On the relationships of DIN$_{xs}$, nitrogen fixation and differential remineralization in the North Atlantic ocean

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Abstract

We use a combination of simple scalings and analytical expressions as well as an idealized numerical model of basin-scale circulation, biogeochemical cycles and ecology, to elucidate and illustrate factors which regulate the distribution of tracer $\text{DIN}_{x,s} = \text{NO}_3^- - 16\text{PO}_4^{3-}$, its temporal variability, and the distribution of diazotrophs in the North Atlantic. We infer that the observed subsurface maximum of $\text{DIN}_{x,s}$ in the subtropical thermocline and increase in temporal variability of $\text{DIN}_{x,s}$ with depth are both consistent with an enhanced remineralization rate for organic phosphorus, relative to organic nitrogen. The observed confinement of diazotrophs largely to warm, tropical waters can be (partly) explained in terms of resource control, competitive in more oligotrophic, nitrogen limited waters, but themselves inviable due to phosphorus limitation in the most oligotrophic waters of the models subtropics.
Introduction

Nitrogen fixation, the biological reduction of dinitrogen gas ($N_2(g)$) to ammonia ($NH_3(g)$), is a significant source of nitrogen in tropical and subtropical oceans (Gruber and Sarmiento, 1997; Karl, 2000; Capone et al., 2005). It is the main source of new nitrogen on the global scale, countered by the nitrogen sink reaction of denitrification. Imbalances between these two, among other secondary sources and sinks, may regulate ocean biogeochemical cycles and climate through modulation of nitrogen limitation of productivity on the global scale (Falkowski, 1997; Karl et al., 2002). Much of the understanding of oceanic nitrogen fixation is based on studies of Trichodesmium (Carpenter, 1983; Capone et al., 1997; Karl et al., 2002). Trichodesmium are the most well studied and probably the most significant nitrogen fixers in the ocean (Karl, 2002). They are free-living, non-heterocystous and filamentous cyanobacteria. Ocean observations indicate that they occur only in the subtropical and tropical oceans at temperatures above 20°C, in oligotrophic and highly stratified waters (Capone et al., 1997). To fix dinitrogen gas ($N_2(g)$) is energetically expensive and thus Trichodesmium (and other diazotrophs, Zehr and Capone, 2002) have a high requirement for light energy, an enriched N:P ratio (Klausmeier et al., 2004), a high requirement for iron (Sanudo-Wilhelmy et al., 2001; Berman-Frank et al., 2001; Kustka et al., 2003), and a slow maximum growth rate relative to other tropical and subtropical phytoplankton (Tyrrell, 1999). They have been observed also to have a few predators (Capone et al., 1997). In consequence Trichodesmium (and other diazotrophs) are only likely to be competitive when the waters are somewhat oligotrophic and nitrogen limited but with phosphorus and iron available (Karl, 2002; Zehr and Capone, 2002; Mills et al., 2004).
Direct observations of nitrogen fixation rates have been, however, too sparse to quantify regional and global rates of nitrogen fixation with accuracy. One of the most precise direct estimates in the North Atlantic, the focus of this study, comes from Capone et al. (2005). They evaluate an areal rate of $1.6-2.4 \times 10^{12}$ molN yr$^{-1}$ for the region, where they interpolate 154 direct measurements located in the Southwest of the basin to the whole region of warm North Atlantic waters (above 20 or 25°C). As a result of sparse direct measurements, integrated rates of nitrogen fixation for global and local studies have been interpreted from the distribution of the geochemical tracer $N^*$ (Gruber and Sarmiento, 1997). Here we will discuss the closely related tracer $\text{DIN}_{xs} = \text{NO}_3^- - 16\text{PO}_4^{3-}$ (Hansell et al., 2004), which differs from $N^*$ only by a constant offset (Deutsch et al., 2001). $\text{DIN}_{xs} = 0$ indicates the transition from nitrate to phosphate limitation in the idealized case of a Redfieldian organism. The relative gradient of $\text{DIN}_{xs}$, or $N^*$ to tracer age along isopycnals is used to infer the integrated contribution of nitrogen fixation and denitrification to those density surfaces (Gruber and Sarmiento, 1997; Deutsch et al., 2001; Hansell et al., 2004). These interpreted rates of nitrogen fixation in the North Atlantic vary between 0.15 and $3.2 \times 10^{12}$ molN yr$^{-1}$ (Capone et al., 2005). They span a significant range largely due to uncertainties in the volume of water in which elevated $\text{DIN}_{xs}$ may be attributed (Hansell et al., 2004). In addition $\text{DIN}_{xs}$ distribution may also reflect other significant processes including denitrification, net transport of $\text{DIN}_{xs}$ into or out of the domain of interest, as well as differential remineralization of the organic nitrogen and phosphorus.

