-W model for August, 1990. Fluxes are in units of μmol m^{-2} d^{-1}.

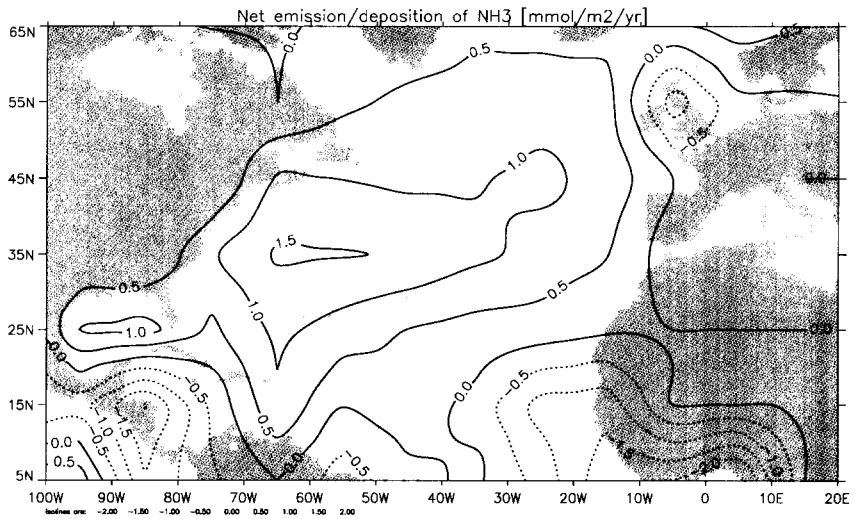


Figure 6. Net annually averaged oceanic ammonia emissions (continuous lines) and depositions (dashed lines) calculated with the Moguntia/HAMOCC3 global models. Fluxes are in mmol m^{-2} yr^{-1} (1 mmol m^{-2} yr^{-1} = 2.7 μmol m^{-2} d^{-1}).

from and to the ocean surface were calculated with the Moguntia/HAMOCC3 global models (Figure 6). Emissions and depositions over continental areas, which are an order of magnitude larger than those in oceanic regions, are not shown in this figure. Net NH_3 deposition occurs in ocean areas that are downwind of continental source regions such as Central America and eastern Africa. In these continentally-derived air masses, the model calculations indicate that ammonia emissions frequently dominate sulfur emissions. Therefore, gas phase NH_3 does not react immediately with acidic sulfate aerosol so that atmospheric residence times are long enough to allow transport to the oceans. Relatively small net fluxes are calculated over the North Sea due to the magnitude of the upward and downward disaggregated fluxes. The presence of significant NH_x (s) concentrations gives rise to large but temporary emission fluxes which are balanced by deposition due to high atmospheric concentrations at other times. The net flux results from the MSC-W model (Figure 7) also suggest a zoning in emission versus deposition during the month considered (August 1990). While the oceanic waters have a uniform emission characteristic, deposition is often dominant in coastal regions that are under the influence of terrestrial sources such as the French coast and the European shelf. Where localized marine concentrations are sufficient, however, net emission can occur such as for the central North Sea.

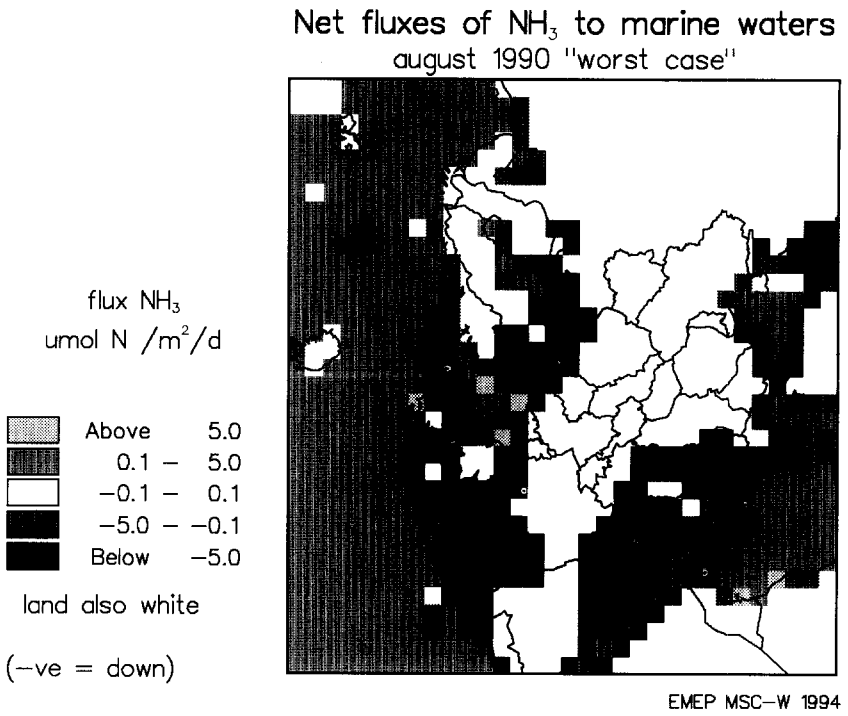


Figure 7. Net fluxes of ammonia for the northeast Atlantic Basin for August 1990 as calculated by the MSC-W model. Fluxes are in units of μmol m^{-2} d^{-1}.

