

A new perspective on environmental controls of marine nitrogen fixation

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Growing slowly, marine N_2 fixers are generally expected to be competitive only where nitrogen (N) supply is low relative to that of phosphorus (P) with respect to the cellular N:P ratio (R) of non-fixing phytoplankton. This is at odds with observed high N_2 fixation rates in the oligotrophic North Atlantic where the ratio of nutrients supplied to the surface is elevated in N relative to the average R (16:1). In this study, we investigate several mechanisms to solve this puzzle: iron limitation, phosphorus enhancement by preferential remineralization or stoichiometric diversity of phytoplankton, and dissolved organic phosphorus (DOP) utilization. Combining resource competition theory and a global coupled ecosystem-circulation model we find that the additional N and energy investments required for exo-enzymatic break-down of DOP gives N_2 fixers a competitive advantage in oligotrophic P-starved regions. Accounting for this mechanism expands the ecological niche of N_2 -fixers also to regions where the nutrient supply is high in N relative to R, yielding, in our model, a pattern consistent with the observed high N_2 -fixation rates in the oligotrophic North Atlantic.

1. Introduction

Nitrogen fixation is essential for maintaining the marine fixed nitrogen (N) inventory which regulates ocean productivity. In spite of its importance, environmental controls of marine N₂ fixation are not well understood. Nutrient requirements and the ability to compete for limiting nutrients strongly affect the regional distribution of different phytoplankton functional types in the ocean [Tilman, 1980; Dutkiewicz *et al.*, 2012; Ward *et al.*, 2013]. N₂ fixers are not limited by dissolved inorganic nitrogen such as nitrate and ammonium because they can utilise the abundant N₂, albeit at a high energetic cost. When considering competition for N and P, resource competition theory [Tilman, 1980; Ward *et al.*, 2013] predicts that, in steady state systems, P-limited N₂ fixers may coexist with N-limited non-fixing phytoplankton only where the N supply is low relative to the supply of P with respect to the cellular N:P ratio of non-fixing phytoplankton (R)(Fig. 1a, $N:P_{supply} < R$), i.e., where positive P*, defined as $P^* = PO_4^{3-} - NO_3^- / R$, is supplied. As N₂ fixers grow and add N to the system they consume P* thus narrowing their own niche (Fig. 1a, reduce α). Then, why do N₂ fixers successfully compete and exhibit high rates of N₂ fixation in the oligotrophic North Atlantic (Fig. 2a) [Capone *et al.*, 2005; Großkopf *et al.*, 2012; Luo *et al.*, 2012] where, the nutrient supply is high in N relative to R? Here, the ratio of nutrients supplied to the euphotic zone, from the thermocline [Gruber and Sarmiento, 1997] and from atmospheric deposition [Krishnamurthy *et al.*, 2009], is well above the average R (N:P=16), and the estimated P* flux [Palter *et al.*, 2011] is not sufficient to fuel N₂ fixation observational estimates (≥ 20 Tg N yr⁻¹, Table 1). N₂ fixers have a high iron requirement [Kustka *et al.*, 2003] and the high aeolian iron inputs into

the North Atlantic [*Mahowald et al.*, 2005] are thought to favour N₂ fixation there [*Moore et al.*, 2009; *Schlosser et al.*, 2014]. Preferential remineralization of phosphorus [*Landolfi et al.*, 2008] and the utilisation of dissolved organic phosphorus (DOP) by diazotrophs [*Dyhrman et al.*, 2006; *Sohm and Capone*, 2006] have also been suggested to support N₂ fixation in the North Atlantic [*Coles and Hood*, 2007]. The ability to competitively hydrolyse semilabile DOP [*Sohm et al.*, 2008; *Orchard, et al.*, 2010; *Orcutt, et al.*, 2013] and access the more refractory phosphonates [*Dyhrman et al.*, 2006] may be the key to diazotrophs's success in P-depleted environments. P depletion demands greater N investments into nutrient uptake machinery (eg. enzymes that, being proteins, contain N and little P) at the expense of cell growth [*Klausmeier et al.*, 2004]. Diazotrophs' unlimited access to N₂ may hence explain their competitive ability to exploit the DOP reservoir better than non-fixing phytoplankton. Such a mechanism has been suggested to explain the occurrence of N₂ fixing plants in phosphorus-limited terrestrial ecosystems [*Houlton et al.*, 2008].