Denitrification, the oxidation of organic matter consuming nitrate in low oxygen conditions, is probably negligible in the well oxygenated open ocean of the North Atlantic. On the other hand, there is evidence of differential cycling of nitrogen and phosphorus in dissolved organic matter (DOM) (Wu et al., 2000; Clark et al., 1998) and particulate organic matter (POM)
(Kolowith et al., 2001), where phosphorus is remineralized faster than nitrogen. When phosphate-stressed, phytoplankton can produce the enzyme alkaline phosphatase which breaks down dissolved organic phosphorus compounds, providing a source of free phosphate to the cells (e.g. Dyhrman and Palenik, 1999). Moreover, preferential removal and utilization of the more refractory pools of DOP (relative to DON) in the oligotrophic gyres is supported by the relative trends of DOP and DON in the surface waters of the subtropical gyres (Wu et al., 2000; Abell et al., 2000; Mahaffey et al., 2004). These observations indicate a reduction of DOP concentrations moving from the gyre boundary to the interior of both North Pacific and North Atlantic subtropical gyres while surface DON is relatively uniformly distributed. Abell et al. (2000) suggest that the consumption of organic phosphorus in this way may balance the nitrogen source from diazotroph activity. In addition it has been suggested that marine bacteria may take up DOP via a mechanism which has an associated export of inorganic phosphorus, providing a source of organic carbon while helping to maintain C:P stoichiometry when utilizing P-rich DOP compounds (Hoppe and Ulrich, 1999). This transfer mechanism is depressed under phosphate limitation but may operate in the mesopelagic and suggests a mechanism for preferential remineralization of phosphorus at depth (Karl and Björkman, 2002).

In this manuscript we will use a hierarchy of idealized models to investigate three questions arising from observations of *Trichodesmium* and DIN$_{ss}$ in the North Atlantic: Firstly, *Trichodesmium* are observed at significant abundances mostly in the warm, tropical surface waters in the North Atlantic basin (Capone et al., 1997; Tyrrell et al., 2003; Carpenter et al., 2004). They are not as abundant in the most oligotrophic waters where one might expect severe nitrogen limitation of other organisms to provide them with the competitive edge. Secondly, DIN$_{ss}$ has relatively high values at the surface (Fig. 1a) where the nitrogen rich organic matter is
produced and most of it is recycled. However, the basin maximum occurs not there but at depths between 100 and 1000m in the subtropical thermocline (Fig. 1b). Thirdly, time-series observations at the Bermuda Atlantic Time-Series Station (BATS) also show that the temporal variability of DIN$_{z,s}$ is much weaker at the surface than in the thermocline where it varies between 1 and 4 µmol kg$^{-1}$ on annual and longer timescales (Fig. 2; Bates and Hansell, 2004). One might expect quite the opposite, where the surface DIN$_{z,s}$ is closely coupled to any variability in diazotrophy through local remineralization of DOM, and where the integrating effects of accumulation smooth out DIN$_{z,s}$ variations in the thermocline.

In the remainder of this manuscript we seek to understand why these three observed signals do not support our initial expectations and hypotheses. We first develop a simple theory based on the prognostic equation for DIN$_{z,s}$ in a regime appropriate to the North Atlantic, which illustrates the possibly important role of preferential remineralization in regulating the vertical profiles of DIN$_{z,s}$ and its variability. We illustrate that the scalings from the simple model hold true in a more complex, yet still idealized, three-dimensional circulation and biogeochemical model of the North Atlantic. In this model we also find, and explain in terms of phosphorus control, the favored tropical habitat of diazotrophs.

A simple theory of DIN$_{z,s}$ dynamics in the North Atlantic

Generalizing the framework laid out by Gruber and Sarmiento (1997), we describe the development of DIN$_{z,s}$ following a water parcel. We use this framework to ask what the necessary conditions are to maintain a subsurface maximum, as well as a weak temporal
surface variability of DIN$_{xs}$ in the open ocean, North Atlantic regime.

We may describe the changes in phosphate and fixed nitrogen following a water parcel in the North Atlantic as the combined effects of photosynthesis, remineralization and nitrogen fixation, assuming that denitrification and atmospheric sources may be neglected in that region. We represent two broad classes of phytoplankton; diazotrophs, $Tri$, based on knowledge of *Trichodesmium*, and all other phytoplankton, $Phy$. Thus $tp$ and $pp$ are their respective rates of primary production. In this highly idealized view we assume that $Tri$ use dinitrogen gas as their sole source of nitrogen and have relatively high N:P ratios (observed to be between 16 and 125) (Deutsch et al., 2001; Krauk et al., 2006). In contrast we assume that $Phy$ have classical Redfieldian stoichiometry, N:P = 16 (Redfield et al., 1963). Thus the Lagrangian (i.e. following the water parcel) prognostic equations for phosphate ($P$) and fixed nitrogen ($N$) are

$$\frac{dP}{dt} = -(pp + tp) + \lambda_P OP$$

$$\frac{dN}{dt} = -16 pp + \lambda_N ON$$

Here $d/dt = \partial/\partial t + u \cdot \nabla$. We represent unresolved microbial processes by which remineralization of organic matter occurs using a linear decay with simple rate coefficient $\lambda$, and $OP$ (or $ON$) the concentration of organic phosphorus (or nitrogen). Combining (1) and (2) leads to a Lagrangian prognostic expression for DIN$_{xs}$:

$$\frac{dDIN_{xs}}{dt} = 16 tp + \lambda_N ON - 16 \lambda_P OP$$

Thus for the idealized North Atlantic regime, the local development of DIN$_{xs}$ represents ideally a balance between nitrogen fixation, physical transport and remineralization. Nitrogen fixation has two positive effects on DIN$_{xs}$: increasing it directly through the *Trichodesmium* uptake of
phosphate ("16 $tp$" term), or indirectly through the remineralization of high N:P organic matter (because the N:P ratio of $Tri$ is greater than 16). Below the euphotic layer the latter effect dominates.

