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

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1. Ammonium / ammonia biogeochemistry

Ammonia (NH_3) is important as the only naturally occurring base in the atmosphere. It's neutralisation of atmospheric acidity is an important process in aerosol and cloud formation, particularly in the marine atmosphere where CCN number is generally low. Any marine source of ammonia is thus of potential climatic significance, and may be important in the geographic redistribution of nitrogen.

In the marine environment the thermodynamic equilibrium between ammonia and ammonium (NH_4^+), is dominated by the latter, which accounts for >90% of total 'NH_X' (at typical seawater temperaure and pH). As well as being a waste product of biological activity, ammonium is an important source of nitrogen nutrition to many phytoplankton species and, under certain conditions, to bacteria (Kirchman, 2000). It is subject to both uptake and regeneration through numerous trophic pathways (Figure 1). The ambient concentration of NH_4^+ (which is rarely greater than 0.5 µM in the surface of the open-ocean) is a balance between all uptake and regeneration processes. Here we present evidence for the temporary decoupling of these processes (and associated ammonium increase) during the declining phase of the spring diatom bloom in the NE Atlantic, leading to a probable basin-scale ammonia emission event.

Data presented here was collected on Leg 1 of RRS Discovery Cruise D253 (FISHES). Brown *et al* (2003) have shown that this study sampled various stages of the declining spring diatom bloom and constructed a 'quasi time series' of bloom decline over the NE Atlantic basin by ordering stations by decreasing silicate concentration.