Using both resource competition theory and a three-dimensional global biogeochemical circulation model we investigate how the above factors affect the distribution of modelled N₂ fixation and assess mechanisms capable of expanding the ecological niche of N₂ fixers in a way to allow N₂-fixation in the P-starved oligotrophic North Atlantic.

2. Methods

The global ocean circulation model employed is based on MOM4, CM2.1 setup [*Gnanadesikan et al.*, 2006], configured on a 3° x 2° grid, forced by monthly heat, freshwater fluxes and wind fields taken from the climatological dataset of the Coordinated

Ocean Reference Experiments (CORE) [Large and Yeager, 2004]. Initial annual mean temperature and salinity are from the World Ocean Atlas [Conkright et al., 2002]. The circulation model is coupled online to a modified version of the NPZD-type ecosystem model of Schmittner et al. (2008) as described in Landolfi et al. [2013] initialized with observed nutrient and oxygen distributions [Conkright et al., 2002]. Briefly, the ecosystem model (details in Supp. Information) has 10 prognostic variables: dissolved oxygen, nitrate, phosphate, non-nitrogen-fixing phytoplankton, nitrogen-fixing phytoplankton (diazotrophs), zooplankton and particulate phosphorus and nitrogen detritus. The experiments DOPU and COST (see below) additionally feature semi-labile dissolved organic phosphorus and nitrogen. Water column denitrification is parameterized as a function of modeled oxygen concentrations. Benthic denitrification (BD) is not explicitly accounted for in our current model that does not resolve continental shelves. Fixing and non-fixing phytoplankton growth has a temperature dependence and is limited by light. Non-fixing phytoplankton is limited by PO_4^{3-} and NO_3^- using a Liebig-type limitation function. Diazotrophs are limited by PO_4^{3-} concentrations, but can also take up NO_3^- . The maximum growth rate of diazotrophs is lower than that of non-fixing phytoplankton. To explicitly account for the additional energetic expenditure on Fe-scavenging, the growth of both phytoplankton types can be further limited by an Fe-limitation factor. Model simulations are restricted to 150 years to limit model drift from observed nutrient and oxygen distributions. The results shown are from model year 150.

We conduct five model experiments: (1) PCOMP, where diazotrophs and non-fixing phytoplankton compete for PO_4^{3-} is our simplest model configuration with no iron lim-

itation and no DOM dynamics. (2) In experiment FELIM diazotrophs and non-fixing phytoplankton growth rates are reduced by a moderate (MEDIUM, Fig. S1c, d), spatially and seasonally varying, iron limitation factor. Sensitivities to different degrees of iron limitation (LOW and HIGH) have been carried out and are described in Suppl. Information. (3) In experiment PREF the particulate phosphorus remineralization rate is doubled in the top 143m. (4) In experiment DOPU growth rates of both diazotrophs and non-fixing phytoplankton are reduced by a moderate iron limitation factor (Fig. S1c, d) and diazotrophs can take up DOP as an alternative P source at no additional cost. (5) Experiment COST differs from experiment DOPU in that DOP uptake is associated with additional energy and N requirement, which apply to both non-fixing phytoplankton and diazotrophs. The extra energetic cost results in a 60% lower maximum growth rate relative to the DOPU run. The additional N-requirement is such that for every P atom the N:P uptake ratio is 1.5 times the cellular N:P (16:1). The N taken up in excess of the cellular N requirement is released instantaneously as DON. The sensitivity of the results to different assumptions about costs in terms of N and energy is investigated and described in the Supplementary Information.

3. Results and Discussions

When competing for PO_4^{3-} in our model experiment PCOMP, N_2 fixers are outcompeted by non-fixing phytoplankton in the North Atlantic (Fig. 2b) where simulated N_2 fixation is low (1.5 Tg N yr^{-1} , Table 1) because of phosphate limitation (Fig. S2a). The major share (78%) of the simulated global N_2 fixation (91 Tg N yr^{-1}) occurs in waters of elevated P^* upwelling from oxygen minimum zones (OMZs) of the eastern equatorial

Pacific. This is in line with the theoretical prediction [Tilman, 1980] and marine biogeochemical studies [Redfield *et al.*, 1963; Tyrrel, 1999; Deutsch *et al.*, 2007], which lead to suggest that marine N₂ fixation is spatially associated with sources of elevated P* caused by denitrification [Deutsch *et al.*, 2007]. However, the simulated low P* supply in the oligotrophic North Atlantic cannot support the N₂ fixation hotspot as observed in this region (Fig. 2a, 3b). Additional surface P* may be provided by benthic denitrification (BD). However, models including this process suggest BD does not contribute to fostering N₂ fixation in the oligotrophic North Atlantic [Weber and Deutsch, 2012]. This is consistent with observational estimates of relatively low rates of North Atlantic BD [DeVries *et al.*, 2013] and resulting P* supply [Palter *et al.*, 2011].