Why is there a subsurface maximum of DIN$_{xs}$? – To answer this question, we rewrite equation (3) in terms of a source of DIN$_{xs}$ due to the remineralization of N-enriched organic detrital remains of diazotrophs. Here $R > 16$ is the N:P ratio of the N-rich organic matter ($ON:OP$), and $\lambda_P$ and $\lambda_N$ the remineralization rate constants for organic phosphorus and nitrogen respectively:

$$\frac{d\text{DIN}_{xs}}{dt} = 16 \, tp + 16 \lambda_N OP \left( R/16 - \frac{\lambda_P}{\lambda_N} \right) \quad (4)$$

If organic nitrogen and phosphorus are remineralized with equal efficiency, $\lambda_P = \lambda_N$, then we expect the maximum value of DIN$_{xs}$ to occur at the surface where the nitrogen enriched organic matter is produced ($tp > 0$) and where most of it will be remineralized. (We illustrate this situation later in the three dimensional model). If there is preferential remineralization of phosphorus, $\lambda_P/\lambda_N > 1$, a local reduction of DIN$_{xs}$ can occur which damps the signature of diazotrophy at the surface and enriches the relative nitrogen content of the remaining organic matter ($R$ increases). This, in turn enhances the net source of DIN$_{xs}$, $(R/16 - \lambda_P/\lambda_N)$, downstream (in the case of dissolved organic matter) or deeper in the water column (in the case of particulate organic matter). This highly simplified analysis suggests that combination of surface oriented nitrogen fixation and preferential remineralization of phosphorus might lead to a maximum of DIN$_{xs}$ below the surface.

What is the relationship between the relative rates of remineralization and the depth of the DIN$_{xs}$ maximum? We consider the idealized case of a one-dimensional water column below the
euphotic layer where lateral advection can be neglected. Also, for simplicity, we take a system where there is only particulate organic matter ($POP$ and $PON$) which sinks gravitationally to be remineralized at depth. At steady state the system is described by three coupled equations:

\[
\begin{align*}
  w \frac{\partial \text{DIN}_{xs}}{\partial z} &\approx \lambda_N PON - 16\lambda_P POP \quad \text{(5)} \\
  w_s \frac{\partial \text{POP}}{\partial z} &\approx -\lambda_P \text{POP} \quad \text{(6)} \\
  w_s \frac{\partial \text{PON}}{\partial z} &\approx -\lambda_N \text{PON} \quad \text{(7)}
\end{align*}
\]

where $w$ is the vertical flow and $w_s$ the sinking speed of organic particles, positive downward. (The full system of equations is detailed in table 1 developed for the 3D model). $w_s$ should be realistically faster than $w$. (6) and (7) then prescribe an exponential decrease of $POM$ with depth:

\[
\begin{align*}
  \text{POP}(z) &\approx \text{POP}_0 \exp(-\lambda_P z/w_s) , \\
  \text{PON}(z) &\approx \text{PON}_0 \exp(-\lambda_N z/w_s) ,
\end{align*}
\]

where the subscript $0$ indicates the concentration at the base of the euphotic layer. A maximum in $\text{DIN}_{xs}$ occurs where $\partial \text{DIN}_{xs}/\partial z = 0$ and $\partial^2 \text{DIN}_{xs}/\partial z^2 < 0$. The first condition applied to (5) leads to

\[
\lambda_N PON = 16\lambda_P POP \quad \text{(8)}
\]

and the second applied to (6), (7) and the derivative of (5), indicates

\[
\partial^2 \text{DIN}_{xs}/\partial z^2 \approx -(\lambda_N^2/w w_s)PON + 16(\lambda_P^2/w w_s)POP < 0 \quad \text{(9)}
\]

These two results, (8) and (9) combine to give a unique condition for a maximum of $\text{DIN}_{xs}$ with depth:

\[
\frac{\lambda_P - \lambda_N}{w w_s} < 0 .
\]
For this to be true it is necessary to have differential remineralization of N and P to find a maximum of DIN$_{xs}$ (below the surface). With $\lambda_P$ greater than $\lambda_N$ such a maximum occurs, in this highly idealized framework, if the vertical velocity $w$ is negative, i.e. in upwelling regions. The depth of the subsurface maximum is also predicted to be

$$z_{max} \approx \frac{w_s}{\lambda_P - \lambda_N} \ln \left( \frac{16 \lambda_P}{R_0 \lambda_N} \right),$$

where $R_0 = PON_0/POP_0$. For the DIN$_{xs}$ maximum to occur at about 500m depth, with a plausible vertical velocity of about 8 m.d$^{-1}$, N:P $\sim 18$ for exported organic particles and $\lambda_N$ of about 0.01 d$^{-1}$, the phosphorus remineralization rate must be around 10% to 50% greater than that of nitrogen (Fig. 3). At higher $R_0$ ratios the depth of the maximum shoals.

