

Magnitude of oceanic nitrogen fixation influenced by the nutrient uptake ratio of phytoplankton

Matthew M. Mills* and Kevin R. Arrigo

The elemental stoichiometry of sea water and particulate organic matter is remarkably similar. This observation led Redfield to hypothesize that the oceanic ratio of nitrate to phosphate is controlled by the remineralization of phytoplankton biomass¹. The Redfield ratio is used universally to quantitatively link the marine nitrogen and phosphorus cycles in numerous biogeochemical applications^{2–4}. Yet, empirical and theoretical studies show that the ratio of nitrogen to phosphorus in phytoplankton varies greatly with taxa^{5,6} and growth conditions^{7–9}. Here we present a dynamic five-box ecosystem model showing that non-Redfield utilization of dissolved nitrogen and phosphorus by non-nitrogen-fixing phytoplankton controls the magnitude and distribution of nitrogen fixation. In our simulations, systems dominated by rapidly growing phytoplankton with low nitrogen to phosphorus uptake ratios reduce the phosphorus available for nitrogen fixation. In contrast, in systems dominated by slow-growing phytoplankton with high nitrogen to phosphorus uptake ratios nitrogen deficits are enhanced, and nitrogen fixation is promoted. We show that estimates of nitrogen fixation are up to fourfold too high when non-Redfield uptake stoichiometries are ignored. We suggest that the relative abundance of fast- and slow-growing phytoplankton controls the amount of new nitrogen added to the ocean.

The notion of a constant nitrogen/phosphorus ratio for both phytoplankton and the deep ocean shapes our current understanding of the balance between nitrogen and phosphorus inventories in the ocean. In this framework, processes that remove oceanic fixed nitrogen (for example, denitrification) and drive the nitrate/phosphate ratio from the canonical Redfield ratio are approximately balanced by nitrogen inputs, primarily from nitrogen fixation^{3,10}. However, field and laboratory data confirm that non-Redfield nutrient utilization is common in phytoplankton, with N/P utilization ratios being below Redfield during blooms^{6,9} and above Redfield in oligotrophic regions dominated by cyanobacteria^{8,9} (including non-diazotrophs). One explanation for this N/P plasticity is that fast-growing cells require abundant P-rich growth machinery and exhibit low cellular N/P ratios^{7,9}. In contrast, resource-limited cells invest in N-rich light and/or nutrient acquisition machinery and have higher N/P ratios^{7,9}.

Despite the prevalence of non-Redfield nutrient utilization, few ecosystem models^{11,12}, and virtually no geochemical or ocean general circulation models that include biological processes, consider non-Redfield nutrient consumption, assuming instead that phytoplankton N/P stoichiometry is Redfield (diazotrophs notwithstanding). Considering the predominance of marine environments that support non-Redfield N/P utilization by non-diazotrophic phytoplankton, a better description of how phytoplankton stoichiometry affects oceanic nutrient inventories is critical to understanding the marine N cycle.

We developed a dynamic five-box ecosystem model (Fig. 1) with three phytoplankton groups (diatoms, picocyanobacteria and diazotrophs) to understand how changes in seawater NO_3/PO_4 stoichiometry, mediated by non-Redfield phytoplankton N/P requirements, influence N_2 fixation and, ultimately, the oceanic inventory of N in the eastern tropical South Pacific Ocean (ETSP). Briefly, the model includes flow between compartments representing the deep ocean, the nearshore subsurface oxygen minimum zone (OMZ) where fixed N is lost through microbial processes, the coastal upwelling zone dominated by diatoms^{13,14} with low N/P requirements⁵, transitional waters between the coastal upwelling and the oligotrophic ocean, and the oligotrophic gyre dominated by picocyanobacteria (for example, *Prochlorococcus*¹⁵) with high N/P requirements⁸. Changes in N and P inventories were simulated over an annual cycle in each box using different assumptions about phytoplankton N/P stoichiometry in each simulation. N_2 fixation was calculated from diazotroph growth and the fraction of the N requirement satisfied by N_2 fixation. We also calculated the amount of N_2 fixation required in each box to restore PO_4 concentrations to the observed World Ocean Atlas (WOA) 2005 climatology¹⁶. Results from the Redfield and non-Redfield simulations were then compared (for model details, see the Methods section).

In the coastal upwelling box, chlorophyll *a* (chl) varies seasonally from 0.5 to 2.0 mg m^{-3} (Supplementary Fig. S1) and is dominated by diatoms (89%; refs 13,14), with picocyanobacteria and diazotrophs making up 10% and 1% of the community, respectively. In the Redfield simulation, diazotrophs obtain 9–25% of their N from N_2 fixation, depending on seasonal variations in NO_3 , and fix $1.5 \times 10^9 \text{ mmol N yr}^{-1}$. Whereas seasonal NO_3 dynamics are consistent with the observed climatology, PO_4 is substantially too high, averaging $1.62 \pm 0.09 \text{ mmol m}^{-3}$ (Fig. 2a, Supplementary Table S2). The modelled NO_3/PO_4 ratio in the upwelling box is below Redfield because of input of NO_3 -depleted waters from the OMZ, as documented throughout the ETSP (refs 3,10). However, the predicted amount of excess PO_4 ($\text{xsPO}_4 = \text{PO}_4 - \text{NO}_3/16$; ref. 10) is 30% higher than observed (Fig. 2b). Sensitivity analyses show that once waters upwell to the surface, xsPO_4 is determined primarily by the phytoplankton N/P ratio (*r*), being much less sensitive to other model parameters (Supplementary Tables S5–S7). Under the Redfield assumption, another 0.26 $\text{mmol PO}_4 \text{ m}^{-3}$ would need to be removed from the upwelling box to bring modelled nutrient inventories into agreement with observed climatologies. This could be achieved only by allowing diazotrophs to consume >25% of the total available PO_4 and fix >13 mmol N m^{-3} , values that far exceed *in situ* observations in upwelling waters¹⁷.

Community composition is similar in the upwelling and transitional boxes, with diatoms, picocyanobacteria and diazotrophs accounting for 85, 10 and 5%, respectively, of the

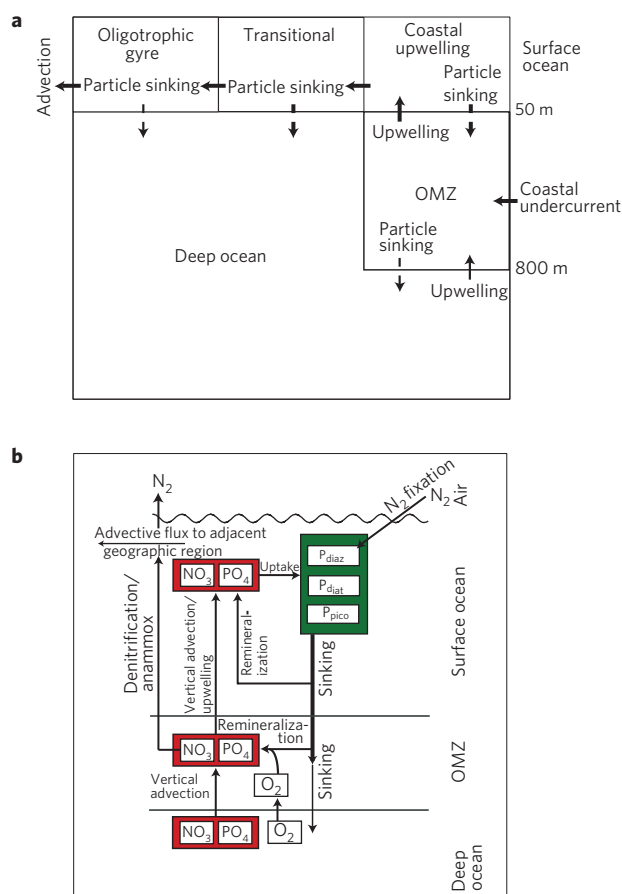


Figure 1 | The ETSP five-box ecosystem model. a, Diagram showing the flows between the different ocean boxes (denoted by solid arrows). The difference between deep flows into the OMZ and out to the coastal upwelling box is equal to the advection of suboxic coastal undercurrent water into the OMZ (Supplementary Table S1). Sinking particulates from the transitional and oligotrophic boxes do not alter nutrient concentrations in the much larger deep ocean box. **b**, Schematic representation of the biological model showing the relationship between state variables and the principal fluxes. Nutrients upwell only into the coastal box.

total chl pool. However, phytoplankton abundance is lower in this box and the annual cycle is dampened ($0.15\text{--}0.23\text{ mg chl m}^{-3}$, Supplementary Fig. S1). In the Redfield simulation, NO_3 agrees well with observations, but modelled PO_4 ($1.26 \pm 0.004\text{ mmol m}^{-3}$) is about twofold too high ($0.64 \pm 0.28\text{ mmol m}^{-3}$), requiring removal of a further $0.63\text{ mmol P m}^{-3}$ to reproduce observed concentrations in the ETSP (Fig. 2a, Supplementary Table S2). Depletion of this residual PO_4 pool requires that diazotrophs remove $>80\%$ of the total PO_4 and fix $\sim 31\text{ mmol N m}^{-3}$, rates far in excess of those documented in surface *Trichodesmium* blooms¹⁸.