6. Sensitivity of the flux calculation to input parameters

A sensitivity study was done to quantify the effect that changes in surface seawater temperature, salinity, pH, NH_x (s) concentration, the atmospheric NH_3 (g) concentration, and V_e have on the calculated flux. The input parameters for the sensitivity calculations were set for a base case of surface seawater temperature equal to 19 °C, salinity equal to 35.75 per mil, pH equal to 8.2, $[NH_x]_s$ equal to 100 nM, $(NH_3)_g$ equal to 1 nmol m^{-3}, and V_e equal to 0.8 cm sec^{-1}. One parameter was varied at a time while the others were kept at the base case values. Input parameters were varied over the range of values expected for the North Atlantic Basin: temperature from 7 to 31 °C, salinity from 34 to 37.5 per mil, pH from 7.8 to 8.5, $[NH_x]_s$ from 10 to 5000 nM, $(NH_3)_g$ from 1 to 500 nmol m^{-3}, and V_e from 0.8 to 2.0 cm sec^{-1}. As shown in Figure 8, for the range of expected values of the input parameters, changes in $[NH_x]_s$ and $(NH_3)_g$ have the largest effect on the absolute magnitude of the flux. Changes in seawater temperature also have a significant effect while changes in salinity, seawater pH, and V_e have minimal effects.