**Why is the temporal variability of DIN$_{xs}$ temporal greater at depth?** – Time-series observations at BATS station show a strong variability of DIN$_{xs}$ in the subtropical thermocline, far exceeding that at the surface, where one would expect a strong coupling to variability in nitrogen fixation and contrary to expectation that the integration of remineralization would damp thermocline signals. However, this observation is also consistent if preferential remineralization of organic phosphorus is significant. Consider again the prognostic expression for DIN$_{xs}$ following a water parcel at the surface, equation (4), and find

$$\frac{\partial\text{DIN}_{xs}}{\partial t} \approx 16tp + 16\lambda_N OP \left( \frac{R}{16} - \frac{\lambda_P}{\lambda_N} \right),$$

here including a local production term, $tp$, due to the uptake of inorganic nutrients by diazotrophs. The observations suggest that a steady state approximation, $\partial/\partial t \sim 0$ may be appropriate at the surface. Hence $tp \approx (\lambda_P/\lambda_N - R/16)\lambda_N OP$; a compensation between the effects of *Trichodesmium* uptake and the remineralization on DIN$_{xs}$. This is possible only if
\( \lambda_P > \lambda_N \), since \( R \geq 16 \) and \( tp > 0 \), suggesting that weak surface variability of DIN\(_{zs}\) is also consistent with a significant role for preferential remineralization.

To summarize, these idealized analytical solutions support the notion that preferential remineralization of phosphorus is an important process in describing DIN\(_{zs}\) distribution in the North Atlantic. It can drive a subsurface maximum of DIN\(_{zs}\) at a depth of up to several hundred meters. Consistently, the simple model is also able to reconcile the increase in variability of DIN\(_{zs}\) with depth in terms of a compensatory effect between differential remineralization of organic matter and the uptake of phosphate by diazotrophs.

However, the analytical model is extremely idealized. In the following sections we illustrate that these predictions and scalings hold true in the more realistic, yet still idealized, context of a three-dimensional model circulation and biogeochemistry model. We go on to use the three-dimensional model to comment on the implications of significant preferential remineralization of phosphorus for estimates of regional nitrogen fixation.

A Basin Scale Model of the Coupled N and P Cycles.

*Circulation* – We configure the MIT ocean circulation model (Marshall et al., 1997a and 1997b) in a coarse resolution, idealized North Atlantic sized basin (described by Follows et al., 2002; 20°S to 72°N, 60° wide at 3°×3° resolution and 15 vertical levels). Here we apply seasonally varying wind stresses and restoring surface boundary conditions for temperature and salinity. Subgrid-scale mixing processes are represented by the Gent and McWilliams (1990) parameterization and boundary layer mixing is represented simply by convective adjustment.
The highly idealized circulation model captures the main large scale physical features of the North Atlantic gyres with plausible density structure, wind driven gyres and ventilated thermocline, and meridional overturning circulation (Figure 4). Due to the closed southern boundary, all deep waters in this idealized basin join the upwelling in the tropics.

**Nutrient cycles** – The ecosystem and biogeochemistry model represents the coupled cycles of nitrogen and phosphorus (Figure 5), including explicit tracers for fixed nitrogen \((N)\), phosphate \((P)\), dissolved organic matter \((DON\) and \(DOP\)) and particulate organic matter \((PON\) and \(POP\)). We do not explicitly represent denitrification assuming a generally well oxygenated basin for the North Atlantic, without a sediment model. Here we describe the effects of denitrification in the wider global ocean by relaxing the \(N\) towards the mean oceanic N:P ratio, i.e. \(14.7 \times P\), in a sponge layer of several gridpoint wide at the Southern boundary of the model domain. This drives an import of “denitrified” waters into the basin as might be envisaged in the North Atlantic. Here we do not specifically represent the iron cycle or the potential effects of iron limitation on diazotrophs. We assume the limit case of an iron replete basin, which is certainly an idealization, but perhaps a reasonable first cut for the Atlantic basin (Sanudo-Wilhelmy et al., 2001; Mills et al., 2004). Finally we do not include the river and atmospheric sources of nitrogen and phosphorus, as we are focusing on the open ocean.

**Ecosystem** – We resolve two classes of phytoplankton; \(Tri\), a diazotroph based on knowledge of *Trichodesmium*, and one "all other" phytoplankton, \(Phy\). \(Tri\) are assumed to fix all their nitrogen and are thus never nitrogen limited. \(Phy\), however may be nitrogen limited, whereas both \(Phy\) and \(Tri\) are subject to phosphate and light limitation. \(Phy\) are again assumed to have classical Redfieldian stoichiometry, \(N:P = 16\), while \(Tri\) higher N:P ratios
We impose a slower intrinsic maximum growth rate for \( Tri \) reflecting the energetic expense of nitrogen fixation (following Tyrrell, 1999 and Hood et al., 2004). Nutrient limitation of growth is parameterized using classical Michaelis-Menten kinetics (MacIsaac and Dugdale, 1969) (Eq. 10 and 11) where the half saturation constant for nitrogen uptake, \( K_N = 16K_P \), the constant for phosphorus uptake. Liebig’s law is used to impose the retardation of growth by the most limiting resource. Hence, under oligotrophic conditions, \( Phy \) are phosphate limited when \( \text{DIN}_{xs} > 0 \), and nitrogen limited when \( \text{DIN}_{xs} < 0 \). We impose a simple, fixed mortality rate, \( M_{Phy} \) and \( M_{Tri} \), for the non-diazotrophs and the \textit{Trichodesmium}, in a highly idealized representation of all loss processes including grazing and other loss mechanisms (Eq. 12 to 17). We assume \( M_{Phy} \) to be greater than \( M_{Tri} \) as has been suggested from observations (Capone et al., 1997). The subsequent detritus is split between a sinking particulate pools, \( PON, POP \), and “semi-labile” dissolved organic pools, \( DON, DOP \), with prescribed lifetimes representing the action of microbial respiration back to inorganic form (\( \lambda_N, \lambda_P \)).