In the oligotrophic box, chl is low ($0.05\text{--}0.07\text{ mg m}^{-3}$, Supplementary Fig. S1) and dominated by picocyanobacteria (55%), with diatoms and diazotrophs comprising the remaining 35% and 10% of phytoplankton biomass, respectively¹⁵. In the Redfield simulation, nutrient assimilation yields reasonable levels of NO_3 , whereas PO_4 concentrations are fourfold higher than observed (Fig. 2a and Supplementary Table S2). As a result of the low NO_3 concentrations in this box, the annual N_2 -fixation rate of $12.6 \times 10^9\text{ mmol yr}^{-1}$ provides $>98\%$ of the N for diazotrophs. However, diazotrophs would need to fix 38 mmol N m^{-3} and remove an extra $0.76\text{ mmol PO}_4\text{ m}^{-3}$ for the Redfield model to match observed nutrient inventories in oligotrophic waters. This is

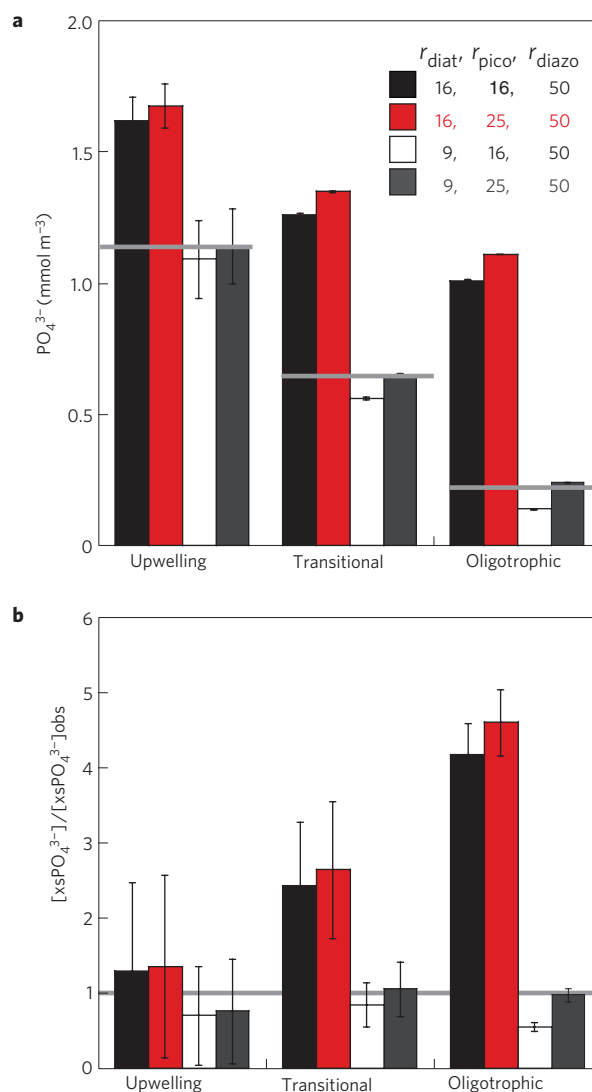


Figure 2 | Effects of phytoplankton nitrate/phosphate (NO_3/PO_4) utilization ratios on PO_4 and xsPO_4 in the ETSP. a, b Mean annual values \pm s.d. for PO_4 concentrations (mmol m^{-3}) (**a**) and the ratio of modelled xsPO_4 to observed xsPO_4 (from the WOA2005; ref. 14) (**b**) for the three surface boxes using different elemental ratios (r_i). The grey lines in **a** represent observed annual means from the WOA2005 and the grey line in **b** represents perfect agreement between the modelled and observed xsPO_4 concentrations. The associated standard deviations of NO_3 and PO_4 used in the calculation of xsPO_4 are propagated as $\text{s.d.}_{\text{xsPO}_4} = \sqrt{(\text{s.d.}_{\text{NO}_3})^2 + (\text{s.d.}_{\text{PO}_4})^2}$.

greater than the observed removal of PO_4 between the transitional and oligotrophic zones by all phytoplankton groups combined (Supplementary Table S2) and is therefore not tenable.

In the non-Redfield simulation, calculated NO_3 in each box was the same as in the Redfield simulation (Supplementary Table S5). However, PO_4 was substantially reduced and in much better agreement with climatology¹⁶ throughout the ETSP (Fig. 2a, Supplementary Table S2). Enhanced PO_4 consumption by diatoms (owing to their low N/P ratio), particularly in the upwelling and transitional boxes, reduced the xsPO_4 (Fig. 2b) available to diazotrophs and resulted in markedly lower N_2 -fixation rates compared with the Redfield simulation (Table 1). This was partially offset by higher than Redfield NO_3/PO_4 consumption by picocyanobacteria in the transitional and oligotrophic boxes,

Table 1 | Comparison of N₂-fixation rates in the three oceanographic regions under the different N/P utilization scenarios and assuming that diazotroph consumption returns xsPO₄ concentrations to observed climatology.

Oceanographic region		Area (10 ⁸ m ²)	N/P = 9, 25, 50*	N ₂ -fixation rate (10 ⁹ mmol yr ⁻¹)		
				16, 16, 50*	16, 25, 50*	9, 16, 50*
Box 3	Upwelling	0.22	1.5	2.1	2.1	1.4
Box 4	Transitional	1.07	7.2	14.0	15.0	6.2
Box 5	Oligotrophic	1.59	12.6	53.0	58.4	7.3
	Total	2.88	21.3	69.1	75.5	14.9
	Mean ± s.d.		7.1 ± 5.6	23.0 ± 26.7	25.2 ± 29.5	5.0 ± 3.1
	Relative to N/P = 9, 25, 50		1.0	3.3	3.6	0.7

*Diatom, picocyanobacteria and diazotroph N/P utilization ratios, respectively.

which slightly increased PO₄ concentrations (Fig. 2a) and N₂ fixation when r_{Pico} was increased from 16 to 25 (Table 1). However, because of diatom dominance, especially in the upwelling box, the net impact of non-Redfield nutrient stoichiometry was to reduce the xsPO₄ (Fig. 2b) available for N₂ fixation downstream. Consequently, in the upwelling box, N₂-fixation rates were 1.5-fold higher in the Redfield simulation than in the non-Redfield run (Table 1). The difference between the two simulations was even larger in the transitional box (twofold higher in the Redfield run) and culminated in N₂-fixation rates in the oligotrophic box that were fourfold higher in the Redfield run than in the non-Redfield simulation. Assumption of non-Redfield nutrient utilization in the ETSP leads to N₂-fixation rates that, although threefold lower than when Redfield stoichiometry is assumed (Table 1), are in agreement with estimates for the equatorial Pacific⁴.

These results show that the relative diatom and picocyanobacteria abundance substantially impacts the amount of xsPO₄ available for diazotrophy. As diatoms dominate upwelling and transitional zones, they exert greater control on PO₄ availability than picocyanobacteria. As a consequence of lower diatom N/P requirements, the xsPO₄ in the upwelling box is reduced by 65% before reaching the oligotrophic box. Our results also clearly demonstrate the importance of considering actual nutrient utilization ratios when calculating N₂-fixation rates from nutrient inventories^{3,10}. This is particularly relevant to productive waters overlying OMZs, such as the coastal waters that upwell off Peru, where observed nutrient ratios show xsPO₄ consumption (ref. 10; Supplementary Table S2). The assumption that NO₃/PO₄ utilization is Redfield in the ETSP probably leads to estimates of N₂ fixation that are up to fourfold too high (Table 1).

Our model, although reasonably mechanistic, makes some important simplifying assumptions, including holding both N/P utilization ratios and phytoplankton community composition fixed over time. Nevertheless, our results changed little when phytoplankton N/P requirements were allowed to vary seasonally (lower during exponential growth and higher at the end of the bloom). This is because the ratios used in the non-Redfield simulations are applicable during the exponential phase of blooms when most nutrients are removed. After the bloom, nutrient utilization ratios may be higher, but nutrient uptake is small, minimizing its impact. Similarly, allowing taxonomic composition to vary seasonally had little effect on xsPO₄ because only the minor taxa in each box were impacted by this assumption.