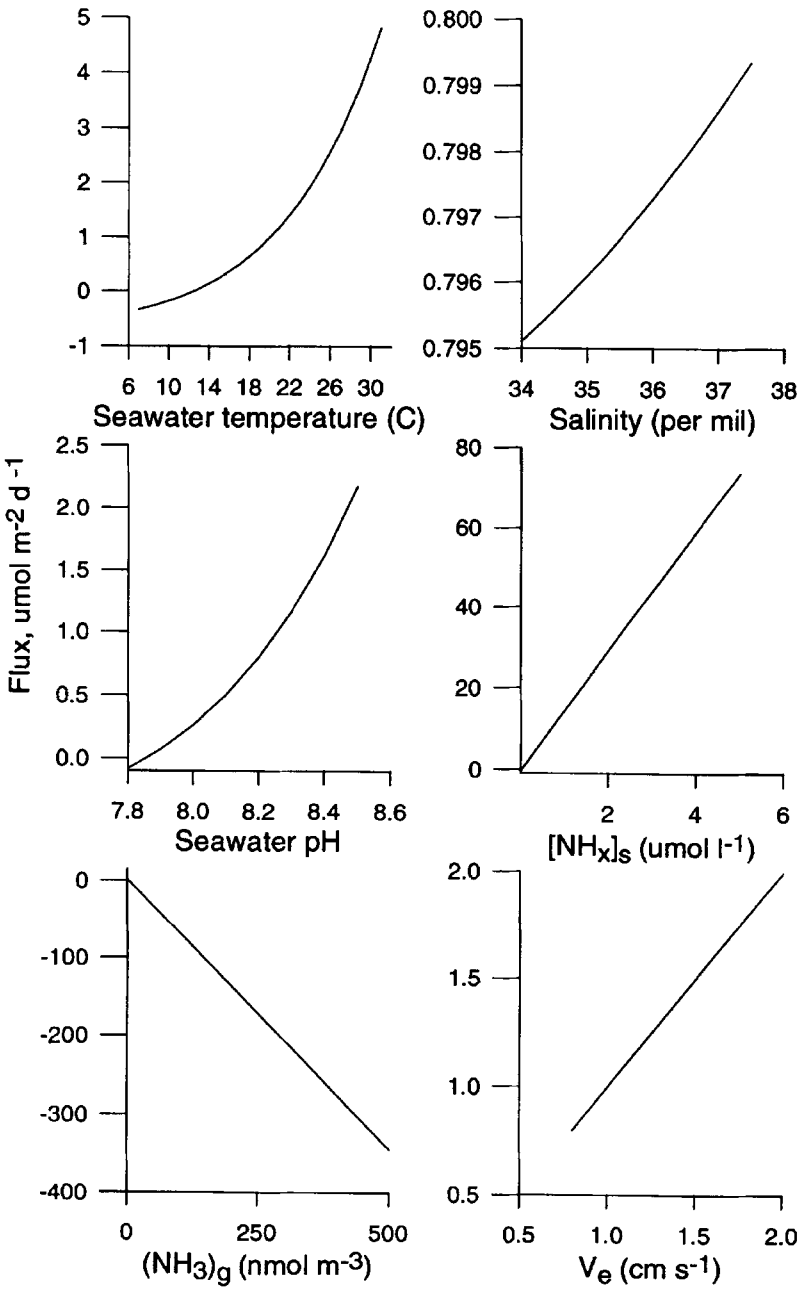


Figure 8. The sensitivity of the calculated flux to changes in surface seawater temperature, salinity, pH, $[NH_x]_s$, atmospheric $(NH_3)_g$, and the exchange velocity, V_e.

7. Conclusions

Presented here is a first attempt to determine the direction and magnitude of the air/sea ammonia flux for different regions of the North Atlantic Basin. Reported seawater and atmospheric ammonia concentrations have been compiled and the measured data have been compared to Moguntia/HAMOCC3 and MSC-W model output. In addition, air/sea NH_3 fluxes have been derived from the measured and modeled seawater and atmospheric concentration data.

Measured seawater NH_x (s) concentrations cover two orders of magnitude ranging from less than 30 to 4300 nM. The highest concentrations are reported for the Caribbean Sea, North Sea, and the Belgium coast. Very few open ocean values have been reported. The HAMOCC3 global model was able to reproduce the measured open ocean concentrations but tended to underestimate coastal values. This most likely is a result of the large scale of the model and an incomplete description within the model of the biological processes controlling the seawater ammonia concentrations. Measured atmospheric NH_3 (g) concentrations have been reported for only four North Atlantic field experiments. The concentrations range from 2 to 500 nmol m^{-3} with the largest values reported for the North Sea, the Caribbean Sea, and the Sargasso Sea. Again, there is a lack of open ocean measurements. In general, measured NH_3 (g) concentrations were larger than those calculated from the MSC-W and Moguntia models. The systematically higher measured values could be due to sample contamination and/or inadequate emission and transport schemes in the models. In addition, Moguntia concentrations are representative of the lowest 0 to 400 m of the atmosphere while the measurements are made at the surface. The difficulty in comparing point measurements with wider-scale models may also contribute to the disagreement.

Air/sea fluxes of ammonia calculated from the measured seawater NH_x (s) and atmospheric NH_3 (g) concentrations are meant to be a first approximation as, in most cases, the seawater and atmospheric concentrations were not measured simultaneously. The North Sea was found to have both atmosphere-to-ocean and ocean-to-atmosphere net fluxes. Fluxes for the Caribbean, Bermuda, and the Sargasso Sea were consistently from the atmosphere to the ocean although those from the Sargasso Sea were about a factor of 15 to 20 larger than those from Bermuda. The lack of agreement between the Bermuda and Sargasso Sea fluxes is disturbing as they are in the same region. It is likely that the NH_3 (g) concentrations measured over the Sargasso Sea (Georgii & Gravenhorst 1977) were contaminated leading to artificially large atmosphere-to-ocean fluxes. The only fluxes calculated from simultaneously measured NH_3 (g) and NH_x (s) concentrations were for the North Sea (Asman et al. 1994) where values ranged from -75 to 43 μmol m^{-2} d^{-1}. The net direction of the flux depends primarily on the highly variable $(NH_3)_g$ as for

other regions under continental influence. Fluxes derived from the measured concentration data were either more negative or more positive than those derived from the modeled concentrations. This difference could be due to sampling artifacts, inadequacies in the models, or difficulties in comparing discrete and time-averaged fluxes.

Sensitivity tests indicate that the flux estimates depend strongly on changes in the seawater NH_x and atmospheric NH_3 concentrations. Therefore, to define the role of oceanic ammonia emissions in the nitrogen budget of the North Atlantic Basin, simultaneous and accurate measurements of $(NH_3)_g$ and $[NH_x]_s$ in several regions are needed. These should be compared to model-derived values over equivalent spatial and temporal scales for validation of the models. The eventual goal is to develop models which are able to simulate accurately the nitrogen dynamics of the North Atlantic Basin. Such models will help to determine the magnitude of oceanic NH_3 emissions on a regional basis, the influence of continental NH_3 emissions on the North Atlantic Basin, and the regional effects of NH_3 on aerosol chemical, physical, and optical properties in the North Atlantic atmosphere.

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