Taking the regional distribution of iron limitation into account in experiment FELIM, we find that iron limitation contributes to the accumulation (Fig. S3a) and transport of P* (Fig. 3c) from the OMZ-associated upwelling regions into non-iron limited waters, where it helps to reduce phosphate limitation of N₂ fixers (Fig. S2b). When increasing the strength of iron limitation, global N₂ fixation is reduced, but regionally N₂ fixation increases in relatively iron-rich regions such as the North Atlantic (Fig. 4a). The advective and vertical P* supply to the surface (Fig. 3c, d) remains, however, insufficient to support observed levels of N₂ fixation in the tropical and subtropical North Atlantic (Fig. 2a,c, Table 1).

Enhancing the availability of PO₄³⁻ by doubling the remineralization rate of organic phosphorus to PO₄³⁻ in experiment PREF, augments surface P* (Fig. S3b) and thereby global N₂ fixation rate (302 Tg N yr⁻¹, Table 1, Fig. 2d). However, as P* fluxes to the

surface oligotrophic (0-30° N) North Atlantic remain low (Fig. 3c, d), only 4% of the global N₂ fixation is simulated to occur in this region, still much less than observational estimates suggest (20%, Table 1). PO₄³⁻ availability may be enhanced also by stoichiometric diversity of non-fixing phytoplankton, which has been shown to expand the niche of N₂ fixers on a global scale [Weber and Deutsch, 2012]. A high cellular N requirement (large R) of non-fixing phytoplankton enlarges the region of N:P_{supply} < R, (high P* supply) (Fig. 1a, larger α). We account for stoichiometric diversity in model experiment, nonRR, implementing two non-fixing phytoplankton types which differ in their maximum growth rates and in their N:P ratios, R=20 and R=9 respectively (Table S1) consistent with the stoichiometric plasticity of, resource-limited and slow growing, and resource-replete and fast growing, phytoplankton, respectively [Klausmeier et al., 2004; Mills and Arrigo, 2010; Weber and Deutsch, 2012]. In experiment nonRR we find that the enhanced P* supply (Fig. S4) is still insufficient to explain the observed patterns of Atlantic N₂ fixation (Fig. 2a, 3b), in agreement with previous studies (Weber and Deutsch, 2012, their supplementary figure S2a,b).

Allowing for DOP-uptake by N₂ fixers in experiment DOPU reduces their region of P-limitation (Fig. S2d) to the core of the subtropical gyres where modeled DOP concentrations are low (Fig. S5b). The simulated global N₂ fixation (170 Tg N yr⁻¹, Fig. 2e, Table 1) doubles compared to the simulation FELIM which does not include DOP dynamics. The largest increase occurs in the Pacific Ocean which contributes 65% to global N₂ fixation. Total P* fluxes to the surface oligotrophic North Atlantic (Fig. 3c, d) support 12 Tg N yr⁻¹, 7% of the global N₂ fixation. However, the simulated distribution

of N_2 fixation in the Atlantic Ocean does not match the observed latitudinal gradient (Fig. 3b).

All mechanisms tested so far in our global model cannot maintain sufficient P^* and DOP supply to support the elevated levels of N_2 fixation in the oligotrophic North Atlantic. To test a N-intensive DOP breakdown strategy [Houlton *et al.*, 2008] we account for the additional N and energy costs associated with exo-enzymatic DOP breakdown by introducing an additional N demand and lower growth rates. We first apply resource competition theory (Fig. 1). The extra N demand for the synthesis of extracellular enzymes requires N uptake in excess of the non-fixing phytoplankton's N:P ratio R (Fig. 1b, black arrow, slope $> R$). We find that, while N_2 -fixers can easily satisfy the extra N demand, non-fixing phytoplankton become more N limited (Fig. 1b, grey arrow). This expands the ecological niche of N_2 fixers into regions where $N:P_{supply} > R$ (Fig. 1b, β ; details in Suppl. Information, Section 2). We now account for the costs for DOP-breakdown in our three-dimensional global biogeochemical circulation model experiment COST. The additional N cost is simulated such that N demand exceeds the cellular N requirement by 50% resulting in N:P uptake ratio of 24:1. The associated energetic cost is simulated such that growth rate is reduced by 60% (see Suppl. Information for details). Accounting for these trade-offs, N_2 fixation is stimulated in the tropical regions of the North Atlantic (Fig. 2f) reaching 35 Tg N yr^{-1} , which is about 25% of the global N_2 -fixation (134 Tg N yr^{-1} , Table 1). The additional energetic and N cost lead to a reduction of DOP-supported growth in waters above oxygen minimum zones reducing in turn particulate organic matter export, denitrification and the associated P^* resupply [Landolfi *et al.*, 2013]. We investigated