Recent studies suggest that the low NO₃/PO₄ ratio of waters that upwell to the surface from suboxic zones stimulates diazotrophy in areas proximal to OMZs, producing a tight spatial coupling between sources and sinks of oceanic fixed N (ref. 10). Tight coupling is predicted to lead to even greater denitrification rates as more organic matter produced through N₂ fixation is exported to depth, resulting in a runaway denitrification/N₂-fixation feedback loop¹⁹. Models can spatially decouple N₂ fixation and N loss by making diazotrophy

inversely proportional to NO₃ availability or by allowing diatoms to outcompete diazotrophs when NO₃ concentrations are high. However, this decoupling does nothing to alter the xsPO₄ inventory when Redfield stoichiometry is invoked. Therefore, previous model-based estimates of areal N₂-fixation rates are 1–9-fold higher than those calculated here^{20,21}. We note that our estimates are conservative and do not include N₂ fixation in the absence of cell growth²². Nevertheless, our analysis suggests that by reducing N₂-fixation rates within both upwelling and transitional zones, non-Redfield nutrient utilization by phytoplankton provides an effective mechanism to spatially decouple areas of N₂ fixation and N loss.

Non-Redfield nutrient utilization by non-diazotrophs may also be responsible for the observed patterns of xsPO₄ in the North Atlantic. xsPO₄ in waters from the Arctic Ocean²³ is reduced significantly during the massive phytoplankton blooms in the North Atlantic (Fig. 3a–h). These blooms are dominated by diatoms and coccolithophores²⁴ with low NO₃/PO₄ utilization ratios⁵. As they are located north of regions with substantial N₂ fixation²⁵, the seasonal reduction in xsPO₄ in these waters is best explained by phytoplankton nutrient drawdown at N/P ratios below Redfield. As in the ETSP, these fast-growing phytoplankton reduce the availability of PO₄ to diazotrophs in the North Atlantic, and thus, significantly diminish potential N₂-fixation rates.

Furthermore, nutrient utilization above Redfield by non-diazotrophs may contribute to the high excess NO₃ (xsNO₃, relative to Redfield proportions) in the subsurface North Atlantic subtropical gyre³. The overwhelmingly dominant autotrophs in these waters (*Prochlorococcus* and *Synechococcus*) have high cellular N/P quotas, and their contribution to export in oligotrophic environments may be significant²⁶. The export and remineralization of this N-rich organic matter probably contribute to elevated xsNO₃ in subsurface waters and should be accounted for when using xsNO₃ to determine basin-scale N₂ fixation³. By similar reasoning, denitrification rates in OMZs that are calculated assuming sinking particulate matter is in Redfield proportions are probably overestimated by an amount proportional to the sinking flux and subsequent remineralization of low-N/P particulate organic matter originating at the surface.

Finally, the results presented here have important implications for understanding controls on global marine N inventories. Current views hold that N₂ fixation increases the N content of the predominantly N-limited oceans, stimulating organic matter production and export, reducing oxygen concentrations in the ocean interior and enhancing the loss of fixed N from the ocean through denitrification and anaerobic ammonium oxidation (anammox). We suggest that the relative abundance of phytoplankton with non-Redfield N/P requirements exerts significant control on the strength of this feedback. Contemporary phytoplankton distributions are such that slow-growing picocyanobacteria dominate oceanic gyres, whereas fast-growing taxa such as diatoms dominate high-nutrient environments such as upwelling waters overlying OMZs. Environmental changes that enhance ocean

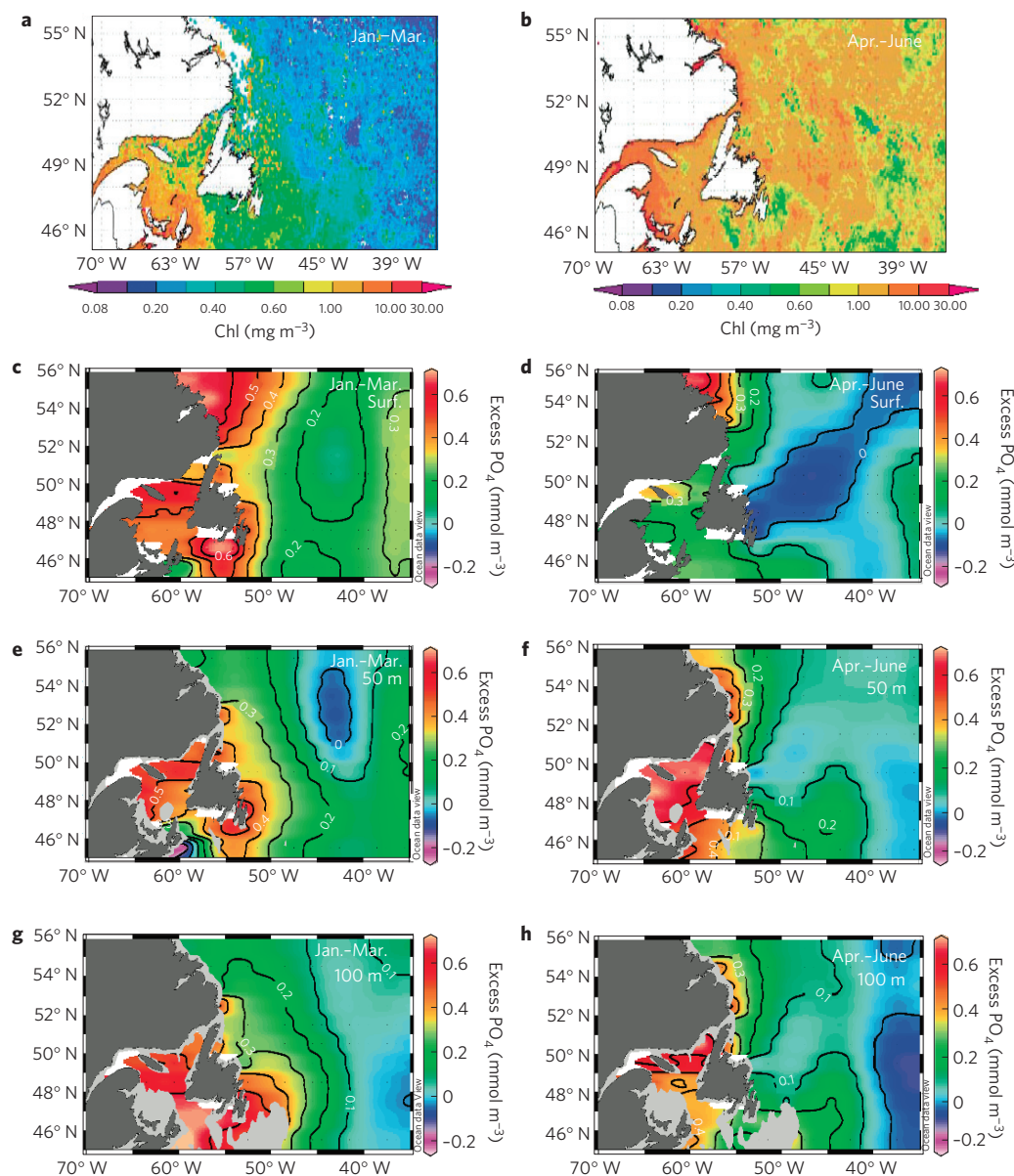


Figure 3 | Seasonal variation in excess PO_4 (xsPO_4 , mmol m^{-3}) and chlorophyll (chl , mg m^{-3}) in the northern North Atlantic Ocean. a–h, Surface chl (a,b) and xsPO_4 at depths of 0 m (c,d), 50 m (e,f) and 100 m (g,h) for January–March (a,c,e,g) and April–June (b,d,f,h). Although wintertime nutrient data are relatively sparse (Supplementary Fig. S4), the seasonal decrease in xsPO_4 in the upper 100 m correlates with the spring diatom blooms in waters north of 40° N where diazotrophs are not typically found. Nutrients, from the WOA2005, are plotted using ODV (<http://www.awi-bremerhaven.de/GEO/ODV>). Chl was determined using the Giovanni Ocean Colour Time-Series Online Visualization software (<http://odv.awi.de/>).

stratification²⁷ will probably increase the area of the ocean's surface that is depleted in macronutrients, thereby expanding the habitat of high-N/P-using picocyanobacteria²⁸. In contrast, perturbations that increase upwelling (for example, increased winds) will expand the habitat of diatoms having lower N/P ratios. The relative magnitude of these two changes could significantly impact xsPO_4 availability for diazotrophs, and hence the amount of new N added to the ocean through N_2 fixation. Therefore, the prevailing paradigm that the marine N inventory is controlled by a simple feedback between global rates of denitrification/anammox and N_2 fixation needs to be modified. Our results indicate that non-Redfield nutrient utilization by non-diazotrophic phytoplankton represents a mechanism that can decouple the processes of N_2 fixation and denitrification, and consequently, the steady-state oceanic N inventory. Furthermore, the reduction in xsPO_4 by diatoms and the corresponding decrease in downstream N_2 fixation may help explain the

apparent imbalance between rates of N_2 fixation and fixed-N loss (which is substantially larger)²⁹ in the contemporary ocean.