The circulation model was integrated for several thousand years to an equilibrium annual cycle. Biogeochemical integrations and sensitivity studies are all based on this circulation with additional integrations of several hundred years, in which time tracer distributions and model ecology are close to equilibrium. The baseline parameter values used in the "control" integration, as well as ranges of values explored in sensitivity studies, are listed in Table 2.

We will examine the relationship of diazotrophy, nitrogen fixation and \( \text{DIN}_{xs} \) in two cases. First the "control run" where the remineralization rates for organic nitrogen and phosphorus are identical. Then we examine a case where the organic phosphorus remineralization rate exceeds that for nitrogen. The experiments test and illustrate our simpler, analytical model and provide comment on the implications of preferential remineralization for regional nitrogen fixation and its
relationship to tracers such as N*.

Basin-scale Model: Community structure, Nitrogen Fixation and Geochemical Signatures

Despite the idealization of the model configuration, and with equal rates of remineralization for organic nitrogen and phosphorus, the distributions of nutrients and phytoplankton abundance are generally plausible (Figure 6) with an oligotrophic subtropical gyre and a seasonally nutrient replete subpolar gyre. Primary production and the annual mean standing stock of biomass are greater in the subpolar and tropical regions where upwelling supplies nutrients (Fig. 7a) also broadly consistent with observations in the Atlantic basin.

Trichodesmium distribution – Modeled Trichodesmium appear primarily in the tropics (Figure 6) with abundances on the order of $10^{-3} \mu \text{molP.kg}^{-1}$ and maximal values at the Equator. Again this seems generally consistent with observations (Capone et al., 2005). In this highly idealized model, phytoplankton growth is not regulated by temperature, light limitation for both diazotrophs and other phytoplankton are the same, and there is no explicit model of the iron cycle. Hence the biogeography of modeled diazotrophs is mainly regulated by competition for phosphorus. Here, due to the energetic constraint imposed on maximum growth rate, diazotrophs will only be competitive with other phytoplankton when the latter are significantly nitrogen limited which must be in the oligotrophic subtropical or tropical oceans. However, there is also a threshold phosphate concentration below which mortality outstrips growth for diazotrophs and they too are unable to flourish in the very oligotrophic, central subtropical gyre.
of the model. This minimum concentration of phosphate for a *Trichodesmium* growth can be seen from the differential equation $\frac{dT_{tri}}{dt} > 0$ (see Table 1 for the equation), which gives

$$P^{T_{tri}} > \frac{KP}{\mu^{T_{tri}}} \left(\frac{1}{1+K_P} \right) - 1.$$  

Hence the modeled diazotrophs occur close to the tropics, where upwelling waters exceed this threshold and have a relatively low $\text{DIN}_{z,s}$, reflecting the influence of "denitrification" on the model’s deeper waters.

This resource control on diazotrophy in the model can be described more formally in terms of the relative "biological reaction time scales" of diazotrophs and other phytoplankton. Here we define the biological reaction time scale, $\tau$, as the relative rate of change of abundance of organism $X$ due to biological processes; $\tau_B = \frac{1}{X} \left(\frac{dX}{dt}\right)_{bio}$. $\tau_B$ for both can be exactly evaluated in the model and mapping the difference between the reaction time scales of $T_{tri}$ and $P_{hy}$ reveals the areas where *Trichodesmium* is potentially competitive, i.e. its local relative biological production rate is faster than that for other phytoplankton (Figure 7b). In the region where $\tau_{T_{tri}} - \tau_{P_{hy}} > 0$, if advection and mixing were negligible and nutrient patterns static, $T_{tri}$ would eventually dominate the plankton population. The region of positive $\tau_{T_{tri}} - \tau_{P_{hy}}$ covers much of the tropical and subtropical region of the model. The region of significant $T_{tri}$ population is coincident to some extent, but not quite, and nowhere it does dominate the phytoplankton population. Its abundance is typically two orders of magnitude less than that of other phytoplankton. This indicates the importance of the advection of phytoplankton which maintains phytoplankton abundance even in the region where $T_{tri}$ could potentially outcompete them.

**Rate of nitrogen fixation** – Over the whole basin (10°S to 50°N), the nitrogen fixation rate averages 0.03 $\mu$molN.kg$^{-1}$.yr$^{-1}$, equivalent to $0.85 \times 10^{12}$ molN.yr$^{-1}$ or 55 $\mu$molN.m$^{-2}$.d$^{-1}$. This
falls within the lower end of the estimates of nitrogen fixation in the North Atlantic basin diagnosed from observations (Capone et al., 2005) which range between $0.15 - 3.2 \times 10^{12}$ molN yr$^{-1}$ (direct and indirect observations).