Figure 1. Ammonium in the marine nitrogen cycle

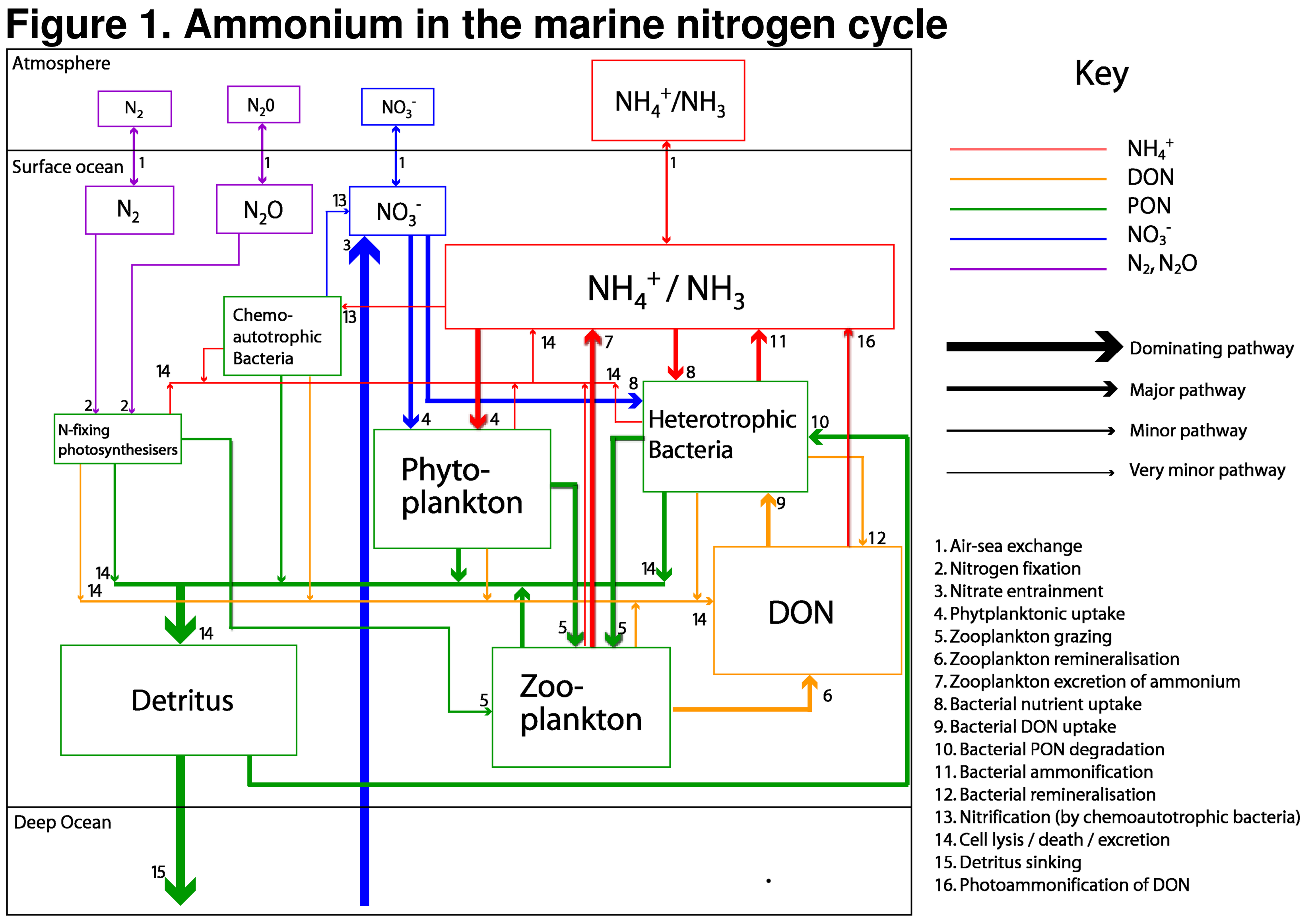
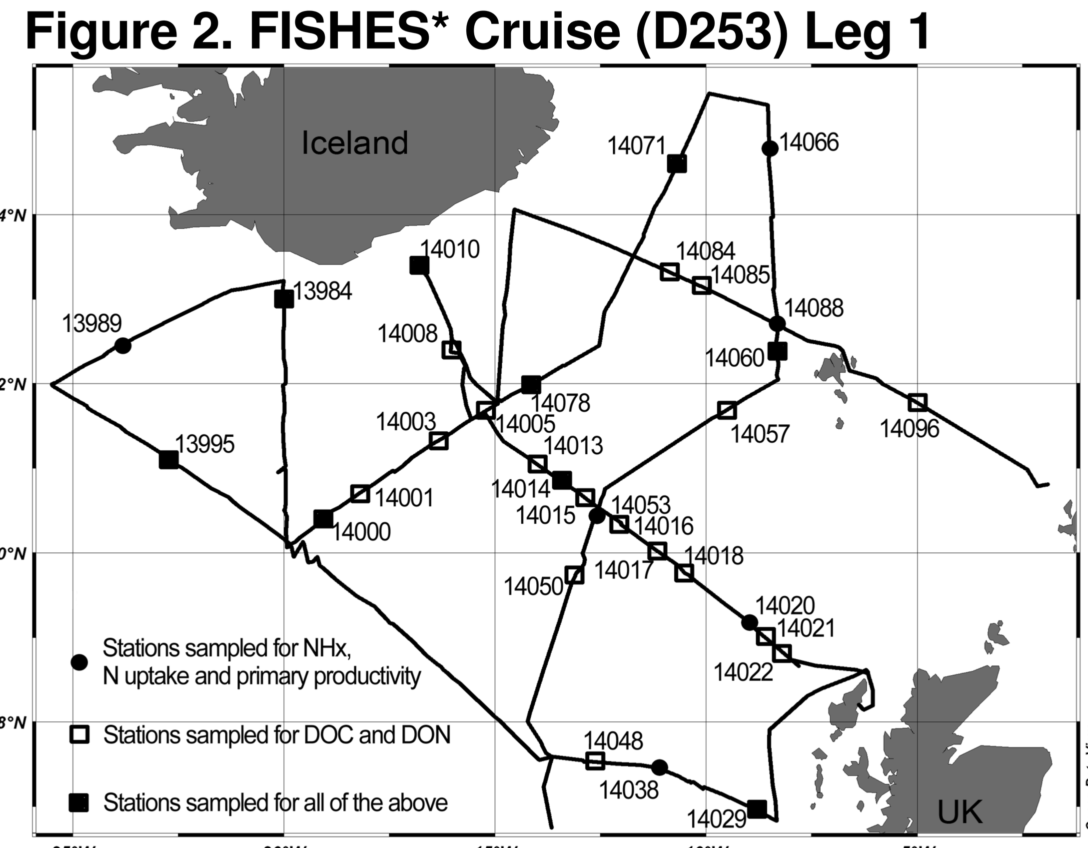


Figure 2. FISHES* Cruise (D253) Leg 1



* Faroes, Iceland, Scotland, Hydrographic and Environmental Survey. May-June 2001.