Methods

In the model, water from the OMZ upwells into the surface coastal box with a low NO_3/PO_4 ratio. We model this input of nutrients as a product of the time-varying advective volume flux (f) and the associated nutrient concentration. Net growth of each phytoplankton group in the surface coastal box is determined from observed changes in chlorophyll a concentrations (from SeaWiFS) (Supplementary Fig. S1) and the proportion that each phytoplankton group contributes to the total phytoplankton population (as determined from published data). This net growth rate for each phytoplankton group is used to calculate uptake of nutrients at the specified utilization ratios. The NO_3/PO_4 utilization ratios (r) for diatoms, picocyanobacteria and diazotrophs are specified to be 16 (r_{diat}), 16 (r_{pico}) and 50 (r_{diaz}), respectively, in the 'Redfield' simulation. In the non-Redfield simulation, NO_3/PO_4 utilization ratios by diatoms ($r_{\text{diat}} = 9$) and picocyanobacteria ($r_{\text{pico}} = 25$) are altered to better conform with our improved understanding of phytoplankton stoichiometry^{5,7,8}. A fraction of the newly formed particulate material (N or P) is remineralized within the surface box and the remainder either sinks below the

surface or advects into the transitional box. This information is used to calculate the inventories of NO_3 and PO_4 over an annual cycle within the box. This scheme is repeated when estimating the nutrient inventories for the transitional box and the oligotrophic box. Although variable surface water remineralization ratios may alter surface nutrient ratios³⁰, we suggest variability in this ratio is small. Finally, mass is conserved in the model by running it to a long-term steady state, at which point all N inputs equal N outputs.

Model details. As shown in Supplementary Equation (1) (Supplementary Table S3), all state variables in the model ($X = \text{NO}_3, \text{PO}_4, \text{O}_2$, or one of the three phytoplankton taxa, P_j , where j = diatoms, picocyanobacteria or diazotrophs) are impacted by both physical (f = advection and mixing) and biological (Q = nutrient uptake, remineralization and sinking) processes. Mixing between the subsurface OMZ box and the surface coastal box is calculated as a function of wind speed (Supplementary Information), as is advection between the surface coastal box, the transition zone box and the oligotrophic box.

The rate of change in phytoplankton biomass ($\text{mg N m}^{-3} \text{d}^{-1}$, Supplementary Equation (2)) in each box is calculated as a function of the phytoplankton growth rate (μ_j, d^{-1}), the daily fraction of P_j that is remineralized within each box (E_j, d^{-1}) and the daily fraction of P_j that sinks out of each box (s_j, d^{-1}). Changes in NO_3 and PO_4 concentration (mg m^{-3} , Supplementary Equations (3a) and (4a), respectively) are calculated as a function of phytoplankton uptake during growth (μ_j) and the remineralization of dead or grazed phytoplankton biomass (E_j, d^{-1}). The currency of the model is N, so changes in PO_4 (Supplementary Equation (4)) are coupled to those of NO_3 (Equation (3)) through the elemental N/P ratio of each phytoplankton taxa (r_j). As Supplementary Equations (3a) and (4a) require knowledge of $\mu_j P_j$ and $E_j P_j$ for each phytoplankton taxa, quantities that are not easily determined, we rearranged Supplementary Equation (2a) to take the form shown in Supplementary Equation (2b). Then we substituted the right side of Supplementary Equation (2b) for the left side and inserted it into Supplementary Equations (3a) and (4a) to yield Supplementary Equations (3b) and (4b), respectively. Supplementary Equations (3b) and (4b) are preferable to Supplementary Equations (3a) and (4a) because they rely only on changes in phytoplankton biomass, which can be derived from SeaWiFS, and phytoplankton sinking rate, a quantity that can be constrained easily using O_2 data and to which model results are relatively insensitive.

As formulated, Supplementary Equation (3a) assumes that all phytoplankton growth is supported by dissolved NO_3 . However, this is not the case for diazotrophs, which use N_2 when NO_3 is low. We account for this in the second line of Supplementary Equation (3b), where κ_{N_2} is the fraction of diazotroph N that comes from N_2 fixation (Supplementary Fig. S2). The instantaneous N_2 -fixation rate (ρ) is then calculated in Supplementary Equation (6).

Finally, the rate of remineralization of sinking phytoplankton organic matter in the OMZ is constrained using observed O_2/P remineralization ratios² such that modelled O_2 concentrations are consistent with the WOA climatology. Changes in O_2 concentration in the model are calculated as in Supplementary Equation (7), where E_{OMZ} ($\text{mg m}^{-3} \text{d}^{-1}$) is the remineralization of particulate matter and $E_{\text{O}_2/\text{P}}$ is the elemental ratio of consumed O_2 to P produced through remineralization (170; ref. 2).

Parameter values used in the model are given in Supplementary Table S4.

Further description of model physics, model parameters and constants, and sensitivity analyses are included in the Supplementary Information.

Received 13 January 2010; accepted 30 March 2010;
published online 16 May 2010

References

1. Redfield, A. C. in *James Johnstone Memorial Volume* (ed. Daniel, R. J.) 177–192 (Univ. Press Liverpool, 1934).
2. Anderson, L. A. & Sarmiento, J. L. Redfield ratios of remineralization determined by nutrient data-analysis. *Glob. Biogeochem. Cycles* **8**, 65–80 (1994).
3. Gruber, N. & Sarmiento, J. L. Global patterns of marine nitrogen fixation and denitrification. *Glob. Biogeochem. Cycles* **11**, 235–266 (1997).
4. Moore, J. K., Doney, S. C., Kleypas, J. A., Glover, D. M. & Fung, I. Y. An intermediate complexity marine ecosystem model for the global domain. *Deep-Sea Res. II* **49**, 403–462 (2002).
5. Quigg, A. *et al.* The evolutionary inheritance of elemental stoichiometry in marine phytoplankton. *Nature* **425**, 291–294 (2003).
6. Arrigo, K. R. *et al.* Phytoplankton community structure and the drawdown of nutrients and CO_2 in the Southern Ocean. *Science* **283**, 365–367 (1999).
7. Geider, R. J. & La Roche, J. Redfield revisited: Variability of C:N:P in marine microalgae and its biochemical basis. *Eur. J. Phycol.* **37**, 1–17 (2002).
8. Bertilsson, S., Berglund, O., Karl, D. M. & Chisholm, S. W. Elemental composition of marine *Prochlorococcus* and *Synechococcus*: Implications for the ecological stoichiometry of the sea. *Limnol. Oceanogr.* **48**, 1721–1731 (2003).

9. Klausmeier, C. A., Litchman, E., Daufresne, T. & Levin, S. A. Optimal nitrogen-to-phosphorus stoichiometry of phytoplankton. *Nature* **429**, 171–174 (2004).
10. Deutsch, C., Sarmiento, J. L., Sigman, D. M., Gruber, N. & Dunne, J. P. Spatial coupling of nitrogen inputs and losses in the ocean. *Nature* **445**, 163–167 (2007).
11. Anderson, T. R. & Pondaven, P. Non-Redfield carbon and nitrogen cycling in the Sargasso Sea: Pelagic imbalances and export flux. *Deep-Sea Res. I* **50**, 573–591 (2003).
12. Christian, J. R. Biogeochemical cycling in the oligotrophic ocean: Redfield and non-Redfield models. *Limnol. Oceanogr.* **50**, 646–657 (2005).
13. Chavez, F. P., Buck, K. R., Service, S. K., Newton, J. & Barber, R. T. Phytoplankton variability in the central and eastern tropical Pacific. *Deep-Sea Res. II* **43**, 835–870 (1996).
14. Bruland, K. W., Rue, E. L., Smith, G. J. & DiTullio, G. R. Iron, macronutrients and diatom blooms in the Peru upwelling regime: Brown and blue waters of Peru. *Mar. Chem.* **93**, 81–103 (2005).
15. Dandonneau, Y. *et al.* Seasonal and interannual variability of ocean colour and composition of phytoplankton communities in the North Atlantic, equatorial Pacific and South Pacific. *Deep-Sea Res. II* **51**, 303–318 (2004).
16. Garcia, H. E., Locarnini, R. A., Boyer, T. P. & Anotov, J. I. in *NOAA Atlas NESDIS 64* (ed. Levitus, S.) (US Government Printing Office, 2006).
17. Voss, M., Bombar, D., Loick, N. & Dippner, J. W. Riverine influence on nitrogen fixation in the upwelling region off Vietnam, South China Sea. *Geophys. Res. Lett.* **33**, L07604 (2006).
18. Capone, D. G. *et al.* An extensive bloom of the N_2 -fixing cyanobacterium *Trichodesmium erythraeum* in the central Arabian Sea. *Mar. Ecol. Prog. Ser.* **172**, 281–292 (1998).
19. Canfield, D. E. Models of oxic respiration, denitrification and sulfate reduction in zones of coastal upwelling. *Geochim. Cosmochim. Acta* **70**, 5753–5765 (2006).
20. Moore, J. K. & Doney, S. C. Iron availability limits the ocean nitrogen inventory stabilizing feedbacks between marine denitrification and nitrogen fixation. *Glob. Biogeochem. Cycles* **21** (2007).
21. Tagliabue, A., Bopp, L. & Aumont, O. Ocean biogeochemistry exhibits contrasting responses to a large scale reduction in dust deposition. *Biogeosciences* **5**, 11–24 (2008).
22. Glibert, P. M. & Bronk, D. A. Release of dissolved organic nitrogen by marine diazotrophic cyanobacteria, *Trichodesmium* spp. *Appl. Environ. Microbiol.* **60**, 3996–4000 (1994).
23. Yamamoto-Kawai, M., Carmack, E. & McLaughlin, F. Nitrogen balance and Arctic throughflow. *Nature* **443**, 43–43 (2006).
24. Lochte, K., Ducklow, H. W., Fasham, M. J. R. & Stienen, C. Plankton succession and carbon cycling at 47° N 20° W during the JGOFS North-Atlantic bloom experiment. *Deep-Sea Res. II* **40**, 91–114 (1993).
25. Staal, M. *et al.* Nitrogen fixation along a north-south transect in the eastern Atlantic Ocean. *Limnol. Oceanogr.* **52**, 1305–1316 (2007).
26. Richardson, T. L. & Jackson, G. A. Small phytoplankton and carbon export from the surface ocean. *Science* **315**, 838–840 (2007).
27. Schmittner, A. Decline of the marine ecosystem caused by a reduction in the Atlantic overturning circulation. *Nature* **434**, 628–633 (2005).
28. Irwin, A. J. & Oliver, M. J. Are ocean deserts getting larger? *Geophys. Res. Lett.* **36**, L18609 (2009).
29. Codispoti, L. A. *et al.* The oceanic fixed nitrogen and nitrous oxide budgets: Moving targets as we enter the anthropocene? *Sci. Marina* **65**, 85–105 (2001).
30. Paulmier, A., Kriest, I. & Oschlies, A. Stoichiometries of remineralisation and denitrification in global biogeochemical ocean models. *Biogeosciences* **6**, 2539–2566 (2009).

