



# Ammonium accumulation during a silicate-limited diatom bloom indicates the potential for ammonia emission events

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## Abstract

Ammonium ( $\text{NH}_4^+$ ) concentration was measured at 15 stations in the NE Atlantic during the declining phase of the spring diatom bloom as part of the FISHERS 2001 cruise. The NE Atlantic temperate spring bloom is one of the largest seasonal events in the oceanic cycle of primary productivity and represents the conversion of large amounts of oxidized nitrogen to organic (reduced) nitrogen by planktonic photosynthesis, much of which is recycled by heterotrophs as reduced N (DON and ammonium). We might expect recycled ammonium to be rapidly re-used by photosynthesizers. However, during the FISHERS cruise the decline of the bloom was accompanied by a substantial buildup of dissolved ammonium (from  $\sim 100$  nM to  $>500$  nM near the sea surface) caused by a temporary imbalance in production and consumption processes. Calculations of air–sea ammonia ( $\text{NH}_3$ ) flux under assumed ‘normal’ ‘peak bloom’ and ‘post-diatom-bloom’ conditions are presented and these demonstrate that over a wide range of temperatures, post-bloom accumulation of ammonium will lead to changes in the magnitude and direction of air–sea ammonia flux. If our results are generally applicable then the seasonal succession of plankton communities may be accompanied by periods of anomalously high ammonium concentration and hence be disproportionately important for air–sea ammonia flux. Once in the atmosphere, ammonia neutralizes acidity and in doing so plays a potentially significant role in climate forcing via aerosol formation.

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## 1. Introduction

### 1.1. Atmospheric importance

Ammonia in the atmosphere is important in the biogeochemical cycling and geographic redistribution of

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nitrogen, as well as in its connections to the sulfur cycle and its role in cloud formation (Liss and Galloway, 1993). As the predominant naturally occurring base in the atmosphere, ammonia is important in neutralization reactions, particularly with acidic sulfate aerosol. It has been shown that new particle formation from sulfuric acid gas is enhanced in the presence of ammonia (McFiggans, 2000; Yu, 2003). Such ammonia-sulfate reactions are of particular interest in the marine boundary layer (MBL), where there are fewer fine-mode particles available to act as cloud condensation nuclei (CCN) than in the terrestrial boundary layer. Over the open ocean, a small increase in CCN number will generally lead to a substantially greater increase in cloud albedo than a similar increase in CCN number in the terrestrial boundary layer (or over coastal seas) where CCN numbers are greater initially (Twomey, 1991; Watson and Liss, 1998). Thus, any marine source of ammonia to the MBL is of potentially great importance to atmospheric chemistry and climate. Ammonia is a soluble gas and thus its air–sea flux, unlike that of other important (relatively insoluble) trace gases such as DMS (dimethylsulfide), is bi-directional, depending on factors such as concentration in sea and air, and pH and temperature at the ocean surface.

### 1.2. Marine ammonium cycling

In the offshore marine environment ammonium originates primarily from the biological decomposition of organic matter by bacteria, either free-living or in the guts of zooplankton or higher organisms (Billen, 1984; Rodrigues, 1998; Kirchman, 2000). Secondly there is some atmospheric input (Duce et al., 1991; Liss and Galloway, 1993; Spokes et al., 2000). The relative contributions of zooplankton and free-living bacteria to ammonium production in the surface ocean is variable (Kirchman, 2000), with previously observed open-ocean bacterial contributions of between 10% (Glibert, 1982) and 95% (Harrison et al., 1983) of total ammonium regeneration.

Ammonium is also an important source of nitrogen nutrition to many phytoplankton species and, under certain conditions, to bacteria (Rodrigues, 1998; Kirchman, 2000). Thus it is subject to both uptake and regeneration through numerous trophic pathways. The ambient concentration of  $\text{NH}_4^+$  (which is usually  $< 1 \mu\text{M}$  in the surface of the open ocean) is thus a balance between all uptake and regeneration processes. We can consider  $\text{NH}_4^+$  concentration as a ‘state variable’ in a system that is complex and turns over rapidly. Close coupling between  $\text{NH}_4^+$  uptake and regeneration is frequently observed in  $^{15}\text{N}$  isotopic tracer studies (Glibert and McCarthy, 1984; Probyn, 1985;

Mengesha et al., 1990) i.e. ammonium regenerated by heterotrophs is commonly rapidly re-assimilated by primary producers. Any temporary decoupling of uptake and regeneration processes may lead to substantial accumulation of ammonium in surface waters, or lack of availability of ammonium to the planktonic community.

### 1.3. Phytoplankton nitrogen nutrition

It is energetically favorable for phytoplankton to meet their nitrogen requirements from ammonium over nitrate; nitrogen in ammonium being in the correct oxidation state ( $-3$ ) for incorporation into amino acids and proteins (Dortch, 1990). The relative uptakes of oxidized and reduced N is the basis of the  $f$ -ratio (Eppley and Peterson, 1979):

$$f = \rho\text{NO}_3 / [\rho\text{NO}_3 + \rho\text{NH}_4^+ (+\rho\text{urea})] \quad (1)$$

Where  $\rho\text{NO}_3$ ,  $\rho\text{NH}_4^+$ , and  $\rho\text{urea}$  are the phytoplanktonic uptake rates of nitrate, ammonium and urea respectively. When the  $f$ -ratio is used with productivity data to estimate carbon export from the mixed layer, it is important to include urea uptake, although methods exist to correct for its influence if not measured (Wafar et al., 1995). In this paper, we are specifically interested in the relative roles of nitrate and ammonium in nitrogen nutrition and so urea uptake is not considered further. The nitrogen source preferences of phytoplankton are constrained by the lowest concentration and temperature at which a cell can take up nutrients, against the availability of the different nitrogen sources (Dortch, 1990; Owens et al., 1991; Reay et al., 1999 and others) and intrinsic growth rates of different species. In this respect, small cells have a competitive advantage relative to larger cells because of their surface-area-to-volume ratio, often expressed in terms of a relative half-saturation constant,  $K_s$ . The fast intrinsic growth rates of large-celled diatoms (e.g., Furnas, 1991; Crosbie and Furnas, 2001) need to be supported by rapid nitrate (and silicate) assimilation. When nitrate or silicate becomes limiting for diatoms, smaller phytoplankton taxa will out-compete them at low N concentrations because of lower  $K_s$  characteristics. This allows them to ‘scavenge’ the remaining  $\text{NO}_3^-$ , but more particularly to utilize  $\text{NH}_4^+$  at low ambient concentrations and in balance with regeneration rates that can satisfy the N demands of their slower growth rates.

### 1.4. Bacterial role

It has been observed that heterotrophic bacteria can play a dual role in the dynamics of ammonium in the

euphotic zone of the ocean. The organic material that they consume, for both respiration and growth, will vary in its C/N (carbon to nitrogen) ratio with factors such as its source; ambient nutrient concentrations; and degree of preprocessing by other bacterial groups. When the C/N ratio of the organic matter the bacteria are metabolizing is low, they will cleave ammonium before assimilation of the organic matter. However, when the C/N ratio is high, they will tend to take up inorganic nitrogen (predominantly in the form of ammonium) to complement the high-carbon material they are consuming (Kirchman, 2000; Rodrigues, 1998 and others).

### 1.5. NE Atlantic spring bloom

The NE Atlantic is subject to a transition from diatom to flagellate community in May, following silica depletion (Kortzinger et al., 2001). The diatom bloom tends to be silica limited in this region because winter nitrate conditions are in excess of winter silicate concentrations and nutrient replete diatoms use N and Si in a 1:1 ratio (Allen et al., 2005; Brzezinski, 1985).

Whilst the general conceptual picture of the evolution from a nitrate reliant to an ammonium reliant community after the spring diatom bloom is well accepted, there exist rather few field data to examine the seasonal cycle of ammonium in high latitude waters, how this interacts with the spring diatom bloom and how these interactions may enhance or suppress the air–sea flux of ammonia.