the sensitivity of our results to variations of the N and energetic costs (details in Suppl. Information, Section 1) and find that increasing these costs further, enhances N₂ fixation in the North Atlantic and increases the contribution of the North Atlantic to global N₂ fixation (Fig. 4b). Too high energetic costs (80% reduction of the growth rates), however, reduce the importance of DOP uptake as an alternative P source (Fig. 4b). N₂ fixation simulated by our model is thus sensitive to the associated metabolic costs. Yet, the inferred regional distribution of N₂ fixation appears robust in our model (Fig. 4b, Table 1). The expansion of the niche of N₂ fixers into regions of low P* supply (Fig. 3c) is possible as long as the N cost for DOP uptake is greater than the direct N supply by N₂ fixers (Suppl. Information equ. 25), such that, non-fixing phytoplankton growth remains limited by NO₃⁻. In experiment COST the additional costs for DOP uptake relative to PO₄³⁻ uptake inhibit DOP-uptake when PO₄³⁻ is available. Growth of both diazotrophs and non-fixing phytoplankton on DOP occurs in regions where DOP is a large fraction of the total dissolved phosphorus pool (>80%, Fig. S5h, Fig. S6). This occurs in the oligotrophic, Fe-abundant, North Atlantic. In Fe-limited regions, the consumption of PO₄³⁻ and DOP is reduced because of Fe limitation. As a result, these nutrients can be transported from Fe-deplete into Fe-abundant regions (Fig. 3c), where they can then fuel biological consumption by both diazotrophs and non-fixing phytoplankton. DOP is consumed, however, depending on phytoplankton's ability to cover the extra N costs associated with DOP uptake.

4. Conclusions

Our results offer a new perspective on the environmental controls of marine N₂ fixers. The competitive success of the slower-growing diazotrophs is generally associated with regions of N-deficiency and of elevated P* supply, where the growth of their faster-growing competitors is suppressed. Here we show that diazotrophs can have a competitive advantage also in regions that are N-rich relative to the cellular needs (R) of their faster-growing competitors. The additional energy and N costs associated with the enzyme-mediated hydrolysis of DOP favour N₂ fixers competitive success in PO₄³⁻-starved regions. This strategy can explain the puzzling persistence of marine N₂ fixers in regions where estimated P* fluxes [Palter *et al.*, 2011] are insufficient to support observation-based N₂ fixation estimates. A N-intensive strategy for P acquisition in oligotrophic systems may also explain the widespread N-limitation of phytoplankton [Moore *et al.*, 2013] as deduced from nutrient addition assays. Even in PO₄³⁻-starved systems experimental PO₄³⁻ addition fails to stimulate phytoplankton growth while N addition does [Tanaka *et al.*, 2011]. The addition of N is found to induce enzyme activity related to DOP-hydrolysis [Tanaka *et al.*, 2011; Mahaffey *et al.*, 2014], suggesting a N-intensive strategy for P-acquisition that ought to be explored. In our simulations Fe-limitation prevents complete P consumption in Fe-limited regions and thereby allows a net transport of DOP and PO₄³⁻ into more Fe-replete regions where they may be consumed. Our findings suggest that global patterns of iron supply facilitate the potential for enhanced diazotrophy within the oligotrophic North Atlantic, while the additional nitrogen and energetic costs associated with DOP hydrolysis, provide diazotrophs with a competitive advantage for P in this relatively N-

rich region. Understanding the factors regulating the distribution of marine N₂ fixation is essential if we are to predict changes in the oceanic N inventory.

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Table 1: Observed, biogeochemical and modelled global and regional N_2 fixation estimates ($TgNy^{-1}$). *Areal rate extrapolated to the oligotrophic North Atlantic region ($25 \times 10^6 km^2$). ^aCompilation of observational data. ^bGeochemical estimate based on diazotrophic N:P of 125:1. ^cModel-based geochemical estimate. ^dGyre-integrated rate estimated from excess phosphate supply. Numbers in brackets are the mean \pm SD of sensitivity experiments FELIM with varying iron-limitation, and COST with varying energetic (growth rate) and fixed N (1.5 fold) costs.