Acknowledgements

We thank G. van Dijken and B. Saenz for help coding the model and L. Thomas for help parameterizing upwelling fluxes. We are also indebted to the members of the Arrigo laboratory and to C. M. Moore for fruitful discussions on nutrient utilization ratios of different phytoplankton and for comments on the manuscript. This work was supported by NSF grant ANT 0732535 and DOE grant DE-FG02-04ER63896 to K.R.A.

Author contributions

All authors contributed equally to this work.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at <http://npg.nature.com/reprintsandpermissions>. Correspondence and requests for materials should be addressed to M.M.M.

Magnitude of oceanic nitrogen fixation is significantly influenced by phytoplankton nutrient uptake ratios

Matthew M. Mills* & Kevin R. Arrigo

Department of Environmental Earth System Science, Stanford University, Stanford, California, 94305, USA

*To whom correspondence should be addressed. E-mail: mmmills@stanford.edu

This file includes:

Figure Legends

References

Tables S1 - S7

Figures S1 – S4

Supplementary figure legends

Figure S1. SeaWiFS 8-day global (9 km) chlorophyll concentrations (mg m^{-3}) in the a) upwelling, b) transitional, and c) oligotrophic boxes. Shown are satellite-derived values during 2008 and modeled concentrations. SeaWiFS data were obtained using the Giovanni Ocean Color Time-Series Online Visualization and Analysis tool at <http://reason.gsfc.nasa.gov/OPS/Giovanni/>.

Figure S2. The inverse relationship between NO_3 concentrations and the fraction of diazotroph N that comes from N_2 -fixation. Data were obtained from Holl and Montoya¹ and fit using the software package LAB Fit (Wilton Pereira da Silva, Brazil).

Figure S3. Effect of non-diazotroph nutrient utilization ratios on surface water nutrient concentrations and N_2 -fixation. The dissolved N:P ratio (N:P_D) of water that upwells through the OMZ is reduced by the microbial processes of denitrification and/or anammox. a) When assuming Redfield nutrient utilization, xsPO_4 concentrations remain high in water that transits away from the upwelling zone. Therefore, xsPO_4 is consumed solely by diazotrophs, whose particulate N:P ratio (N:P_P) is typically 50 or higher, resulting in enhanced rates of N_2 -fixation. Remineralization of N-rich diazotroph biomass below the surface layer returns deep water N:P_D to Redfield proportions. b) In contrast, phytoplankton utilization of $\text{NO}_3\text{:PO}_4$ in non-Redfield proportions can increase ($\text{N:P}_{\text{Diat}} < 16$) or decrease ($\text{N:P}_{\text{Pico}} > 16$) surface N:P_D depending on the relative abundance of diatoms and picocyanobacteria. Because diatoms generally dominate the upwelling and transitional zones of the ETSP, less xsPO_4 is available for diazotrophs and rates of N_2 -fixation are reduced relative to (a). This figure is a revised version of one originally published in Capone and Knapp².

Figure S4. The number of PO_4^{3-} observations in the northern North Atlantic from the WOA 2005 database³. Data shown are for the (A, C, E) Jan.–Mar. and the (B, D, F) Apr.–Jun. seasons at

three different depths (Surface, 50m, 100m). Data were obtained from <http://iridl.ldeo.columbia.edu/SOURCES/.NOAA/.NODC/.WOA05/>. In support of Fig. 3, we note that additional evidence showing lower than Redfield N:P drawdown in the northern North Atlantic can be found in Louanchi and Najjar⁴. Their Table 2 shows that the seasonal N:P drawdown between Jan-Mar and Jul-Sep in the Sub-Arctic Atlantic averages 12.9.

References

1. Holl, C. M. & Montoya, J. P. Interactions between nitrate uptake and nitrogen fixation in continuous cultures of the marine diazotroph *Trichodesmium* (Cyanobacteria). *Journal of Phycology* **41**, 1178-1183 (2005).
2. Capone, D. G. & Knapp, A. N. Oceanography - A marine nitrogen cycle fix? *Nature* **445**, 159-160 (2007).
3. Garcia, H. E., R. A. Locarnini, T. P. Boyer, and J. I. Antonov, 2006. World Ocean Atlas 2005, Volume 4: Nutrients (phosphate, nitrate, silicate). S. Levitus, Ed. NOAA Atlas NESDIS 64, U.S. Government Printing Office, Washington, D.C., 396 pp.
4. Louanchi, F. & Najjar R. G. Annual cycles of nutrients and oxygen in the upper layers of the North Atlantic Ocean. *Deep-Sea Research II* **48**, 2155 (2001).

Table S1. Dimensions, Ekman transport, and residence time of each box in the non-Redfield nutrient utilization model.

						Ekman transport (m ² d ⁻¹)		Residence time (y)	
						Non-upwelling period	Upwelling period	Non-upwelling period	Upwelling period
		°S	°W	Depth (m)	Area (m ²)				
Box 2	OMZ	15	76-80	50-300	0.22 x 10 ⁸	2.37 x 10 ⁴	9.72 x 10 ⁴	12.5	3.0
Box 3	Upwelling	15	76-80	0-50	0.22 x 10 ⁸	2.37 x 10 ⁴	9.72 x 10 ⁴	1.4	0.3
Box 4	Transitional	15	80-100	0-50	1.07 x 10 ⁸	2.37 x 10 ⁴	9.72 x 10 ⁴	18.5	4.5
Box 5	Oligotrophic	20	100-130	0-50	1.59 x 10 ⁸	2.37 x 10 ⁴	9.72 x 10 ⁴	26.0	6.3

The upwelling period was between July 1st and September 30th.

Table S2. Comparison of NO_3^\dagger and PO_4 concentrations obtained from WOA 2005 climatology and those modeled here using N:P utilization ratios of 9, 25, and 50 for diatoms, picocyanobacteria and diazotrophs respectively.