Fasham et al. (1993) modeled the annual cycle of plankton growth and nitrogen metabolism (based on data from JGOFS campaigns in the early 90s) at Ocean Weather Station India (OWSI) at 60°N, 20°W; a station southwest of the FISHERS study region. No ammonium data were collected during the JGOFS campaign at OWSI, but data from the NABE site (48°N, 20°W) show a seasonal evolution of ammonium immediately after the spring diatom bloom, associated with bacterial remineralization. This accumulation of ammonium is reproduced by Fasham et al. (1993) in their model of OWSI, who ascribed it to zooplankton grazing, with bacterial activity a sink for ammonium due to the high C/N ratio of the modeled DOM pool.

In this paper we present the first field evidence that substantial ammonium accumulation is indeed associated with the decline of the spring diatom bloom *at the basin scale*, and we examine the reasons underlying its occurrence before presenting sample calculations to examine its effect on air–sea ammonia flux. This is undertaken by considering data acquired on the Faeroes, Iceland, Scotland Hydrographic and Environmental

Survey (FISHES) cruise of the Iceland basin in 2001. As demonstrated by Brown et al. (2003), the dataset collected on this cruise presents a unique opportunity to investigate the effects of spring bloom on the NE Atlantic Basin — they identify that, in spite of basin-scale variability in water column and community structure, the biological measurements made can be used to order the stations into a quasi-time-series of diatom bloom decline.

## 2. Methods

### 2.1. Study area

Fieldwork was carried out during the first leg of the FISHERS cruise (RRS Discovery cruise D253), from 4 to 31 May 2001. One station each day was selected for detailed study of the plankton community; the timing of these stations was such that sample collection occurred as close to dawn as possible. Seawater was collected in 20-litre Go-Flo bottles mounted on a rosette sampler. The PAR (photosynthetically active radiation) sensor on a Chelsea Instruments fast repetition rate fluorometer (FRRF), deployed immediately before CTD casts, was used to determine sampling depths at 97%, 45%, 17.6%, 8.0%, 2.9%, 1.3% and 0.1% of surface PAR. Fifteen of these stations were sampled for ammonium concentration, other inorganic nutrients, and nitrogen and carbon assimilation rates (Fig. 1).

### 2.2. Ammonium concentration

Seawater total ammonium (NH<sub>x</sub>, the sum of ammonia and ammonium) concentrations were measured using the fluorescence method outlined by Holmes et al. (1999). Full details of the method used in this study can be found elsewhere (Johnson, 2004). In brief, sampling was conducted from surface CTD Niskin bottles and from the ship's non-toxic supply (NTS, intake at approximately 5 m depth). OPA (ortho-phthalaldehyde) was introduced to samples in the form of a 'working reagent' containing OPA in ethanol, di-sodium tetraborate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) buffer and sodium sulfite (to inhibit reaction of OPA with primary amines) prepared as described by Holmes et al. (1999). Water samples of approximately 25 ml were taken in clean 50 ml Coming centrifuge tubes and immediately inoculated with 2 ml of working reagent. Holmes et al. (1999) use a much larger working reagent to sample volume ratio for the measurement of coastal and freshwater samples, but the ratio used here was found to give a linear response to ammonium concentrations up to approximately 5 μM

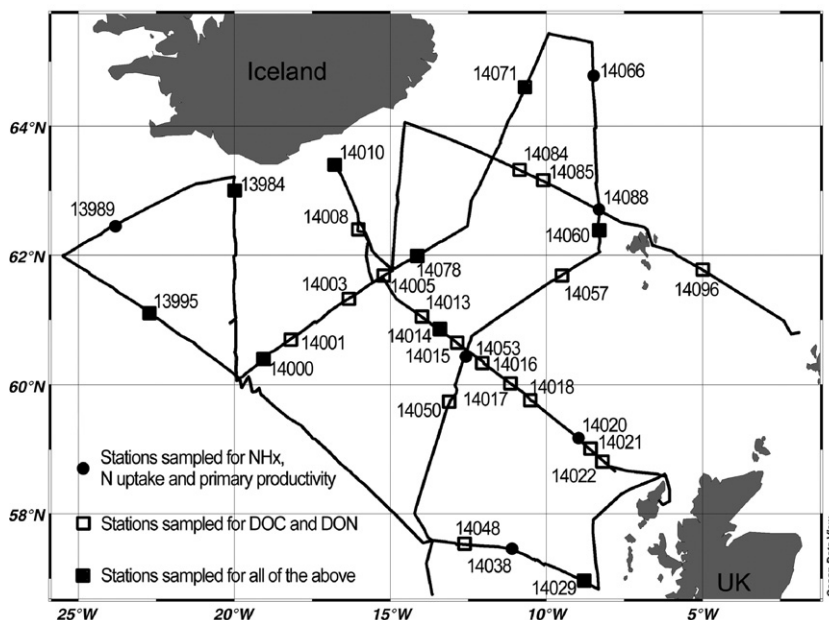


Fig. 1. Cruise track of the first leg of the FISHES cruise and stations sampled.

(the highest observed concentration during this study being approximately  $1.5 \mu\text{M}$ ). No interference from primary amines was observed in spite of the smaller amount of sulfite introduced into the samples (Johnson, 2004). Calibration was by 5 standard additions of 25 ml aliquots of surface seawater, covering a range of concentrations up to  $2.5 \mu\text{M}$ . The fluorescence of the samples was measured using a Jasco-750 spectrofluorometer (excitation 380 nm, emission 420 nm), after the samples had been stored in the dark for 3 to 24 hours (or occasionally longer). A calibration was performed each time a set of samples was taken, which ensured that samples could be analyzed at any stage in the development-plateau-decay fluorescence cycle. Measurements of sample concentration had an associated expanded uncertainty of  $\pm 4.8\%$  of sample concentration (Johnson, 2004). This relatively small uncertainty is due to high reproducibility of repeat measurements and results in a detection limit of approximately 2 nM.

### 2.3. Other measurements

Primary productivity was measured using the  $^{14}\text{C}$  technique outlined in Parsons et al. (1984) and full details are given in Brown et al. (2003). Nitrate and ammonium uptake rates were measured using the  $^{15}\text{N}$  stable isotope tracer technique described by Bury et al. (2001). Nutrient analyses (nitrate, nitrite, silicate and phosphate) were performed on a Skalar SanPlus continuous flow autoanalyzer using standard sampling

and colorimetric techniques described by Kirkwood (1995), and Sanders and Jickells (2000). DOC/DON concentrations were determined using a Shimadzu TOC-V high temperature combustion system including a Shimadzu TN detector. The method is described in full in Mathis et al. (2005).

### 2.4. Air–sea ammonia flux calculation

Air–sea ammonia fluxes were calculated according to the flux equation presented in Johnson (2004), after Gibb et al. (1999) and McKee (2001). In brief: the flux of ammonia across the ocean–atmosphere interface can be calculated according to Liss and Slater (1974).

$$F = k_g \{ (\text{NH}_3(g)) - H[\text{NH}_3(\text{sw})] \} \quad (2)$$

where  $F$  is the ocean–atmosphere flux ( $\text{pmol}/\text{m}^2/\text{s}$ ),  $k_g$  is the gas phase transfer velocity (m/s) and  $H$  is the dimensionless Henry's law coefficient for ammonia (the ratio of gas phase to liquid phase concentration at equilibrium). The concentrations of gas phase and dissolved ammonia must be in the same units (e.g.,  $\text{pmol}/\text{m}^3$ ). The gas phase transfer velocity is calculated as a function of wind speed according to Duce et al. (1991).

$$k_g = u / [770 + 45(\text{RMM})^{1/3}] \quad (3)$$

where  $u$  is the wind speed (m/s) and RMM is the relative molecular mass of the gas (17.03 in the case of