Reference	Global ($TgNy^{-1}$)	Pacific ($TgNy^{-1}$)	Indian ($TgNy^{-1}$)	Atlantic ($TgNy^{-1}$)	NA ($TgNy^{-1}$)	NA-Lat. °N
Luo et al. 2012 ^a	137 \pm 9	102 \pm 20	-	34 \pm 7	27*	0-30
Gruber and Sarmiento 1997 ^b	110 \pm 40	-	-	-	25*	0-30
Deutsch et al. 2007 ^c	137	95	22	20	8*	0-30
Palter et al. 2011 ^d	-	-	-	-	4.6-5.5	-
This Study Model Experiment						
PCOMP	91	71	13	7	1.5	0-30
FELIM	85(83 \pm 7)	65(61 \pm 8)	12(11 \pm 0.6)	8(7.3 \pm 0.2)	2.5(2.2 \pm 0.5)	0-30
PREF	302	210	39	53	11	0-30
DOPU	170	110	25	35	12	0-30
COST	134(198 \pm 106)	56(106 \pm 68)	40(48 \pm 24)	39(42 \pm 22)	35(23 \pm 12)	0-30

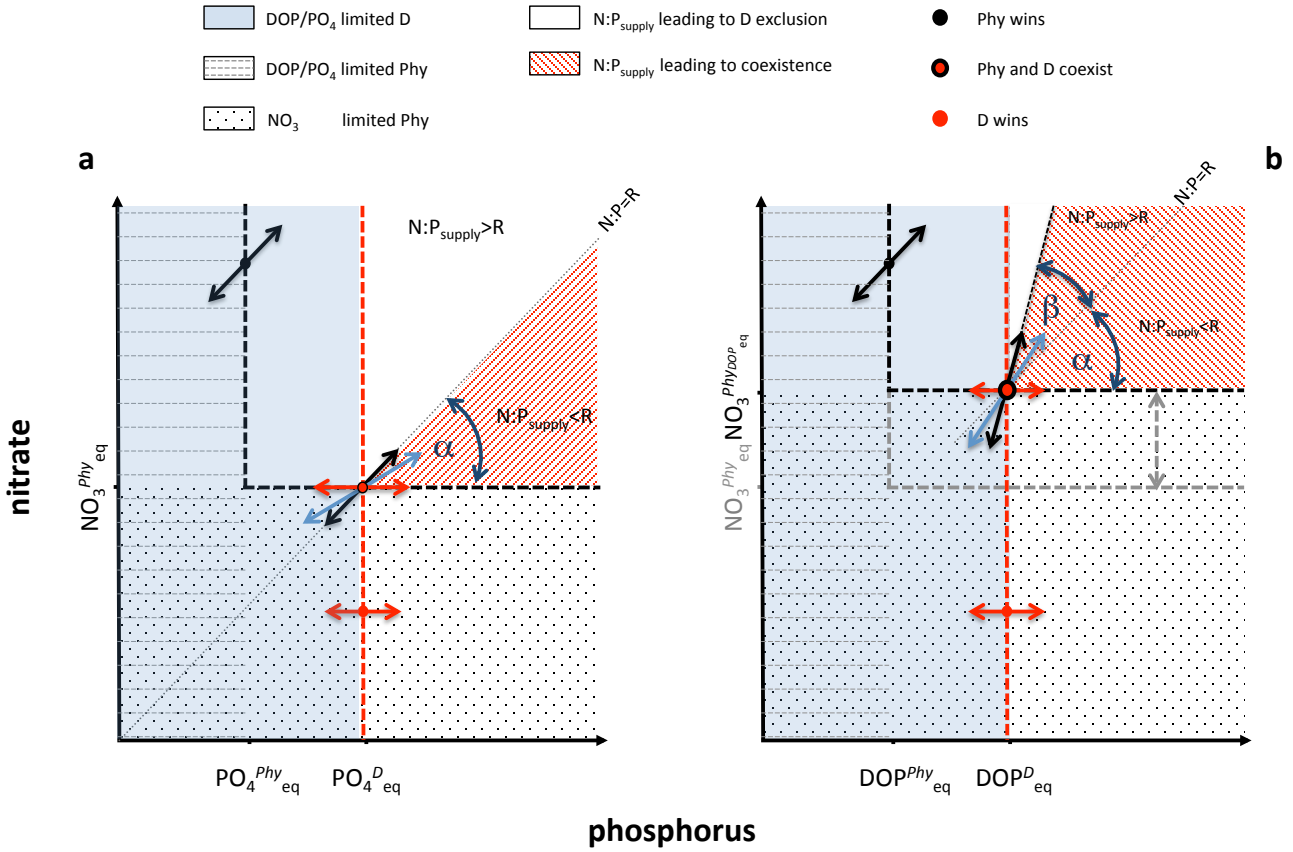


Figure 1: Illustration of the resource competition theory [Tilman, 1980]. Non-fixing phytoplankton (Phy, black) and diazotrophs (D, red) grow drawing down nutrient concentrations to their equilibrium nutrient requirements (NO_{3eq} , PO_{4eq} and DOP_{eq}) reaching steady state (growth balanced by mortality) on the zero net growth isoclines (ZNGI, black and red dashed lines). If nutrient concentrations are drawn below the algae equilibrium requirement, their growth is limited by nutrient availability (shaded areas) and the algae will be competitively excluded (mortality > growth). Stable coexistence (red-dot-black-circle) of Phy and D occurs at the interception of the ZNGIs where the growth of Phy is limited by NO_3 and that of D is limited by PO_4 . (a) Phy consume resources (black arrow) in their cellular (R) proportions (i.e. following the slope of the thin black-dotted line $N:P=R$, where R can differ from 16:1).