	Data			Model		
	NO_3 [mmol m^{-3}]	PO_4 [mmol m^{-3}]	$\Delta\text{NO}_3:\Delta\text{PO}_4$	NO_3 [mmol m^{-3}]	PO_4 [mmol m^{-3}]	$\Delta\text{NO}_3:\Delta\text{PO}_4$
Box 2: OMZ						
Jan-Mar	20.20 \pm 5.14	2.40 \pm 0.34				
Apr-Jun	20.88 \pm 4.92	2.33 \pm 0.37				
Jul-Sep	23.20 \pm 6.24	2.45 \pm 0.39				
Oct-Dec	18.13 \pm 7.92	2.40 \pm 0.37				
Avg. \pm SD	20.60 \pm 12.34	2.39 \pm 0.74		20.65 \pm 0.03	2.45 \pm 0.0002	
Box 3: Upwelling						
Jan-Mar	5.07 \pm 3.90	1.19 \pm 0.47	12.53 \pm 8.02			
Apr-Jun	7.03 \pm 3.82	1.17 \pm 0.41	11.90 \pm 7.80			
Jul-Sep	12.17 \pm 3.23	1.59 \pm 0.32	12.83 \pm 11.04			
Oct-Dec	6.46 \pm 1.46	1.48 \pm 0.37	12.71 \pm 11.40			
Avg. \pm SD	7.68 \pm 6.51	1.36 \pm 0.79	12.41 \pm 9.57	7.63 \pm 1.40	1.14 \pm 0.14	9.97 \pm 1.52
Box 4: Transitional						
Jan-Mar	3.6 \pm 1.37	0.64 \pm 0.11	2.73 \pm 7.90			
Apr-Jun	2.1 \pm 1.12	0.53 \pm 0.11	7.73 \pm 8.14			
Jul-Sep	4.6 \pm 2.60	0.75 \pm 0.20	9.02 \pm 6.32			
Oct-Dec	2.1 \pm 1.08	0.62 \pm 0.12	5.10 \pm 3.13			
Avg. \pm SD	3.10 \pm 3.33	0.64 \pm 0.28	6.14 \pm 6.37	2.95 \pm 0.05	0.65 \pm 0.005	9.35 \pm 3.95
Box 5: Oligotrophic						
Jan-Mar	0.07 \pm 0.08	0.23 \pm 0.05	8.47 \pm 4.10			
Apr-Jun	0.07 \pm 0.12	0.24 \pm 0.04	7.07 \pm 4.78			
Jul-Sep	0.24 \pm 0.16	0.26 \pm 0.05	8.85 \pm 6.50			
Oct-Dec	0.09 \pm 0.05	0.26 \pm 0.05	5.53 \pm 3.64			
Avg. \pm SD	0.12 \pm 0.22	0.25 \pm 0.09	7.48 \pm 4.75	0.11 \pm 0.02	0.24 \pm 0.003	6.95 \pm 0.16

[†]Modeled NO_3 concentrations were insensitive to N:P utilization ratios and were thus the same for all specified r_j .

Table S3. Equations used in the box model of the eastern tropical South Pacific.

Eq. #	Description	Equation
1	Rate of change in state variable X	$\frac{\partial X}{\partial t} = Q_X + fX$
2a	Biological change in phytoplankton taxa j	$Q_{P_j} = \mu_j P_j - E_j P_j - s_j P_j$
2b	2a rearranged	$\mu_j P_j - E_j P_j = Q_{P_j} + s_j P_j$
3a	Biological change in NO_3	$Q_{\text{NO}_3} = \sum_{j=1}^3 P_j (E_j - \mu_j)$
3b	Biological change in NO_3	$Q_{\text{NO}_3} = -Q_{P_{\text{Diat}}} - s_{\text{Diat}} P_{\text{Diat}} - Q_{P_{\text{Pico}}} - s_{\text{Pico}} P_{\text{Pico}}$ $-(1 - \kappa_{N_2}) (Q_{P_{\text{Diaz}}} - s_{\text{Diaz}} P_{\text{Diaz}}) + E_{\text{Diaz}} \kappa_{N_2} P_{\text{Diaz}}$
4a	Biological change in PO_4	$Q_{P_{\text{O}_4}} = \sum_{j=1}^3 P_j \left(\frac{E_j - \mu_j}{r_j} \right)$
4b	Biological change in PO_4	$Q_{P_{\text{O}_4}} = \sum_{j=1}^3 \left(\frac{-Q_{P_j} - s_j P_j}{r_j} \right)$
5	Fraction of diazotroph N from N_2 -fixation	$\kappa_{N_2} = ae^{(-b[\text{NO}_3])}$

6 N₂-fixation rate

$$\rho = \kappa_{N_2} \left(Q_{P_{Diaz}} + E_{Diaz} P_{Diaz} + s_{Diaz} P_{Diaz} \right)$$

7 Biological change in O₂ in OMZ

$$Q_{O_2} = E_{OMZ} \left(s_{Diat} \frac{P_{Diat}}{r_{Diat}} + s_{Pico} \frac{P_{Pico}}{r_{Pico}} + s_{Diaz} \frac{P_{Diaz}}{r_{Diaz}} \right) E_{O_2:P}$$

Table S4. Model parameters and constants.

Symbol	Description	Value
r_{Diat}	Diatom $\text{NO}_3:\text{PO}_4$ utilization ratio	9, 16 (non-Redfield, Redfield)
r_{Pico}	Picocyanobacterial $\text{NO}_3:\text{PO}_4$ utilization ratio (mol:mol ⁻¹)	16, 25 (non-Redfield, Redfield)
r_{Diazo}	Diazotroph $\text{NO}_3:\text{PO}_4$ utilization ratio (mol:mol ⁻¹)	50
$E_{O_2:P}$	$\text{O}_2:\text{P}$ remineralization ratio (mol:mol ⁻¹)	170
S_{Diat}	Sinking fraction of diatom biomass	0.009-0.04
S_{Pico}	Sinking fraction of picocyanobacterial biomass	0.004-0.04
S_{Diazo}	Sinking fraction of diazotroph biomass	0.001-0.02
E_{Diaz}	Remineralized fraction of diazotroph biomass that comes from N_2 -fixation	0.1
E_{OMZ}	Fraction of phytoplankton biomass that is remineralized in the OMZ	0.05
κ_{N-loss}	Fraction of NO_3 that is lost due to denitrification/anammox in the OMZ	0.000041

Table S5. Nutrient concentrations (mmol m⁻³) in each box under different nutrient utilization ratios for the different phytoplankton taxa.

N:P Ratio				Box 2	Box 3	Box 4	Box 5
r_{diat}	r_{pico}	r_{diaz}		OMZ	Upwelling	Transitional	Oligotrophic
9	25	50	NO ₃	20.64 ± 0.027	7.65 ± 1.396	2.96 ± 0.048	0.11 ± 0.012
			PO ₄	2.45 ± 0.0002	1.14 ± 0.141	0.65 ± 0.005	0.25 ± 0.002
9	16	50	NO ₃	20.64 ± 0.027	7.65 ± 1.396	2.96 ± 0.048	0.11 ± 0.012
			PO ₄	2.45 ± 0.0002	1.09 ± 0.146	0.56 ± 0.006	0.14 ± 0.003
9	25	16	NO ₃	20.64 ± 0.027	7.65 ± 1.396	2.96 ± 0.048	0.11 ± 0.012
			PO ₄	2.45 ± 0.0002	1.14 ± 0.141	0.62 ± 0.005	0.21 ± 0.002
9	25	100	NO ₃	20.64 ± 0.027	7.65 ± 1.396	2.96 ± 0.048	0.11 ± 0.012
			PO ₄	2.45 ± 0.0002	1.14 ± 0.141	0.66 ± 0.005	0.26 ± 0.002
16	16	50	NO ₃	20.64 ± 0.027	7.65 ± 1.396	2.96 ± 0.048	0.11 ± 0.012
			PO ₄	2.44 ± 0.0002	1.62 ± 0.088	1.26 ± 0.004	1.00 ± 0.001
16	25	50	NO ₃	20.64 ± 0.027	7.65 ± 1.396	2.96 ± 0.048	0.11 ± 0.012
			PO ₄	2.44 ± 0.0001	1.67 ± 0.083	1.35 ± 0.003	1.11 ± 0.002
16	16	100	NO ₃	20.64 ± 0.027	7.65 ± 1.396	2.96 ± 0.048	0.11 ± 0.012
			PO ₄	2.45 ± 0.0002	1.62 ± 0.088	1.27 ± 0.004	1.02 ± 0.001
12	20	50	NO ₃	20.64 ± 0.027	7.65 ± 1.396	2.96 ± 0.048	0.11 ± 0.012
			PO ₄	2.45 ± 0.0002	1.42 ± 0.110	1.01 ± 0.004	0.70 ± 0.001
Annual Observed							
			NO ₃	20.65 ± 0.03	7.63 ± 1.40	2.95 ± 0.05	0.11 ± 0.02
			PO ₄	2.45 ± 0.0002	1.14 ± 0.14	0.65 ± 0.005	0.24 ± 0.003