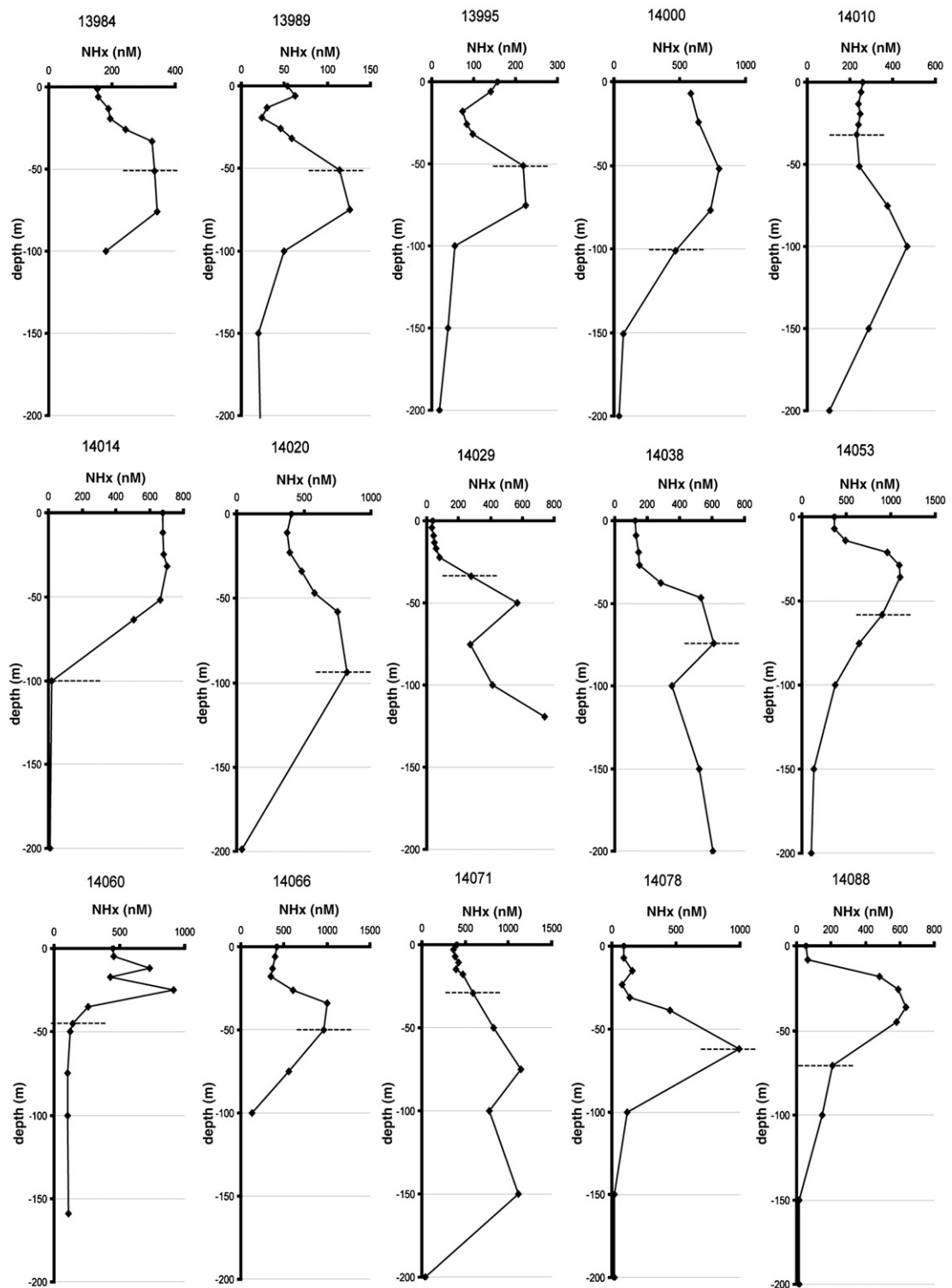


Fig. 2. Ammonium profiles from the fifteen stations considered in this study, in chronological order. Dashed lines indicate the depth of the photic zone: i.e. the depth at which photosynthetically active radiation was at 0.1% of its surface value. Standard (expanded) uncertainty is <5% in all data. Note that the concentration scales vary between stations to highlight within-station variability.

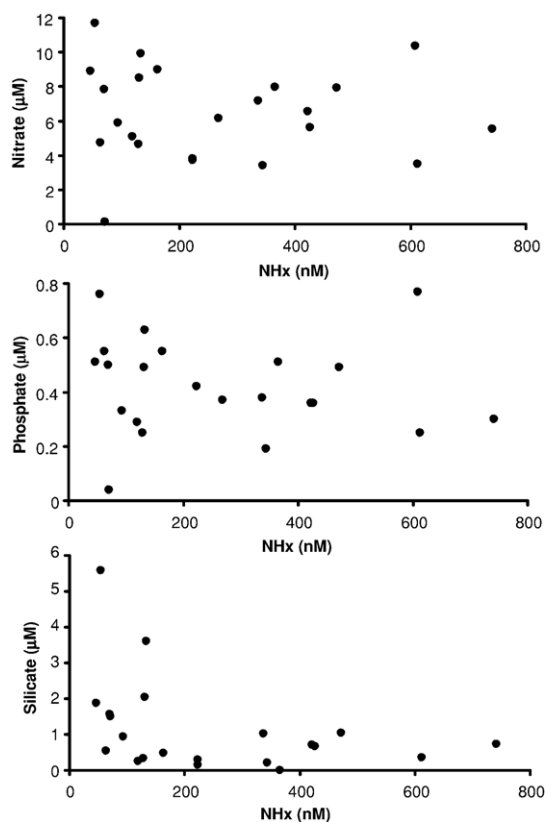


Fig. 3. Sea-surface nitrate, phosphate and silicate concentrations against sea-surface ammonium concentration. Only silicate shows a trend with ammonium. Standard uncertainty in nutrient assay is less than  $\pm 5\%$  in all cases.

ammonia). The concentration of dissolved non-solvated ammonia is given by:

$$[\text{NH}_{3(\text{sw})}] = [\text{NH}_{4(\text{sw})\text{TOT}}^+] K_a / (K_a + [\text{H}^+]) \quad (4)$$

Where  $[\text{NH}_{4(\text{sw})\text{TOT}}^+]$  (the sum of the concentrations of ammonia and ammonium in seawater) is in the units of  $\text{pmol}/\text{m}^3$ ,  $[\text{H}^+] = 10^{-\text{pH}}$  and  $K_a = 10^{-\text{p}K_a}$ .  $\text{p}K_a$  is calculated according to Khoo et al. (1977), from measured values of the dissociation of ammonium in seawater over a range of temperature and salinity. The gas over liquid form of the Henry's law coefficient,  $H$ , is calculated according to McKee (2001).

$$H = \left[ 17.93 \times \frac{T}{273.15} \times e^{\left[ \frac{4092}{T} - 9.70 \right]} \right]^{-1} \quad (5)$$

### 3. Results

#### 3.1. Phytoplankton community

The phytoplankton community observed during the FISHES cruise is discussed in greater detail in Moore et al. (2005) and Brown et al. (2003), who find the waters sampled to be diatom dominated and, with the exception of 1 station (not considered in this work), the diatom bloom was at peak levels (Station 13984) or in various stages of decline.

#### 3.2. Ammonium concentrations

There is considerable spatial heterogeneity in surface ammonium concentrations (Fig. 2), which range from

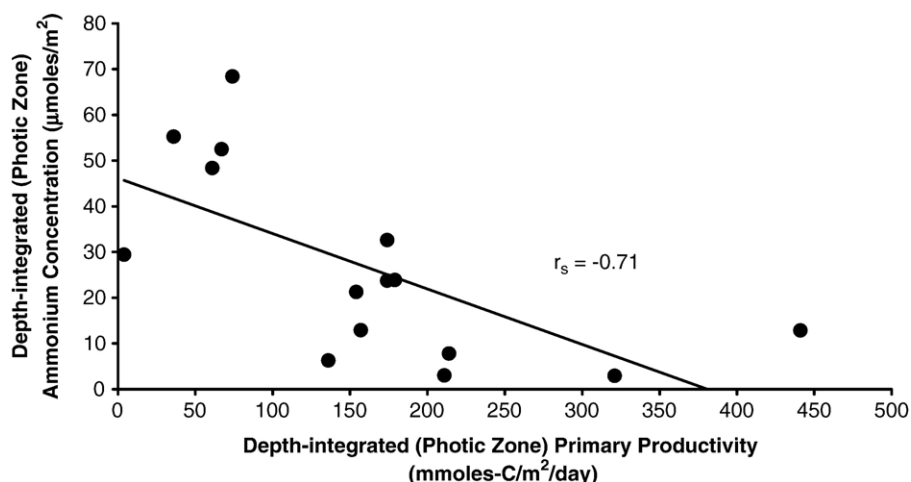


Fig. 4. The relationship between depth-integrated ammonium concentration and primary productivity from all stations, demonstrating that high total water column ammonium is associated with low primary productivity (i.e., post-bloom conditions). The Spearman's rank coefficient ( $r_s$ ) of  $-0.71$  is statistically significant at the 99% confidence limit for  $n=15$ .

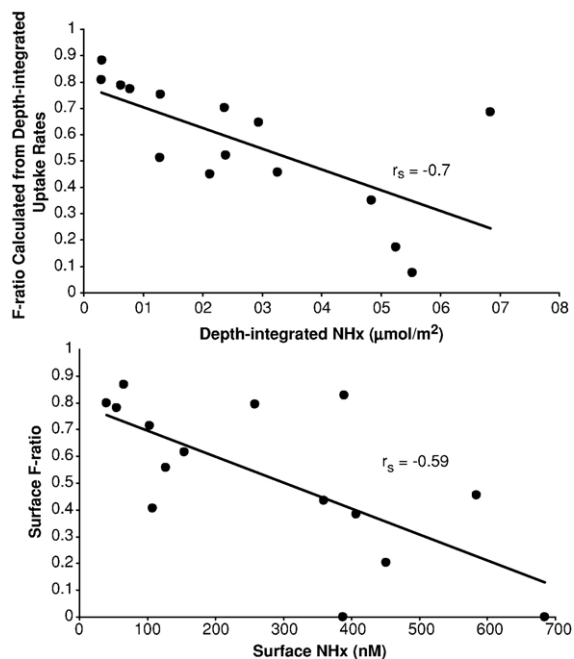


Fig. 5. The decrease in  $f$ -ratio as ammonium accumulates. The Spearman's rank coefficient of  $-0.77$  in depth-integrated data is statistically significant at the 99% confidence limit. Surface data show the same relationship, although weaker. The Spearman's rank coefficient ( $r_s$ ) of  $-0.59$  is significant at the 95% confidence limit. It is important to note that the two values where the  $f$ -ratio is plotted as zero are points where surface nitrate uptake was below detection limit. Real values are unlikely to be exactly zero. However, if these data points are disregarded the Spearman's rank coefficient ( $-0.56$ ) is still significant at the 95% confidence limit.

approximately 40 to 700 nM, and in photic-zone concentrations, which range from 20 to 1100 nM. The vertical structure of the profiles also varied substantially, with surface maxima observed on some occasions and deep maxima on others. Depth-integrated (photic zone) concentrations varied from approximately 3 mmol/m<sup>2</sup> to 70 mmol/m<sup>2</sup>.

### 3.3. Inorganic nutrient concentrations

Inorganic nutrient concentrations (Fig. 3) support the general picture that the declining phases of the spring (Si limited) diatom bloom were sampled; with silica concentrations ranging from 5 µM to below detection limit. In contrast, nitrate and phosphate concentrations were, with the exception of one station, greater than 3 and 0.2 µM respectively, suggesting that nitrate and phosphate were not limiting to growth. High ammonium concentrations occurred only at depleted silicate concentrations (Fig. 3), indicating that ammonium concentration was related to bloom state.

### 3.4. Primary productivity

An inverse relationship is observed between primary production and ammonium concentration (Fig. 4). As production decreased, depth-integrated ammonium concentrations increased from between <1 and 20 to between 40 and 70 µmol/m<sup>2</sup>, indicating that the declining phase of the spring diatom bloom is accompanied by an accumulation of dissolved ammonium throughout the photic zone.

## 4. Discussion

### 4.1. Ammonium accumulation

Ammonium accumulation was observed throughout the NE Atlantic basin over a sampling period of several weeks, covering various stages of bloom decline. Thus it seems that this was not a transient state but rather a condition that persisted for some days or even weeks at each station. We provide evidence below that suggests the accumulation of ammonium over the cruise region is due to decoupling of the processes taking up and regenerating ammonium, as the bloom declined and regeneration exceeded uptake by the mixed algal/ bacterial community.

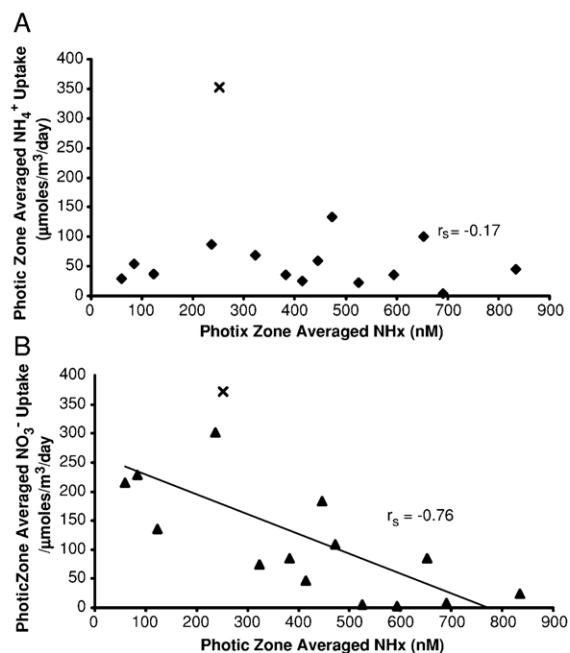


Fig. 6. Ammonium uptake (A) and nitrate uptake (B) against ammonium concentrations over the declining diatom bloom. A Spearman's rank coefficient ( $r_s$ ) of  $-0.76$  is significant at the 99% confidence limit. In both plots the station identified as representing the peak of the spring bloom (Station 13984) is marked with an 'x'.

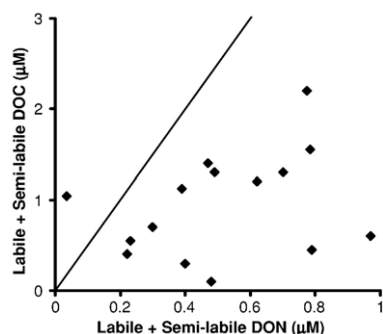


Fig. 7. Labile and semilabile DON vs DOC pools. A C/N ratio of 5 (approximately the C/N ratio of marine bacteria) is marked by the solid line. A C/N ratio of less than 5 in the DOM metabolized by heterotrophic bacteria is likely to lead to ammonium release.

#### 4.2. *F*-ratio

In order to investigate this further we consider the nitrogen metabolism of the mixed plankton community. As the bloom declined and ammonium accumulated, the *f*-ratio declined, as observed in both surface and depth-integrated data (Fig. 5), indicating an increased reliance on ammonium relative to nitrate as a nitrogen source. This is consistent with our conceptual understanding of seasonal phytoplankton community evolution from one dominated initially by ‘new’ nitrate-based production (mostly diatoms) to one characterized by ‘regenerated’ (reduced N) production (mostly dinoflagellates) as nutrients become limiting during summer in the stratified water column. We consider both surface and depth-integrated data here as it is possible that the bulk photic zone plankton community might have been behaving differently from that in the surface sub-layer. The ammonium depth profiles shown in Fig. 2 suggest that there are often differences in the processes modifying ammonium concentration between the surface and at depth (i.e. concentrations often change rapidly near the surface). However, although the relationship between declining *f*-ratio and ammonium accumulation is weaker in the surface data than in depth-integrated data, it is still statistically significant (see caption, Fig. 5).

Contrary to what we might expect with a decreasing *f*-ratio, measured ammonium uptake rates varied relatively little over the course of the study, and with no discernable trend with either primary production or ammonium concentration (Fig. 6). The outlying point in Fig. 6A is the high ammonium uptake at Station 13984, identified by Brown et al. (2003) as representing the peak of the spring bloom. Note that the corresponding nitrate uptake is also high (Fig. 6B). Primary produc-

tivity was also greatest at this station (Fig. 4). The decline in *f*-ratio therefore appears to be the result of a decline in nitrate uptake, rather than an increase in ammonium uptake.

The technique used to quantify ammonium uptake rates (Bury et al., 2001), using the equation presented by Dugdale and Goering (1967) does not account for the effects of isotope dilution (by regeneration of  $\text{NH}_4^+$ ) on apparent uptake rates. It has been shown recently that the ‘classic’ approach applied here consistently underestimates ammonium uptake by up to 40% compared to a more complex model, although major changes in uptake rates associated with the seasonal cycle were well reproduced (Tungazara et al., 2005). It is thus possible that ammonium uptake in fact *increased* with increasing ammonium concentration, but that the signal was masked by increasing regeneration as the bloom declined.

With the exception of one observation, the C/N ratio of the accumulated labile and semilabile dissolved organic matter<sup>1</sup> (DOM) in the photic zone was below 5 (Fig. 7). This low C/N ratio is consistent with bacterial release of ammonium (Goldman and Dennet, 2000; Anderson, 1992; Tezuka, 1990).

#### 5. Implications for air–sea ammonia flux

The observed increase in surface-water ammonium concentrations will lead to an increase the concentration (and partial pressure) of  $\text{NH}_3(\text{sw})$  at the air–sea interface, favoring fluxes from the ocean into the atmosphere.  $\text{CO}_2$  assimilation is likely to lead to a deficit in surface-water  $\text{pCO}_2$  and an increase in pH, causing  $\text{NH}_x$  equilibrium to shift further towards  $\text{NH}_3(\text{sw})$ . This increase in pH can sometimes be as much as 1 pH unit (Brussaard et al., 1996). The numerical model of Yakushev and

<sup>1</sup> To calculate the C/N ratio of the accumulated dissolved organic matter pool we have examined profiles of DOC and DON for each of the stations shown in Fig. 1, each of which showed a surface accumulation of both DOC and DON above 100 m. Below 100 m the profiles were rather constant with depth. We have therefore subtracted the deep value, assuming that this represents the refractory pool which is present throughout the water column with the additional surface maxima being assumed to represent the semi-labile and labile pools turned over on timescales of less than one year. The surface pools of DOC and DON were then integrated separately and the resultant integrated DOC and DON were divided by the integration depth to produce accumulations in units of micromoles per liter which can be compared to estimate the molar ratio of these two pools and hence the C/N ratio of the pool of labile and semi-labile material. It is important to recognize that the C/N ratio of this pool does not represent the C/N ratio of the pool metabolized by bacteria but it is not unreasonable to suppose that it might be close to it.

Mikhailovsky (1995) predicts more moderate increases of 0.2 to 0.3 pH units, sustained over periods of up to 100 days during and after high latitude ocean blooms of various phytoplankton species. To investigate the effect of this associated increase in ammonium and pH on the magnitude and direction of air–sea ammonia flux, a set of calculations is presented, comparing the air–sea ammonia flux under ‘normal’ and ‘post-diatom-bloom’ conditions.

To calculate air–sea ammonia flux we need to know i) the concentrations of ammonium in seawater and ammonia in the atmosphere; ii) pH; iii) temperature; iv) salinity and v) wind speed. Whilst wind speed will enhance a flux of ammonia in either direction (through the transfer velocity,  $k_g$ ), it cannot influence the direction of the flux (“Eq. (2)”). Wind speed is thus not considered here, and fixed at 5 m/s. Salinity (over the range commonly observed in the open ocean) has a negligible effect on the air–sea ammonia flux (Johnson, 2004) and is fixed at 35.

The potential effects of the sea-surface microlayer are not considered here for two reasons: Firstly, other studies of air–sea ammonia exchange do not consider microlayer effects and thus we follow this to ensure comparability of results (results from other studies quoted below are directly comparable due to their similarity of approach, methodology and flux calculations); secondly, the various microlayer-related effects (enrichment, inhibition of gas transfer and irreversible thermodynamic considerations) are largely unknown for ammonia and are difficult to quantify, although assessment of the available data suggests that in the open ocean effects are likely to be minimal (Johnson, 2004).

Gas phase ammonia concentrations were not measured during this fieldwork, so two values are assumed here: the commonly quoted ‘background’ concentration of  $3 \text{ nmol/m}^3$  (Ayers and Gras, 1980; Warneck, 1988) is compared with a concentration of  $1 \text{ nmol/m}^3$ , which is probably a more realistic background concentration, after observations in the NE Atlantic (S. Gibb unpublished results; Johnson 2004). The sea-surface temperatures recorded by the ship’s sensors during the cruise range from approximately 4 to  $15 \text{ }^\circ\text{C}$ ; for the majority of the cruise track they were between 10 and  $15 \text{ }^\circ\text{C}$ . Three surface temperatures are considered here: 5, 10 and  $15 \text{ }^\circ\text{C}$ . For each temperature and gas phase concentration, three scenarios of sea-surface  $\text{NH}_4^+$  concentration and pH are considered. Normal conditions (sea-surface  $[\text{NH}_4^+] = 100 \text{ nM}$ , after frequency analysis of observed surface concentrations in Johnson, 2004) are compared with post-bloom conditions ( $500 \text{ nM}$ ,

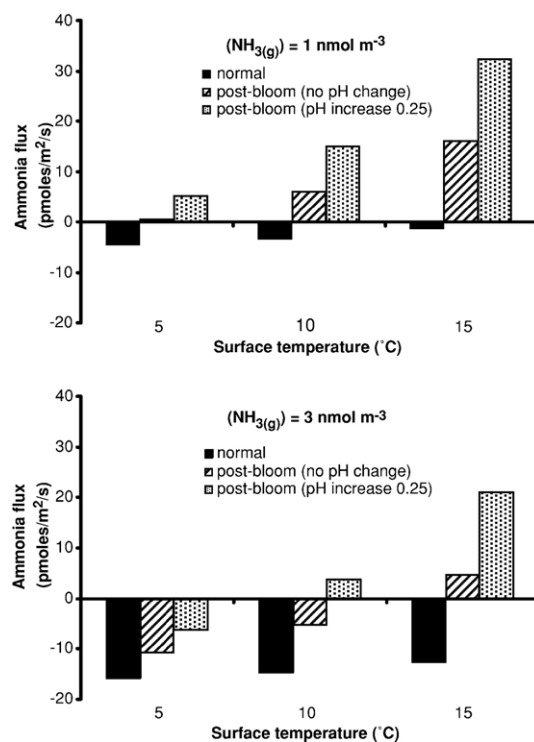


Fig. 8. Enhancement of air–sea ammonia flux during post-bloom ammonium accumulation, relative to normal conditions. A range of temperatures and gas phase ammonia concentrations are considered. Calculation and assumptions are described in the main text.

after the surface concentrations (top 5 m) observed during the FISHES cruise). Fluxes under post-bloom conditions are considered with and without a modification of pH by 0.25 pH units, from 8.0 to 8.25.

The results of this calculation, presented in Fig. 8, clearly demonstrate the potential of bloom events to modify the magnitude and direction of air–sea ammonia flux over a range of typical temperatures and remote MBL gas phase concentrations. This is the case in spite of the strong temperature dependence of the air–sea ammonia flux. This temperature dependence manifests itself in Fig. 8 as the greater difference between normal and post-bloom fluxes at higher temperatures, i.e. low temperatures reduce the effect of bloom events on air–sea ammonia flux. The effect is further inhibited by higher gas phase ammonia concentrations ( $3 \text{ nmol/m}^3$  case, Fig. 8). It should be noted that at  $5 \text{ }^\circ\text{C}$  and with a gas phase concentration of  $3 \text{ nmol/m}^3$  a bloom-driven increase of ammonium concentration to  $500 \text{ nM}$  is insufficient to drive a positive flux even with the concurrent bloom-related pH increase. However, as stated above, more recent measurements of marine boundary layer ammonia concentration suggest that the commonly quoted background concentration of  $3 \text{ nmol/m}^3$  is probably an

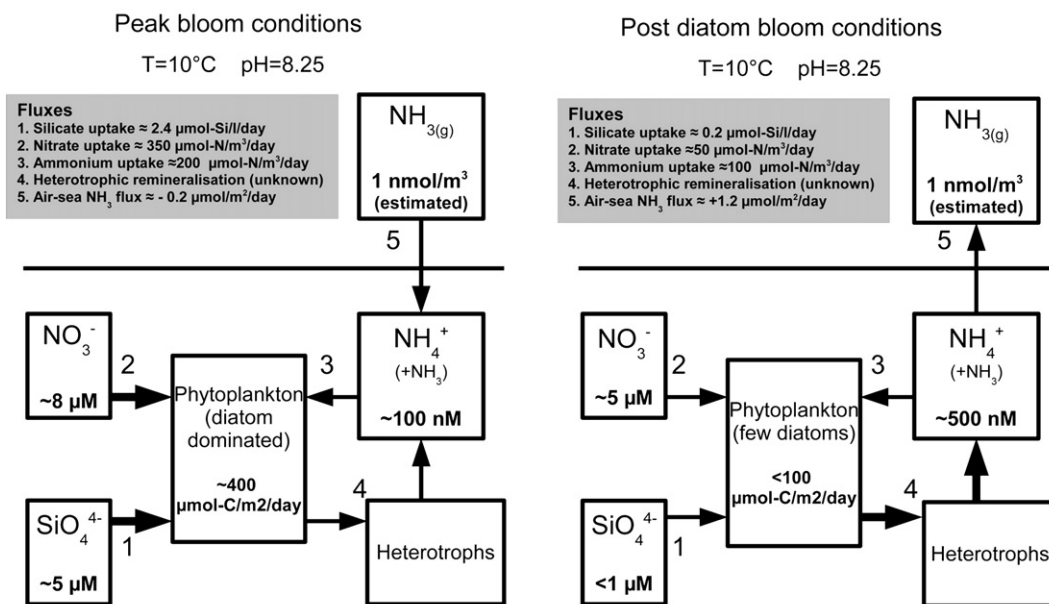


Fig. 9. Budgets to demonstrate the differences between peak- and post-bloom conditions using data measured and calculated during this study.

overestimate. It is clear from Fig. 8 that even at low temperatures and enhanced gas phase concentrations, the equilibrium between seawater and gas phase ammonia is finely poised. The equilibrium between ammonium and ammonia in seawater is sensitive to pH (Johnson, 2004) and the sea-to-air fluxes in Fig. 8 are particularly enhanced when the effect of pH increase due to the phytoplanktonic uptake of  $\text{CO}_2$  is considered.

That it is specifically the decline of the diatom bloom which results in ammonium accumulation in surface waters and consequent emission of ammonia to the atmosphere is demonstrated by the budgets presented in Fig. 9, which synthesize the relevant concentrations and fluxes for the ‘peak bloom’ and ‘post diatom bloom’ conditions observed during the cruise. Peak bloom conditions are based on the two stations with highest primary productivity (13984 and 14010), and post-bloom conditions on the four stations with lowest primary productivity (1400, 14014, 14020 and 14053). The parameters used to calculate air–sea ammonia flux in the peak bloom scenario are similar to the normal conditions used in the calculations for Fig. 8; the difference being an elevated pH (8.25, assumed).

Between peak- and post-bloom conditions we see an order of magnitude decrease in nitrate and silicate uptake (Brown et al., 2003), with a more moderate (factor of 2) decrease in ammonium uptake rates (high peak bloom ammonium uptake having been observed at station 13984, see Fig. 6). Silicate decreases to a

concentration at which it is limiting to diatom growth and primary production decreases by a factor of 4. Nitrate is not depleted to limiting concentrations, suggesting that non-diatom based primary production will increase at some future point to utilize the available nitrate before the summer recycling-based community structure emerges. During this lag in the succession of phytoplankton species, ammonium buildup occurred. We presume that heterotrophic remineralization at least remained at peak bloom rates and more likely increased with increasing numbers of dying cells as the diatom bloom declined. The post-bloom sea to air ammonia flux of  $1.2 \mu\text{mol}/\text{m}^2/\text{day}$  (quoted in these units for comparison with uptake data in Fig. 9) equates to a flux of approximately  $14 \text{ pmol}/\text{m}^2/\text{s}$ , which compares well to the post-bloom fluxes predicted in Fig. 8.

All previously observed air–sea ammonia fluxes from  $>55^\circ\text{N}$  are between approximately  $-200$  and  $-1 \text{ pmol}/\text{m}^2/\text{s}$  (Johnson, 2004; S. Gibb, unpublished results), with extreme negative values being attributable to situations where ammonia from terrestrial sources substantially enhanced gas phase concentrations. These values are exclusively negative (from air to sea) whereas the post-bloom ammonium flux predicted here is positive and of the order of  $15 \text{ pmol}/\text{m}^2/\text{s}$ , suggesting that in a region where the flux is predominantly negative, biological processes can reverse this. It is important to note here that during periods where air is advected over the NE Atlantic from nearby terrestrial sources

(Northern Europe and Iceland), gas phase concentrations of up to  $10 \text{ nmol/m}^3$  are not uncommon (Johnson 2004, S. Gibb, unpublished results). During these events such biologically driven effects will tend to be overwhelmed, particularly at lower temperatures.

Quinn et al. (1990) report sea to air ammonia fluxes observed over the range 20 to  $170 \text{ pmol/m}^2/\text{s}$  in the central Pacific. These large fluxes relative to those predicted by the above calculations can be explained by the extremely low gas phase concentrations ( $\sim 0.01 \text{ nmol/m}^3$ ) observed over the remote central Pacific by Quinn et al. (1990), and because warmer sea-surface temperatures favor efflux of gases from the ocean. McKee (2001) predicts a comparable  $10 \text{ pmol/m}^2/\text{s}$  flux from sea to air for the Central Atlantic, where higher temperatures may have counteracted lower observed surface seawater ammonium concentrations to give a similar flux to that predicted in this study for post-bloom conditions in the NE Atlantic.

It is also interesting to estimate the amount of ammonia emitted to the atmosphere over the cruise region (considered here to be represented by the region between  $58\text{--}64^\circ\text{N}$  and between  $25\text{--}5^\circ\text{W}$ , an area of approximately  $720 \times 10^3 \text{ km}^2$ ) during the decline of the spring bloom. Assuming a per-area post-bloom flux of  $15 \text{ pmol/m}^2/\text{s}$  persisting for two weeks in the region described above, the total flux of ammonia out of the ocean is  $1.3 \times 10^7$  moles (approximately  $2 \times 10^5 \text{ kg}$  of nitrogen). Assuming a 'normal conditions' flux of  $-10 \text{ pmol/m}^2/\text{s}$  for the other 50 weeks of the year yields a total ammonia flux over the region of  $2.1 \times 10^8$  moles per year from atmosphere to ocean; approximately a 10% decrease in magnitude from the net annual flux in the case of a normal flux throughout the year. This very simple calculation does not account for other seasonal changes (temperature, wind speed etc) but it does serve to highlight the potentially disproportionate significance of short periods of bloom-driven effluxes in regions where the norm is influx.

Jickells et al. (2003) present isotopic evidence for a marine ammonia source in the mid to high latitude open oceans in both hemispheres. This is somewhat at odds with recent field observations of high latitude air–sea ammonia fluxes (Johnson, 2004, S. Gibb, unpublished results), which measured solely negative fluxes (i.e. fluxes from air to sea) at  $>55^\circ\text{N}$  in the northeast Atlantic, northern North Sea and Arctic Ocean. The ammonium aerosol data used by Jickells et al. (2003) was collected in June in the northeast Atlantic, and September–October in the southern hemisphere. Thus we suggest that the data presented by Jickells et al. (2003) may be biased by the influence of the spring bloom on the air–sea ammonia flux.

## 6. Conclusion

The implication of our results is that an accumulation of ammonium commonly occurs when a silicate-limited diatom bloom declines. The phenomenon of post-bloom ammonium accumulation was observed throughout the NE Atlantic Basin, and probably occurs on a wider scale. It is possible that such events are repeated at other periods in the seasonal cycle in regions such as the NE Atlantic, leading to greater total emissions. For instance, there is some evidence of ammonium accumulation in the autumn in the NE Atlantic (S. Gibb, unpublished results), as a second nitrate-driven bloom declined, the bloom having been fueled by increased flux of nutrients from depth as the summer thermocline broke down.

The calculations presented in Fig. 8 suggest that at lower temperatures, bloom effects are unlikely to effect changes in air–sea ammonia flux direction. However, data presented by Johnson (2004) suggests that at high latitudes ( $>65^\circ\text{N}$ ) where spring and summer temperatures are low, ammonium concentration tends to be higher (normal conditions of up to  $250 \text{ nM}$  and peak surface concentrations of up to  $>1 \mu\text{M}$ ), which will somewhat counteract the effect of low temperatures. Conversely, at mid-latitudes, temperatures are warmer, but ammonium concentrations tend to be lower (Johnson 2004; McKee, 2001, Gibb et al., 1999), further widening the latitudinal band where ocean–atmosphere ammonia equilibrium is finely balanced and thus ammonium accumulation in surface waters is likely to be significant to air–sea flux direction.

The model data of Fasham et al. (1993) predict that similar ammonium accumulation will occur as the spring diatom bloom declines as a result of nitrate limitation, where the bacteria behave as ammonium utilizers; indicating that ammonium accumulation may occur independently of the role of the bacteria (as net utilizers or remineralizers of ammonium). If such accumulation is not reliant on silicate limitation, then there is the potential for this effect to be ubiquitous in oceans where there is a defined seasonal cycle. If so it may contribute significantly to the net global air–sea flux of ammonia, as it is a substantial deviation from 'ambient' conditions. In terms of global nitrogen biogeochemistry, it is probably not of great significance, as any emission to the remote marine atmosphere is likely to be rapidly converted to particulate phase ammonium and deposited locally.

However, it is in this gas-to-particle conversion that the effect of bloom-related ammonia emission events are of potential importance to MBL chemistry (through neutralization of atmospheric acidity) and to climate (through formation of cloud condensation nuclei).

Late spring and early summer is the period when DMS emissions from the ocean are at their peak, also associated with the phytoplankton seasonal cycle (e.g., Kloster et al., 2006; Kettle et al., 1999). The presence of gas phase ammonia in the atmosphere is likely to enhance the nucleation rate of new particles, through neutralization of oxidized sulfur that has originated from DMS emission. For instance, Yu (2003) predicts a factor of  $10^7$  increase in pseudo-steady-state nucleation rate with a factor of 10 increase in  $\text{NH}_3(\text{g})$  concentration in a kinetic model. To quantify 1) the global significance of bloom-related ammonia emissions and 2) their effect on MBL chemistry (nucleation rate, cloud formation), detailed open ocean time-series data (marine and atmospheric) will be required.

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### References

- Allen, J.T., Brown, L., Sanders, R., Moore, C.M., Mustard, A., Fielding, S., Lucas, M.I., Rixen, M., Savidge, G., Henson, S., Mayor, D., 2005. Diatom carbon export enhanced by silicate upwelling in the northeast Atlantic. *Nature* 437 (7059), 728–732.
- Anderson, T.R., 1992. Modeling the influence of food C:N ratio, and respiration on growth and nitrogen excretion in marine zooplankton and bacteria. *Journal of Plankton Research* 14 (12), 1645–1671.
- Ayers, G.P., Gras, J.L., 1980. Ammonia gas concentrations over the Southern Ocean. *Nature* 284, 539–540.
- Billen, G., 1984. Heterotrophic utilization and regeneration of nitrogen. In: Hobbie, J.E., Williams, P.I.B. (Eds.), *Heterotrophic Activity in the Sea*. Plenum press, New York, pp. 313–356.
- Brown, L., Sanders, R., Savidge, G., Lucas, C.H., 2003. The uptake of silica during the spring bloom in the Northeast Atlantic Ocean. *Limnology and Oceanography* 48 (5), 1831–1845.
- Brussaard, C.P.D., Gast, G.J., vanDuyf, F.C., Riegman, R., 1996. Impact of phytoplankton bloom magnitude on a pelagic microbial food web. *Marine Ecology — Progress Series* 144 (1–3), 211–221.
- Brzezinski, M.A., 1985. The Si:C:N ratio of marine diatoms. Interspecific variability and the effect of some environmental variables. *Journal of Phycology* 21, 347–357.
- Bury, S.J., Boyd, P.W., Preston, T., Savidge, G., Owens, N.J.P., 2001. Size-fractionated primary production and nitrogen uptake during a North Atlantic phytoplankton bloom: implications for carbon export estimates. *Deep-Sea Research. Part 1. Oceanographic Research Papers* 48 (3), 689–720.
- Crosbie, N.D., Furnas, M.J., 2001. Net growth rates of picocyanobacteria and nano-/microphytoplankton inhabiting shelf waters of the central (17 degrees S) and southern (20 degrees S) Great Barrier Reef. *Aquatic Microbial Ecology* 24 (3), 209–224.
- Dortch, Q., 1990. The interaction between ammonium uptake and nitrate uptake in phytoplankton. *Marine Ecology. Progress Series* 61, 183–201.
- Duce, R.A., Liss, P.S., Merrill, J.T., Atlas, E.L., Buat-Menard, P., Hicks, B.B., Miller, J.M., Prospero, J.M., Arimoto, R., Church, T.M., Ellis, W., Jickells, T.D., Knap, A.H., Reinhardt, K.H., Schneider, B., Soudine, A., Tokos, J.J., Tsunogai, S., Wollast, R., Zhou, M., 1991. The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles* 5 (3), 193–259.
- Dugdale, R.C., Goering, J.J., 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. *Limnology and Oceanography* 12, 196–206.
- Eppley, R.W., Peterson, B.J., 1979. Particulate organic matter flux and planktonic new production in the deep ocean. *Nature* 282, 677–680.
- Fasham, M.J.R., Sarmiento, J.L., Slater, R.D., Ducklow, H.W., Williams, R., 1993. Ecosystem behaviour at Bermuda Station S and Ocean Weather Station India — a general circulation model and observational analysis. *Global Biogeochemical Cycles* 7 (2), 379–415.
- Furnas, M.J., 1991. Net insitu growth-rates of phytoplankton in an oligotrophic, tropical shelf ecosystem. *Limnology and Oceanography* 36 (1), 13–29.
- Gibb, S.W., unpublished results.  $\text{NH}_x$  concentrations, speciations and air-sea exchange measured during Poseidon cruise 211, NE Atlantic 1995, OMEX programme.
- Gibb, S.W., Mantoura, R.F.C., Liss, P.S., 1999. Ocean-atmosphere exchange and atmospheric speciation of ammonia and methylamines in the region of the NW Arabian Sea. *Global Biogeochemical Cycles* 13 (1), 161–178.
- Glibert, P.M., 1982. Regional studies of daily, seasonal and size fraction variability in ammonium remineralization. *Marine Biology* 70, 209–222.
- Glibert, P.M., McCarthy, J.J., 1984. Uptake and assimilation of ammonium and nitrate by phytoplankton-indexes of nutritional status for natural assemblages. *Journal of Plankton Research* 6 (4), 677–697.
- Goldman, J.C., Dennett, M.R., 2000. Growth of marine bacteria in batch and continuous culture under carbon and nitrogen limitation. *Limnology and Oceanography* 45 (4), 789–800.
- Harrison, W.G., Douglas, D., Falkowski, P.G., Rowe, G., Vidal, J., 1983. Summer nutrient dynamics of the Middle Atlantic bight: nitrogen uptake and regeneration. *Journal of Plankton Research* 5 (4), 539–556.
- Holmes, R., Aminot, A., Kerouel, R., Hooker, B.A., Peterson, B.J., 1999. A simple and precise method for measuring ammonium in marine and freshwater ecosystems. *Canadian Journal of Fisheries and Aquatic Science* 56, 1801–1808.
- Jickells, T.D., Kelly, S.D., Baker, A.R., Biswas, K., Dennis, P.F., Spokes, L.J., Witt, M., Yeatman, S.G., 2003. Isotopic evidence for a marine ammonia source. *Geophysical Research Letters* 30 (7), 1374.
- Johnson, M.T., 2004. The air–sea flux of ammonia, PhD Thesis, University of East Anglia, Norwich.
- Kettle, A.J., Andreae, M.O., Amouroux, D., Andreae, T.W., Bates, T.S., Berresheim, H., Bingemer, H., Boniforti, R., Curran, M.A.J., DiTullio, G.R., Helas, G., Jones, G.B., Keller, M.D., Kiene, R.P., Leck, C., Levasseur, M., Malin, G., Maspero, M., Matrai, P., McTaggart, A.R., Mihalopoulos, N., Nguyen, B.C., Novo, A., Putaud, J.P., Rapsomanikis, S., Roberts, G., Schebeske, G., Sharma, S., Simo, R., Staubes, R., Turner, S., Uher, G., 1999. A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of

- latitude, longitude, and month. *Global Biogeochemical Cycles* 13 (2), 399–444.
- Khoo, K.H., Culbertson, C.H., Bates, R.G., 1977. Thermodynamics of the dissociation of ammonium ion in seawater from 5 to 40 °C. *Journal of Solution Chemistry* 6 (4), 281–290.
- Kirchman, D.L., 2000. Uptake and regeneration of inorganic nutrients by marine heterotrophic bacteria. In: Kirchman, D.L. (Ed.), *Microbial Ecology of the Oceans*. Wiley Series in Ecological and Applied Microbiology. Wiley, New York, pp. 261–289.
- Kirkwood, D.S., 1995. The SanPlus Segmented Flow Autoanalyser and its Applications. Skalar Analytical BV publication.
- Kloster, S., Feichter, J., Maier-Reimer, E., Six, K.D., Stier, P., Wetzel, P., 2006. DMS cycle in the marine ocean–atmosphere system — a global model study. *Biogeosciences* 3, 29–51.
- Kortzinger, A., Koeve, W., Kahler, P., Mintrop, L., 2001. C:N ratios in the mixed layer during the productive season in the northeast Atlantic Ocean. *Deep-Sea Research. Part 1. Oceanographic Research Papers* 48 (3), 661–688.
- Liss, P.S., Galloway, J.N., 1993. Air–sea exchange of sulphur and nitrogen and their interaction in the marine atmosphere. In: Wollast, R., Mackenzie, F.T., Chou, L. (Eds.), *Interactions of C, N, P and S Biogeochemical Cycles and Global Change*. NATO ASI Series. Springer-Verlag, Berlin, pp. 259–281.
- Liss, P.S., Slater, P.G., 1974. Flux of gases across the air–sea interface. *Nature* 247, 181–184.
- Mathis, J.T., Hansel, D.A., Bates, N.R., 2005. Strong hydrographic controls on spatial and seasonal variability of dissolved organic carbon in the Chukchi Sea. *Deep-Sea Research II* 52, 3245–3258.
- McFiggans, G., 2000. A modelling study of marine boundary layer chemistry. PhD Thesis, University of East Anglia, Norwich.
- McKee, C.M., 2001. Biogeochemical cycles of ammonia and dimethylsulphide in the marine environment. PhD Thesis, University of East Anglia, Norwich.
- Mengesha, A., Dehairs, F., Elskens, N., Goeyens, L., 1990. Phytoplankton nitrogen nutrition in the Western Indian Ocean: ecophysiological adaptations of neritic and oceanic assemblages to ammonium supply. *Estuarine, Coastal and Shelf Science* 48, 589–598.
- Moore, C.M., Lucas, M.I., Sanders, R., Davidson, R., 2005. Basin-scale variability of phytoplankton bio-optical characteristics in relation to bloom state and community structure in the Northeast Atlantic. *Deep-Sea Research. Part 1. Oceanographic Research Papers* 52 (3), 401–419.
- Owens, N.J.P., Priddle, J., Whitehouse, M.J., 1991. Variations in phytoplanktonic nitrogen assimilation around South Georgia and in the Bransfield Strait (Southern Ocean). *Marine Chemistry* 35, 287–304.
- Parsons, T.R., Maita, Y., Lalli, C.M., 1984. *A manual of Chemical and Biological Methods for Seawater Analysis*. Pergamon Press.
- Probyn, T.A., 1985. Nitrogen uptake by size-fractionated phytoplankton populations in the southern Benguela upwelling system. *Marine Ecology. Progress Series* 22, 249–258.
- Quinn, P.K., Bates, T.S., Johnson, J.E., 1990. Interactions between the sulfur and reduced nitrogen cycles over the central Pacific Ocean. *Journal of Geophysical Research* 95 (D10), 16405–16416.
- Reay, D.S., Nedwell, D.B., Priddle, J., Ellis-Evans, J.C., 1999. Temperature dependence of inorganic nitrogen uptake: reduced affinity for nitrate at suboptimal temperatures in both algae and bacteria. *Applied and Environmental Microbiology* 65 (6), 2577–2584.
- Rodrigues, R.M.N.V., 1998. Interaction between the bacterial and phytoplanktonic inorganic nitrogenous nutrition, PhD Thesis, University of Wales, Bangor.
- Sanders, R., Jickells, T.D., 2000. Total organic nutrients in Drake Passage. *Deep-Sea Research. Part 1. Oceanographic Research Papers* 47, 997–1014.
- Spokes, L.J., Yeatman, S.G., Cornell, S.E., Jickells, T.D., 2000. Nitrogen deposition to the eastern Atlantic Ocean. The importance of south-easterly flow. *Tellus* 52B, 37–49.
- Tezuka, K., 1990. Bacterial regeneration of ammonium and phosphate as affected by the carbon:nitrogen:phosphorus ratio of organic substrates. *Microbial Ecology* 19 (3), 227–238.
- Tungaraza, C., Brion, N., Baeyens, W., 2005. Comparison of two models in the estimation of nitrogen uptake rates using data from 15-N incubation experiments. *Oceanologia* 47 (3), 387–403.
- Twomey, S., 1991. Aerosol, clouds and radiation. *Atmospheric Environment* 25 (11), 2435–2442.
- Wafar, N.V.M., Lecorre, P., Lhelguen, S., 1995. F-rations calculated with and without urea uptake in nitrogen uptake by phytoplankton. *Deep-Sea Research. Part 1. Oceanographic Research Papers* 42 (9), 1669–1674.
- Warneck, P., 1988. *Chemistry of the Natural Atmosphere*. Academic Press.
- Watson, A.J., Liss, P.S., 1998. Marine biological controls on climate via the carbon and sulfur geochemical cycles. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences* 353 (1365), 41–51.
- Yakushev, E., Mikhailovsky, G., 1995. Mathematical modelling of marine biota on the carbon dioxide ocean–atmosphere exchange in high latitudes. In: Jaehne, B., Monahan, E. (Eds.), *Air–water Gas Transfer, Selected Papers from the International Symposium on Air–water Gas Transfer, 1995, July 24–27, Heidelberg*. AEON Verlag and Studio, Hanau.
- Yu, F., 2003. Nucleation rate of particles in the lower atmosphere: estimated time needed to reach pseudo-steady state and sensitivity to H<sub>2</sub>SO<sub>4</sub> gas concentration. *Geophysical Research Letters* 30 (10), 1526.