Figure 1: cont. D consume only phosphate (red arrow). Blue arrows pointing towards the axis origin are the total nitrate and phosphate consumption vectors that, at steady state, are balanced by the nutrient supply vectors (pointing away from the axis origin). For $N:P_{supply} < R$, i.e. region α , nitrate concentrations will be drawn down to $NO_3^{Phy}_{eq}$ by Phy and phosphate to $PO_4^{D}_{eq}$ by D leading to the stable coexistence (red-dot-black-circle). The larger the R , the larger is the coexistence region (larger α). For $N:P_{supply} > R$ both species are limited by PO_4 , and Phy, with the lowest PO_4_{eq} , reduce phosphate concentrations too low for the survival of D (black dot). D outcompete Phy where nitrate concentrations are too low to meet $NO_3^{Phy}_{eq}$ (red dot). **(b)** When accounting for the extra energetic and N cost for DOP uptake, Phy require higher nitrate at equilibrium ($NO_3^{Phy_{dop}_{equ}} > NO_3^{Phy}_{equ}$, grey arrow) increasing the nitrate-limited growth area (dotted area) and consume nitrate (black arrow) in proportions exceeding R . The region of coexistence becomes larger ($\alpha + \beta$) and D can survive also for $N:P_{supply} > R$ (β). Details in Suppl. Information.

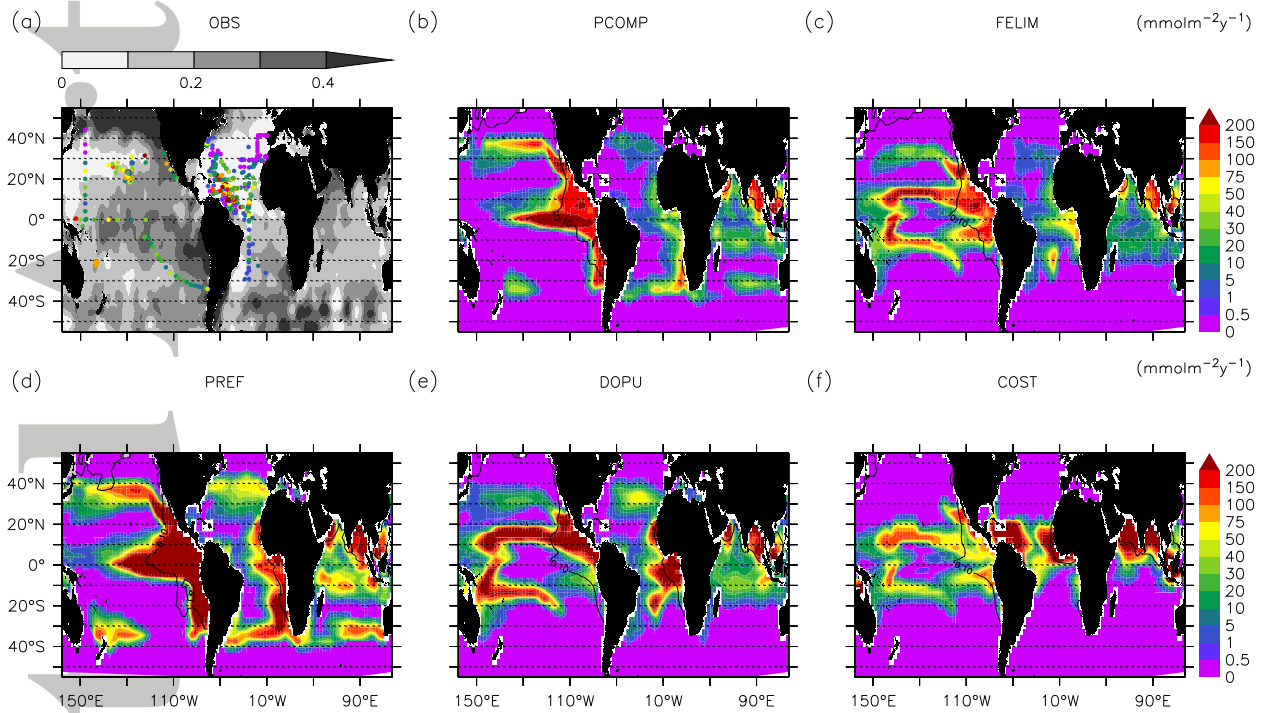


Figure 2: Observed [Luo *et al.*, 2012] N_2 fixation ($\text{mmol N m}^{-2} \text{yr}^{-1}$; coloured dots) and P^* surface distribution (mmol P m^{-3} ; grey shade) based on climatological data [Conkright *et al.*, 2002] (a). N_2 fixation rates ($\text{mmol N m}^{-2} \text{yr}^{-1}$) from PCOMP (b), FELIM (c), PREF (d), DOPU (e) and COST (f) simulations. Black contours represent the $0.1 \text{ mol N m}^{-2} \text{yr}^{-1}$ denitrification isoline.

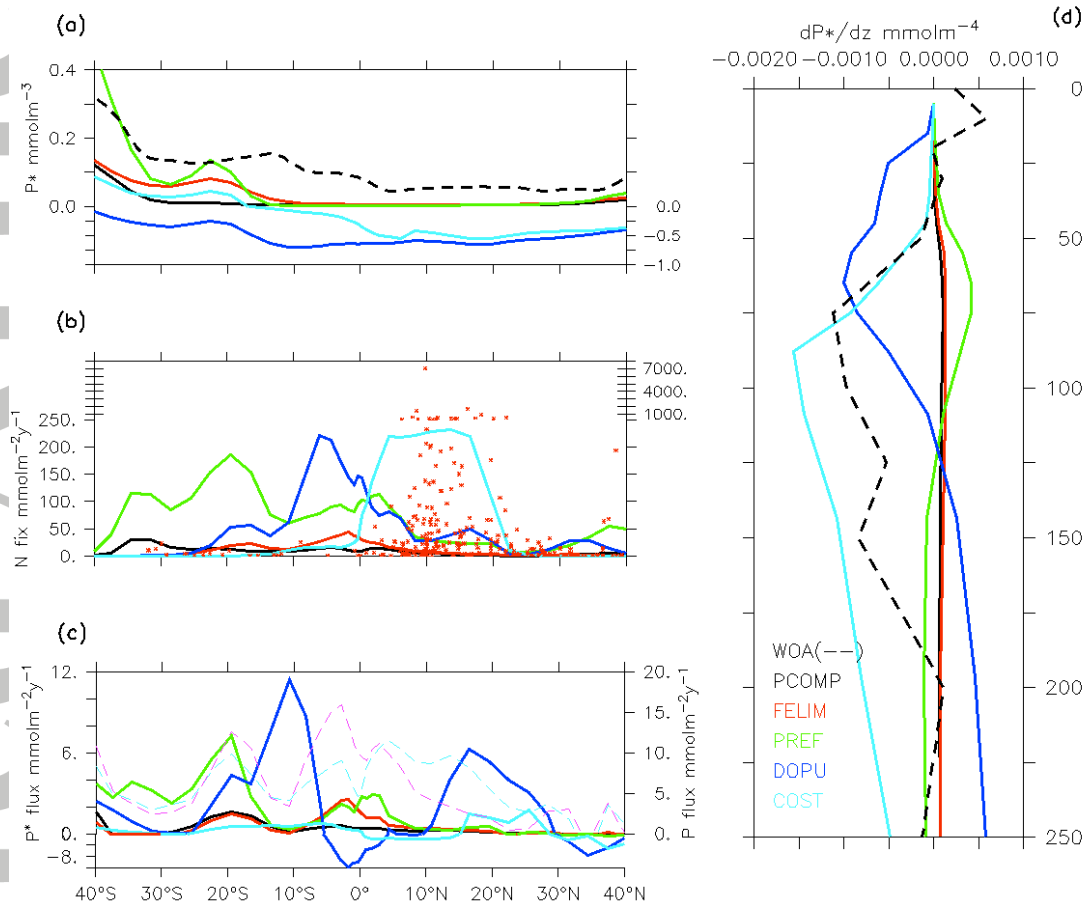


Figure 3: Atlantic Ocean zonal average of climatological (dash) [Conkright *et al.*, 2002] and simulated surface P^* (mmol P m^{-3}) (a), Observed (red star) [Luo *et al.*, 2012] and zonal average of simulated N_2 fixation ($\text{mmol N m}^{-2} \text{yr}^{-1}$) (b), Zonal average of simulated P^* (solid lines, left y-axis) and TP ($\text{PO}_4^{3-} + \text{DOP}$) (dashed lines, right y-axis) advective flux ($\text{mmol P m}^{-2} \text{yr}^{-1}$). Pink line represents the COST simulation without the Fe limitation constrain (c). Please note broken y-axes in (a-c), labels are given on left and right side of the panels, respectively. North Atlantic average (0-30°N) climatological and simulated vertical P^* gradient (d).

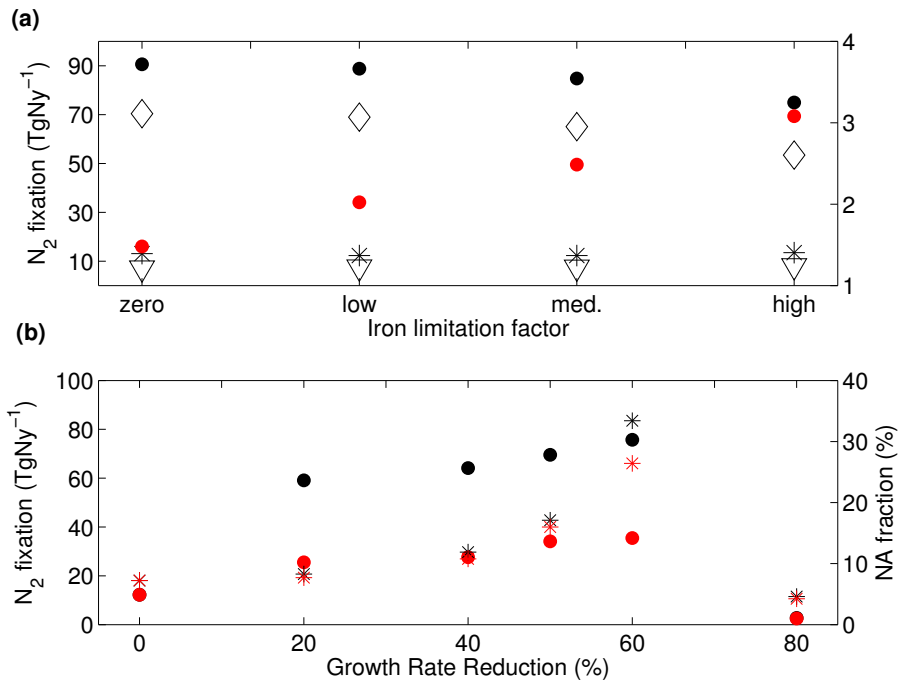


Figure 4: Global and basin N_2 fixation rate ($TgNy^{-1}$) as a function of iron limitation factor in the FELIM experiment with the respective LOW, MEDIUM, HIGH iron limitation factors. Zero corresponds to PCOMP experiment. ●=Global; ◇=Pacific; ★=Indian; ▽= Atlantic; ●=North Atlantic (NA) ($0-30^\circ N$). The 2nd y-axis is for North Atlantic data (and has the same units as the 1st y-axis) (a). NA N_2 fixation rate ($TgNy^{-1}$) as a function of growth rate reduction for a 1.5 fold (●) and 2.5 fold (●) increase in the N cost in COST, and its percent contribution (*), (*) to global N_2 fixation from the same experiments (b).