**Geochemical signature of nitrogen fixation** – The model's surface DIN$_{xs}$ distribution qualitatively captures the large scale features of the observed North Atlantic with lower (more negative) values in the tropics and subpolar regions, where denitrified waters are supplied to the surface by Ekman suction (Figure 1a). Modeled DIN$_{xs}$ is elevated (Figure 6) in a band crossing the subtropical gyre, from west to east. The surface distribution of DIN$_{xs}$ and *Trichodesmium* are not correspondent (Figure 6). The diazotrophs occur in a narrow band in the tropics, whereas higher DIN$_{xs}$ is in the subtropical gyre, in agreement with both their observed relative distributions in the North Atlantic. In the model this separation reflects two processes: firstly, the advection of nitrogen rich dissolved organic matter from the nitrogen fixing region in the tropics to the subtropical gyre where it is remineralized (as first suggested to these authors by Dennis Hansell, 2000, pers. comm.), and secondly, the "diluting" effect of deeper, denitrified waters in the upwelling tropics.

A meridional section through the model (in the control case) reveals a monotonic decrease of DIN$_{xs}$ with depth. Maximum values occur at the surface of the subtropical gyre. A signature of the surface nitrogen fixation is transported to mid- and high-latitudes where it is ventilated into the thermocline and deep waters (Fig. 8a) and ultimately reduced by mixing with remotely denitrified waters. This contrasts with observed meridional sections in the North Atlantic (Figures 1b and 1c) which also show a signature of ventilation of higher values in deep waters but consistently exhibit a subsurface maximum of DIN$_{xs}$, at depths around 500 m. It is this signal
in the thermocline which has been assumed to reflect diazotrophy and interpreted as a measure
of the basin wide nitrogen fixation rate. Though our model has a broadly realistic representation
of the basin scale circulation and explicit, plausible parameterization of diazotrophs and nitrogen
fixation, it cannot reproduce the subsurface maximum of \( \text{DIN}_{\text{zs}} \). Sensitivity studies reveal the
surface (and not subsurface) maximum of the model to be a very robust result. In the model,
though nitrogen rich \( POM \), produced by \textit{Trichodesmium} in the euphotic zone, sinks into the
thermocline the particle flux decays roughly exponentially with depth (Martin et al., 1987) so the
majority of this organic matter is remineralized in the near surface waters. Thus the excess
nitrogen source is surface oriented in the model creating the a maximum of \( \text{DIN}_{\text{zs}} \) there and not
deeper.

This suggests that a process significant in shaping the distribution of \( \text{DIN}_{\text{zs}} \) is missing in the
control run of the model. This process is probably differential remineralization between nitrogen
and phosphorus, as anticipated by our simple analytical theory. The control run shows that
apparently reasonable rates of nitrogen fixation may be associated without quite different
subsurface patterns of \( \text{DIN}_{\text{zs}} \). In the control run case, most of the new nitrogen from diazotrophy
is remineralized in the surface layers of the ocean and is stirred or advected into the subsurface
leading to a monotonic vertical gradient. This scenario points out that any nitrogen added
directly in the surface of the ocean can not be seen in subsurface \( \text{DIN}_{\text{zs}} \) anomalies. This
suggests then that previous indirect methods based on \( N^* \) or \( \text{DIN}_{\text{zs}} \) might underestimate
nitrogen fixation rates, because they do not consider sources in the surface layers.
The Role of Preferential Remineralization of Phosphorus

Subsurface maximum of DIN_{xs} – In the basin model, we also examine the case when organic phosphorus is remineralized faster than nitrogen, here when \( \lambda_P = 1.5 \lambda_N \) as suggested by the scaling argument. In these circumstances, a subsurface maximum of DIN_{xs} does indeed occur (Fig. 8b; see Table 2 for the other parameters). The DIN_{xs} maximum occurs at about 500m consistent with the analytical model and plausible in the light of the North Atlantic observations. Further sensitivity studies with the numerical model suggest that nitrogen fixation and preferential remineralization are both necessary to account for the observed maximum of DIN_{xs} in the thermocline.

Increased nitrogen fixation and primary productivity – In addition driving the maximum of DIN_{xs} into the thermocline, preferential remineralization of phosphorus also enhances diazotrophy at the surface. Faster remineralization of organic phosphorus in the near surface waters can relieve phosphorus limitation and stimulate further nitrogen fixation. We examine the impact on diazotrophy of a preferential remineralization of phosphorus sufficient to drive a plausible subsurface maximum of DIN_{xs} (Figure 8b). Here \( \lambda_P = 1.5 \lambda_N = 0.045 \text{ d}^{-1} \), and basinwide nitrogen fixation, evaluated directly in the model, is 0.11 \( \mu \text{molN.kg}^{-1}.\text{yr}^{-1} \), equivalent to

\[ 3.80 \times 10^{12} \text{ molN.yr}^{-1} \text{ or } 245 \mu \text{molN.m}^{-2}.\text{d}^{-1}. \]