2. Spring diatom bloom decline

The NE Atlantic is subject to a transition from diatom to flagellate community in late spring, following silica depletion (Moore *et al*, 2005). 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).

A strong negative relationship is observed between ammonium concentration and primary productivity over the declining diatom bloom (Figure 3a), suggesting that over the course of the diatom bloom decline, ammonium accumulated. This is supported by the observation that high ammonium concentrations are associated with depleted silicate (Figure 3b).

Figure 3. Evidence for ammonium accumulation

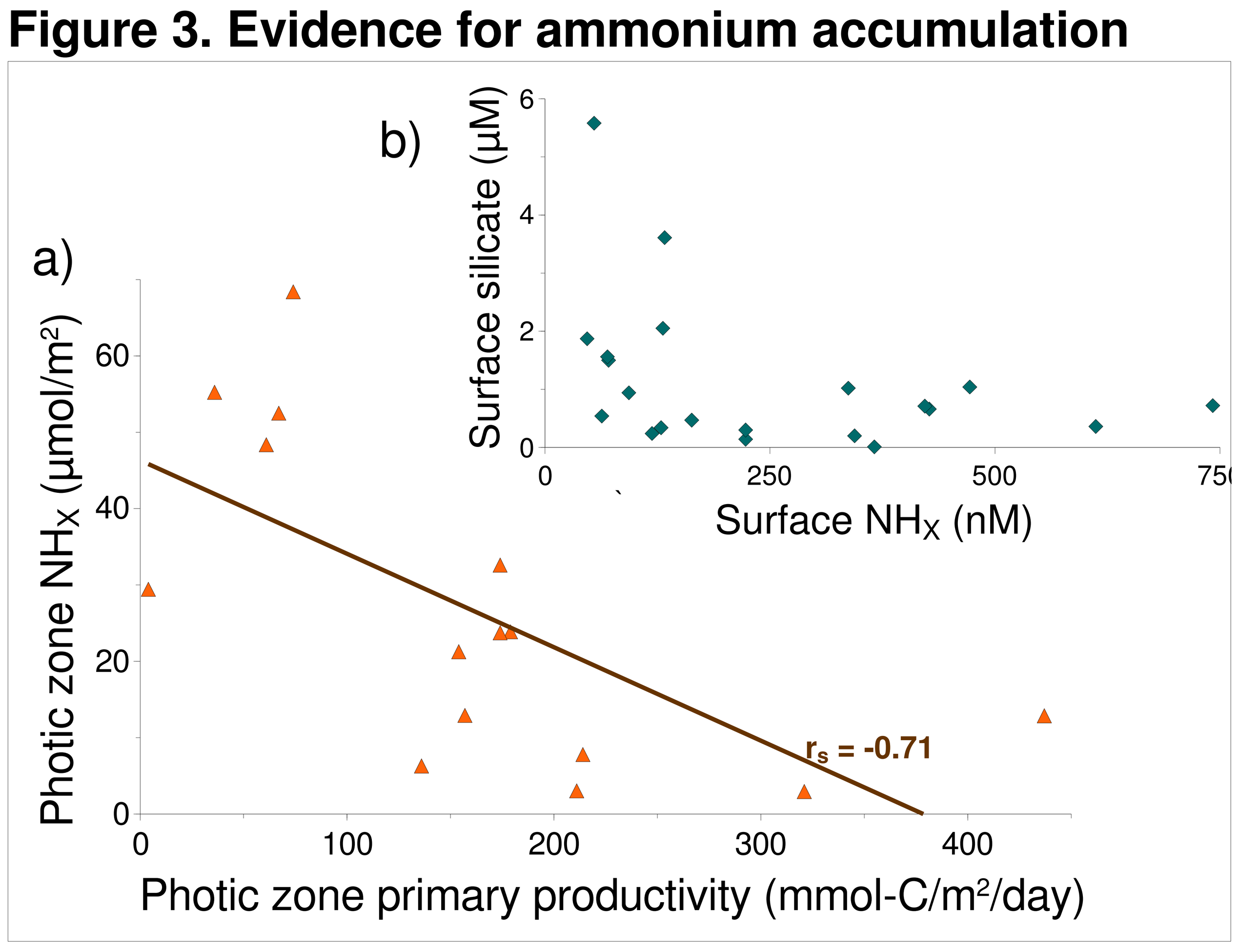
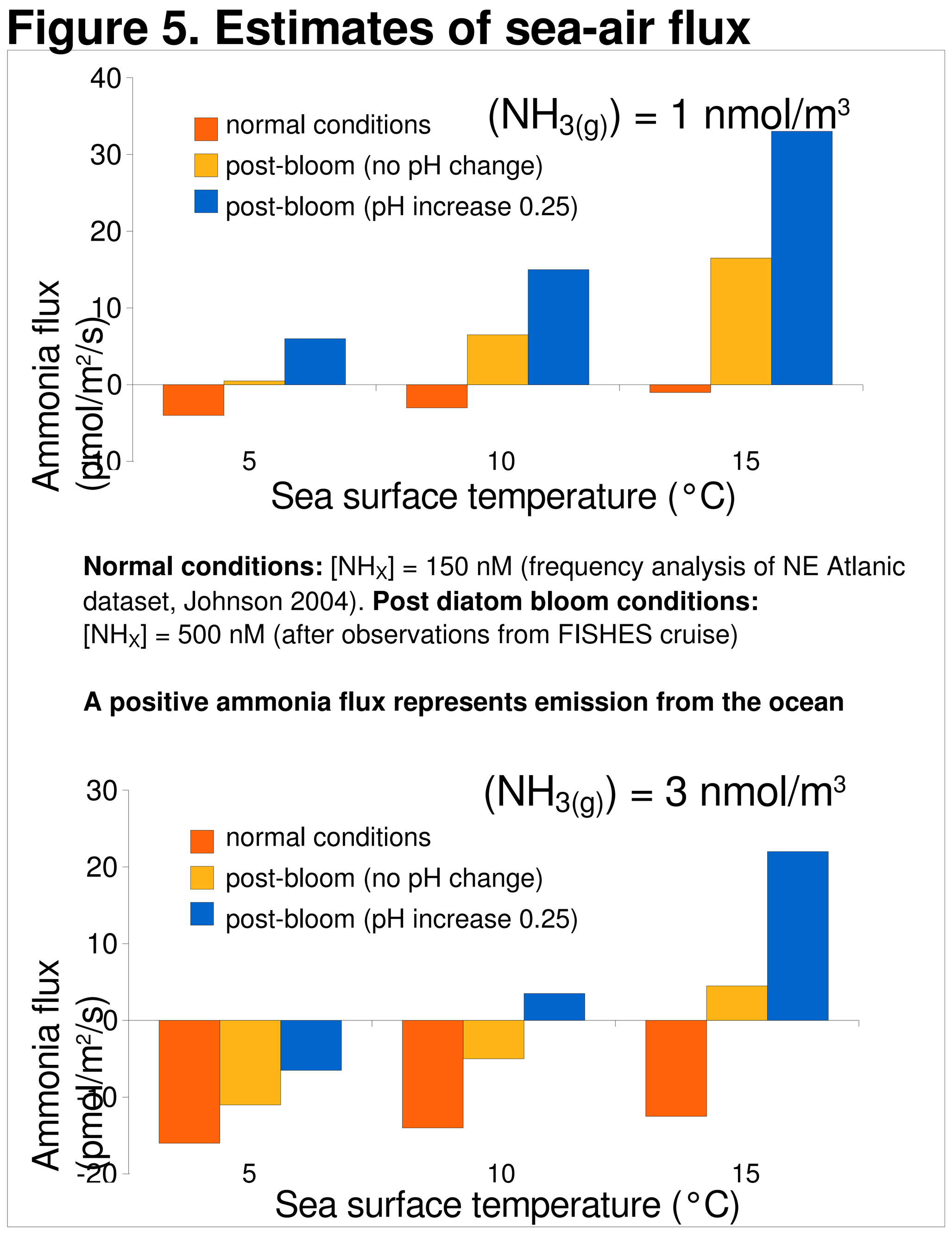


Figure 5. Estimates of sea-air flux



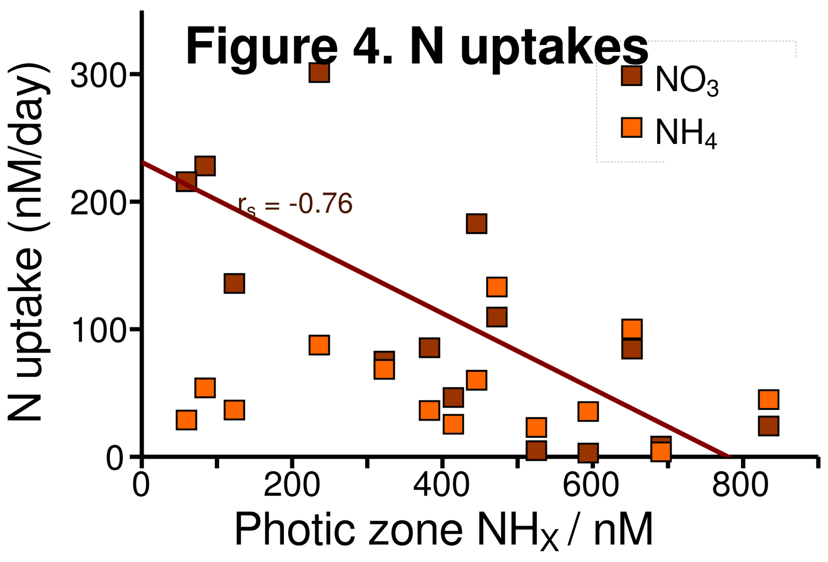
Normal conditions: $[NH_X]$ = 150 nM (frequency analysis of NE Atlanic dataset, Johnson 2004). **Post diatom bloom conditions:** $[NH_X]$ = 500 nM (after observations from FISHES cruise)

A positive ammonia flux represents emission from the ocean

3. F-ratio and nitrogen uptake rates

The f-ratio (the ratio of nitrate uptake to total N uptake) was seen to decrease as the bloom declined; with strong negative relationships between ammonium concentration and f-ratio in surface and photic zone integrated data (not shown). Figure 4 demonstrates that this is attributable to a *decrease in nitrate uptake rather than an increase in ammonium uptake*, in spite of increasing ammonium availability. Thus it seems that there was a lag between diatom decline and flagellate population growth in apparently nutrient replete conditions: at no point did nitrate or phosphate approach limiting levels. We speculate that grazing pressure and/or light limitation (due to turbidity or cloudiness) prevented the rapid growth of the flagellate community. The timescale and area over which the data was collected suggests that this decoupled state may have occurred for a number of weeks.

Figure 4. N uptakes



4. Sea-air ammonia fluxes

No atmospheric data were available from this cruise, so no direct flux calculations can be made. However, calculations are presented in Figure 5 using estimated gas phase concentrations of 1 and 3 nmol/m³, based on typical marine atmosphere ambient concentrations (Johnson, 2004).

The calculations in Figure 5 compare predicted air-sea fluxes under assumed 'normal' and 'post-bloom' conditions based on ammonium concentrations and temperatures observed during the FISHES cruise, and an assumed pH increase in the post-bloom case due to CO_2 uptake. Figure 5 demonstrates that over a range of temperatures and gas phase concentrations, bloom-related increase in ammonium in surface waters will lead to emission of ammonia in a region where, due primarily to low water temperature, the ocean would normally be a sink.

Figure 6 presents a simple budgeting exercise to compare conditions at station #13984, identified as representing close-to-peak-bloom conditions, with post-bloom conditions averaged over a series of low-primary-productivity, high ammonium stations. This highlights the 'lag' in primary productivity before the flagellate bloom, and the temporary decoupling of uptake and regeneration leading to a reverse in flux direction.

Methods: Marine NH_X concentrations were measured using a slightly modified version of the OPA method described by Holmes *et al* (1999), full details of which can be found in Johnson (2004). Other data were measured using standard methods.