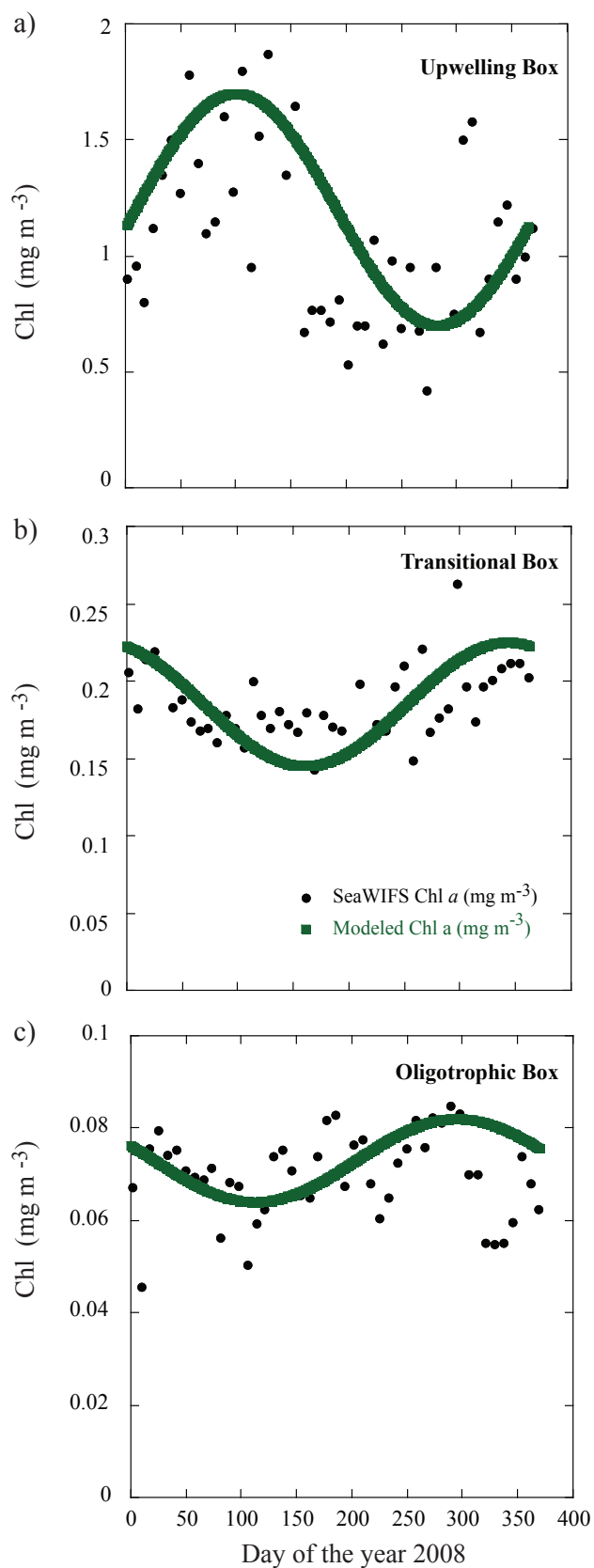
Table S6. Sensitivity of modeled nutrient concentrations (mmol m⁻³) in each box to the percent composition of the phytoplankton community in box 3¹.

Box 3 % <i>Diat</i> , % <i>Pico</i> , % <i>Diazo</i>			Box 2 OMZ	Box 3 Upwelling	Box 4 Transitional	Box 5 Oligotrophic	
89	10	1	NO ₃	20.65 ± 0.027	7.65 ± 1.396	2.96 ± 0.048	0.11 ± 0.012
			PO ₄	2.45 ± 0.0002	1.14 ± 0.141	0.65 ± 0.005	0.25 ± 0.002
79	20	1	NO ₃	20.66 ± 0.027	6.54 ± 1.498	2.07 ± 0.044	0.007 ± 0.009
			PO ₄	2.45 ± 0.0002	1.18 ± 0.136	0.69 ± 0.005	0.29 ± 0.002
59	40	1	NO ₃	20.67 ± 0.026	5.02 ± 1.634	0.91 ± 0.039	0.004 ± 0.006
			PO ₄	2.44 ± 0.0002	1.29 ± 0.122	0.80 ± 0.005	0.40 ± 0.002
79	10	11	NO ₃	20.64 ± 0.027	9.34 ± 1.217	4.41 ± 0.031	1.19 ± 0.013
			PO ₄	2.45 ± 0.0002	1.25 ± 0.129	0.76 ± 0.005	0.37 ± 0.002
59	10	31	NO ₃	20.64 ± 0.027	12.03 ± 0.929	6.09 ± 0.018	3.22 ± 0.014
			PO ₄	2.44 ± 0.0002	1.47 ± 0.104	0.98 ± 0.005	0.59 ± 0.002
Annual Observed			NO ₃	20.65 ± 0.03	7.63 ± 1.40	2.95 ± 0.05	0.11 ± 0.02
			PO ₄	2.45 ± 0.0002	1.14 ± 0.14	0.65 ± 0.005	0.24 ± 0.003

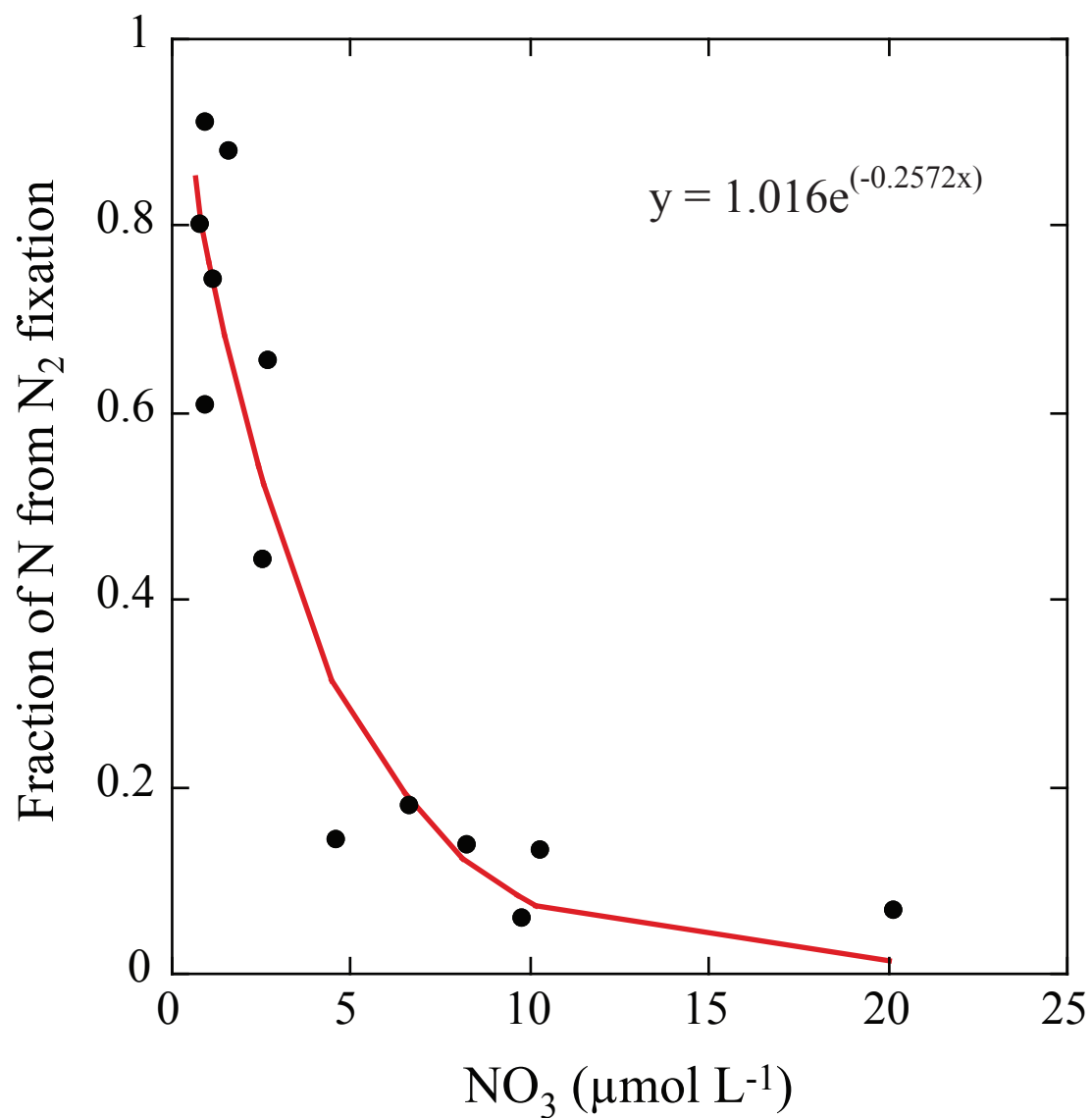
¹Results for the two remaining boxes (4 and 5, the transitional and oligotrophic boxes respectively) are virtually identical. For example, a decrease in diatom percent composition in any of the boxes results in less drawdown of PO₄ in that box and thus less exported to downstream boxes. When this biomass decrease is compensated for by an increase in the picocyanobacteria percent composition more NO₃ is drawn down while compensation through increased diazotroph percent composition results in higher NO₃ concentrations.

Table S7. Sensitivity of modeled average (\pm SD) annual nutrient concentrations (mmol m^{-3}) in each box, and oxygen concentration (mmol m^{-3}) in the OMZ, to the doubling or halving of the sinking rate parameter (s_i) (relative to the standard run) for the different phytoplankton taxa in box 3

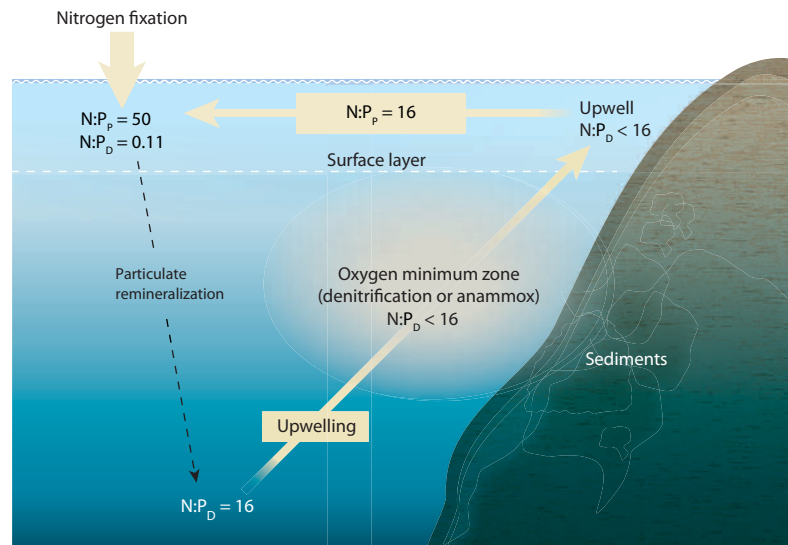
Box 3 sinking (s_i)		Box 2 OMZ	Box 3 Upwelling	Box 4 Transitional	Box 5 Oligotrophic
Standard Run	NO ₃	20.65 \pm 0.027	7.63 \pm 1.40	2.95 \pm 0.050	0.11 \pm 0.020
	PO ₄	2.45 \pm 0.0002	1.14 \pm 0.014	0.65 \pm 0.005	0.24 \pm 0.003
	O ₂	17.79 \pm 0.040			
$s_{Diat} \times 2$	NO ₃	20.75 \pm 0.025	1.99 \pm 1.770	0.01 \pm 0.013	0.003 \pm 0.005
	PO ₄	2.46 \pm 0.0005	0.27 \pm 0.217	0.001 \pm 0.002	0.00 \pm 0.000
	O ₂	15.73 \pm 0.077			
$s_{Diat} \times 0.5$	NO ₃	20.60 \pm 0.028	12.96 \pm 0.923	7.72 \pm 0.059	4.04 \pm 0.015
	PO ₄	2.44 \pm 0.0001	1.74 \pm 0.088	1.25 \pm 0.005	0.85 \pm 0.002
	O ₂	18.82 \pm 0.021			
$s_{Pico} \times 2$	NO ₃	20.67 \pm 0.027	5.60 \pm 1.581	1.34 \pm 0.041	0.01 \pm 0.007
	PO ₄	2.48 \pm 0.0003	1.06 \pm 0.148	0.57 \pm 0.005	0.17 \pm 0.002
	O ₂	17.65 \pm 0.043			
$s_{Pico} \times 0.5$	NO ₃	20.63 \pm 0.027	8.68 \pm 1.302	3.83 \pm 0.694	0.74 \pm 0.012
	PO ₄	2.46 \pm 0.0002	1.19 \pm 0.137	0.69 \pm 0.005	0.30 \pm 0.002
	O ₂	17.87 \pm 0.039			
$s_{Diaz} \times 2$	NO ₃	20.74 \pm 0.025	7.63 \pm 1.397	2.95 \pm 0.048	0.10 \pm 0.012
	PO ₄	2.46 \pm 0.0004	1.14 \pm 0.141	0.65 \pm 0.004	0.25 \pm 0.002
	O ₂	15.73 \pm 0.077			
$s_{Diaz} \times 0.5$	NO ₃	20.63 \pm 0.027	7.65 \pm 1.395	2.97 \pm 0.048	0.11 \pm 0.012
	PO ₄	2.46 \pm 0.0002	1.14 \pm 0.141	0.65 \pm 0.005	0.26 \pm 0.002
	O ₂	17.79 \pm 0.040			



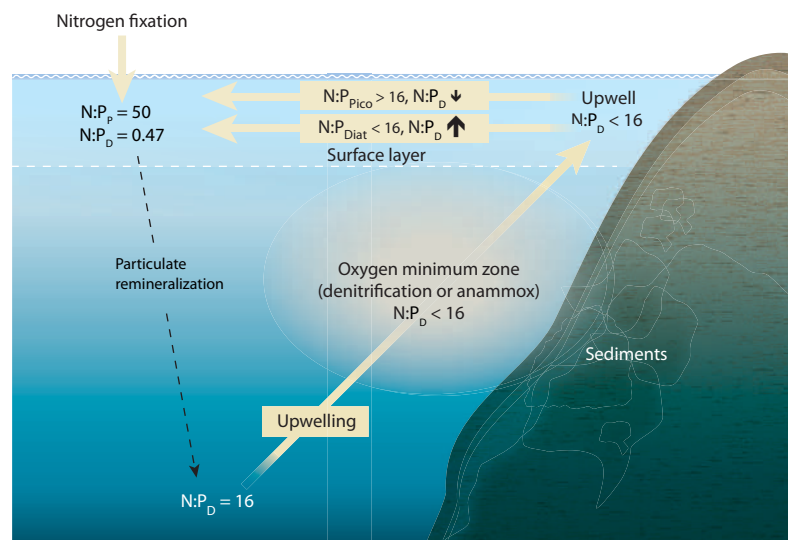
14



a)



b)

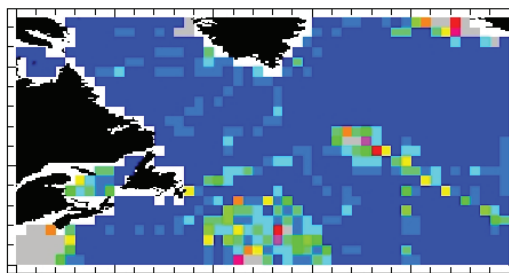


Surface

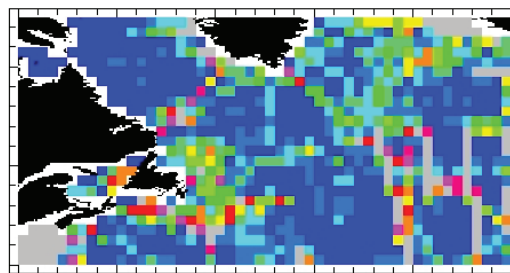
Jan-Mar

Apr-Jun

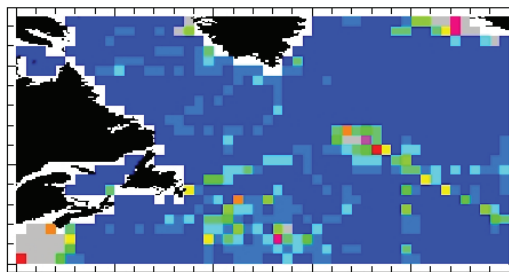
A.

Latitude
60 °N
50 °N
40 °N

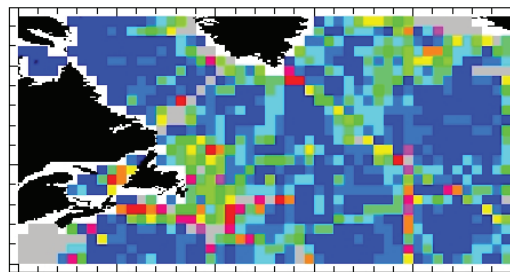
B.

**50 m**

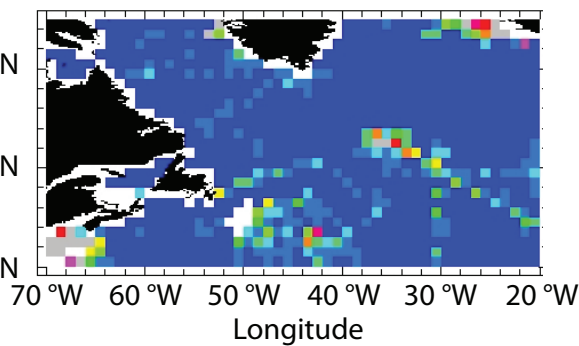
C.

Latitude
60 °N
50 °N
40 °N

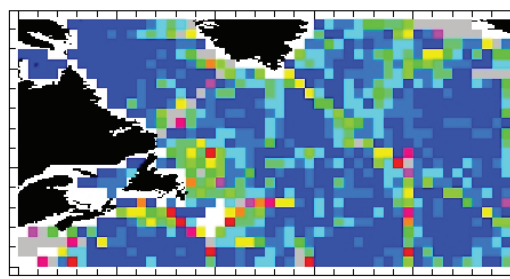
D.

**100 m**

E.

Latitude
60 °N
50 °N
40 °N

F.

Number of PO₄³⁻ observations