This is an order of magnitude greater than our control case with equal remineralization rates for N and P. A further consequence of the additional nitrogen fixation is an enhancement of non-diazotrophic production by 26% and an increase in basinwide primary production of 31% (Figure 9).
Underestimation of nitrogen fixation from $N^*$ or DIN$_{xs}$ – Current estimates of basinwide nitrogen fixation rates based on $N^*$ or DIN$_{xs}$ anomalies do not account for other sources of nitrogen in the euphotic layer and for the possibility of preferential remineralization of phosphorus. It is difficult to estimate the undervaluation made by neglecting source of nitrogen fixation occurring directly in the surface, since DIN$_{xs}$ is also controlled there by diazotrophy uptake. However, it is possible to develop an expression of the underestimate made when differential remineralization is not considered. Thus we expect that diagnostics of nitrogen fixation based on observations DIN$_{xs}$ or $N^*$ which do not take this into account might underestimate the integrated diazotrophy. We can describe this relationship again using a simple model derived from equation (3). We consider only the subsurface waters and specify the rate of nitrogen fixation, $J_{NF}$. We distinguish organic matter from $Tri$ and $ Phy$, in order to define $J_{NF} = \lambda_N ON^{Tri}$, where the superscript $Tri$ indicates Trichodesmium. The DIN$_{xs}$ prognostic equation then becomes:

$$\frac{d\text{DIN}_{xs}}{dt} = \lambda_N (ON^{Tri} + ON^{Phy}) - 16\lambda_P (OP^{Tri} + OP^{Phy}).$$

This can be simplified as:

$$\frac{d\text{DIN}_{xs}}{dt} = (\lambda_N - \lambda_P) ON^{Phy} + J_{NF} - 16\lambda_P OP^{Tri}$$

since $ON^{Phy}/OP^{Phy}$ is equal to 16. Factorizing $J_{NF}$ from each term of the right hand side,

$$\frac{d\text{DIN}_{xs}}{dt} = J_{NF} \left( 1 - \frac{\lambda_P}{\lambda_N} \right) \frac{ON^{Phy}}{ON^{Tri}} + J_{NF} - J_{NF} \left( \frac{16}{R^{Tri}} \frac{\lambda_P}{\lambda_N} \right)$$

where $R^{Tri}$ is the N:P ratio of Trichodesmium, $ON^{Tri}/OP^{Tri}$. Assuming now that $ON^{Phy}/ON^{Tri}$ is negligible, meaning that if nitrogen fixation is to occur there should be more organic nitrogen originating from Trichodesmium than from non-diazotrophs, since the former
have a high N:P ratio, we get:

\[
\frac{d\text{DIN}_{xs}}{dt} \approx J_{NF} \left( 1 - \frac{16}{R_{tri} \lambda_N} \right) \Rightarrow J_{NF} \approx \left( \frac{R_{tri}}{R_{tri} - 16 \lambda_P / \lambda_N} \right) \frac{d\text{DIN}_{xs}}{dt}.
\]

Without differential remineralization (\(\lambda_P = \lambda_N\)), the rate of nitrogen fixation is estimated to be:

\[
J_{NF}(\text{equal } \lambda) = \frac{R_{tri}}{(R_{tri} - 16)} \frac{d\text{DIN}_{xs}}{dt}
\]

which is equivalent to the expression of the nitrogen fixation rate described by Gruber and Sarmiento (1997). The ratio between the two estimates shows that when the preferential remineralization of phosphorus is neglected, the inferred rate \(J_{NF}\) is smaller for a given rate of change of \(\text{DIN}_{xs}\). The ratio between the preferential and equal remineralization rate expressions is:

\[
\frac{J_{NF}(\text{equal } \lambda)}{J_{NF}} \approx \frac{1 - \frac{16}{R_{tri} \lambda_P / \lambda_N}}{1 - \frac{16}{R_{tri}}}
\]

\[
\approx 1 + \frac{16}{R_{tri} - 16} \left( 1 - \frac{\lambda_P}{\lambda_N} \right)
\]

\[
\approx 1 - \frac{1}{R_{tri} / 16 - 1} \left( \frac{\lambda_P}{\lambda_N} - 1 \right) \epsilon.
\]

Since \(\lambda_P > \lambda_N\) and \(R_{tri} > 16\), the estimate with equal rate of remineralization underestimates nitrogen fixation by a factor \(\epsilon\). Using averaged values of \(R_{tri} = 30\) and \(\lambda_P / \lambda_N = 1.5\) (suggested by the analytical scalings), we find a difference of \(\epsilon \approx 0.57\), indicating that nitrogen fixation could be underestimated by at least 50% if preferential remineralization is occurring but unaccounted for.

Hence, because we believe that the subsurface maximum of \(\text{DIN}_{xs}\) is attributable to preferential remineralization, we suggest that estimates of nitrogen fixation in the North Atlantic based on \(N^*\) or \(\text{DIN}_{xs}\) could significantly underestimate the actual rate by not accounting for this effect. (Hansell and Bates (2005) discuss other sources of uncertainty which may have the opposite sign).
Conclusion

Here we explore the relationships between nitrogen fixation, preferential remineralization of phosphorus and geochemical tracers such as N* or DIN$_{xs}$, for the North Atlantic region which is known to have a high Trichodesmium activity. We employ highly idealized scaling arguments and a three-dimensional circulation and biogeochemistry model.