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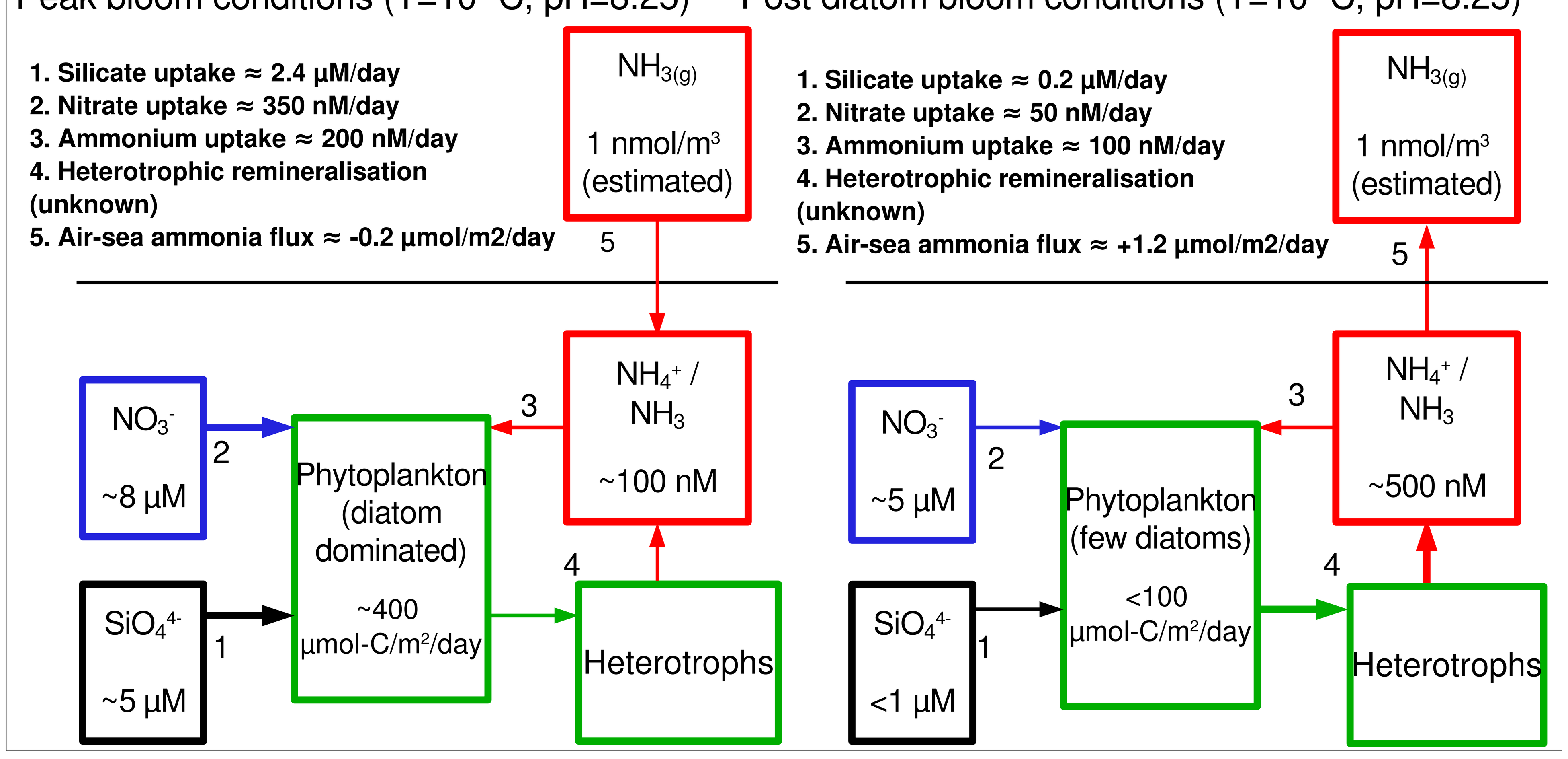
Figure 6. Comparison of peak bloom and post bloom conditions



5. Conclusions

We provide evidence of episodic ammonia emission events at the basin scale, related to the decline of a silicate limited diatom bloom. This is of particular interest as such periods are also likely to be associated with emission of DMS to the atmosphere and ternary nucleation involving ammonia has been shown to be up to 7 orders of magnitude more rapid than that of a binary H_2SO_4-H_2O system (Yu *et al*, 2003). Thus such events may enhance cloud formation from marine sulphur emissions. An interesting question is whether ammonium accumulation would have occurred had the diatom bloom been nitrate rather than silicate limited – in this case would heterotrophic bacteria have consumed the regenerated ammonium?

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