In the three-dimensional model, we find that due to phosphorus constraints, the modeled Trichodesmium inhabit only the tropics, with a concentration averaging $10^{-3}$-$10^{-2}$ µmol.kg$^{-1}$. Moreover, we learn neither the observed subsurface maximum of DIN$_{zs}$ nor the observed subsurface increase in its temporal variability can be explained by nitrogen fixation alone, but are both easily reconciled if preferential remineralization of phosphorus is occurring. Analytical as well as numerical solutions confirm these two ideas.

Finally and interestingly, our simplified three dimensional model exhibits a basin wide rate of nitrogen fixation between $0.85$-$3.80 \times 10^{12}$ molN.yr$^{-1}$ depending on whether the remineralization rates of organic nitrogen and phosphorus are different. Both end-members fall within the range of direct and indirect estimates based on ocean observations ($0.15$-$3.2 \times 10^{12}$ molN.yr$^{-1}$; Capone et al., 2005). We suggest that if the process of differential remineralization is not taken into account, indirect estimates of nitrogen fixation developed from N* or DIN$_{zs}$ would lead to an underestimation of regional nitrogen fixation rates by as much as a factor of two, all else being equal.
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Table 1: Prognostic equations of the model. $\mu^\text{Phy}$ and $\mu^\text{Tri}$ are maximum specific growth rates of the non-diazotroph and diazotroph phytoplankton ($\text{Phy}$ and $\text{Tri}$) respectively. $I$ is the light intensity. $K_I$, $K_P$ and $K_N$ are half saturation constants for light, phosphate and fixed nitrogen, with $K_N = 16K_P$. $pp$ and $tp$ are the rates of photosynthesis, and $M^\text{Phy}$ and $M^\text{Tri}$ the mortality rates, both for $\text{Phy}$ and $\text{Tri}$ respectively. $R^\text{Phy}$ and $R^\text{Tri}$ impose the fixed N:P stoichiometry of $\text{Phy}$ (the classical Redfield ratio, 16) and $\text{Tri}$ (>16). $f_{\text{POM}}$ is the fraction of detritus partitioned into the POM pool, the rest going into DOM. $w_s$ is the sinking rate of the POM. Nitrogen is restored at the South wall to a DIN$_{xs}$ equal to the local mean oceanic DIN$_{xs}$ (=3) with a relatively fast time scale (=1 yr).

\[
\frac{d\text{Phy}}{dt} = \mu^\text{Phy} \frac{I}{I + K_I} \times \min\left\{ \frac{P}{P + K_P} : \frac{N}{N + K_N} \right\} \text{Phy} - M^\text{Phy} \text{Phy}
\]

\[
\frac{dTri}{dt} = \mu^\text{Tri} \frac{I}{I + K_I} \times \frac{P}{P + K_P} \text{Tri} - M^\text{Tri} \text{Tri}
\]

\[
\frac{dP}{dt} = - (pp + tp) + \lambda_P \left( \text{DOP + POP} \right)
\]

\[
\frac{dN}{dt} = -R^\text{Phy} pp + \lambda_N \left( \text{DON + PON} \right)
\]

\[
\frac{d\text{DOP}}{dt} = (1 - f_{\text{POM}}) (M^\text{Phy} \text{Phy} + M^\text{Tri} \text{Tri}) - \lambda_P \text{DOP}
\]

\[
\frac{d\text{DON}}{dt} = (1 - f_{\text{POM}}) (R^\text{Phy} M^\text{Phy} \text{Phy} + R^\text{Tri} M^\text{Tri} \text{Tri}) - \lambda_N \text{DON}
\]

\[
\frac{d\text{POP}}{dt} = -w_s \frac{\partial \text{POP}}{\partial z} + f_{\text{POM}} (M^\text{Phy} \text{Phy} + M^\text{Tri} \text{Tri}) - \lambda_P \text{POP}
\]

\[
\frac{d\text{DON}}{dt} = -w_s \frac{\partial \text{PON}}{\partial z} + f_{\text{POM}} (R^\text{Phy} M^\text{Phy} \text{Phy} + R^\text{Tri} M^\text{Tri} \text{Tri}) - \lambda_N \text{PON}
\]
Table 2: Parameter values for the control case model integration. The sponge layer of denitrification is 100 km wide, over the all column and with a relaxing timescale of a year. (a) Deutsch et al. (2001), (b) Tyrrell (1999); Dutkiewicz et al. (2001); Hood et al. (2001); Fennel et al. (2002), (c) Capone et al. (1997), (d) Libes (1992).

<table>
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<th>Symbol</th>
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<td>0.006-0.15&lt;sup&gt;b&lt;/sup&gt;</td>
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(a) Surface DIN$_{xs}$

(b) DIN$_{xs}$ section along the transect A20.

Figure 1:
Figure 2:
With $R_o = [16.5:30]$ and $\lambda/\lambda_N = 0.02 \, d^{-1}$

$R_o = 16.5$

$R_o = 30$

With $R_o = [16.5:30]$ and $\lambda/\lambda_N = 1.5$

$R_o = 16.5$

$R_o = 30$

Figure 3:
Figure 4:
Figure 5:
Figure 6:
Figure 7:
Figure 8:
Figure 9: