

Nutrient Ratios as a Tracer and Driver of Ocean Biogeochemistry

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nutrient cycles, nitrogen, phosphorus, phytoplankton, Redfield ratio, nitrogen fixation, denitrification

Abstract

Microbial life in the ocean contains immense taxonomic and physiological diversity, yet its collective activity yields global cycles of the major biolimiting elements N and P that are tightly linked. Moreover, the availability of N and P in seawater is closely matched to the metabolic demands of “average” plankton, as if plankton composition and the oceanic nutrient reservoirs were mutually influenced. These simple observations have broad implications for the function of nutrient cycles within the Earth system, which can operate either as a biological homeostat that buffers ocean fertility against large changes or as an amplifier of climate perturbations, by alleviating or exacerbating the nutrient limitation of biological productivity and ocean C storage. A mechanistic understanding of these observations and dynamics must draw upon diverse fields, from physiology and evolution to physical oceanography and paleoceanography, and must account for processes spanning a wide range of spatial and temporal scales. Here we summarize this understanding from the perspective of the nutrient distributions themselves and their changes over time. We offer a synthesis view in which ocean circulation communicates the resource constraints of stoichiometrically distinct planktonic biomes across large spatial scales, allowing geochemical constancy to emerge from rich biological diversity.

1. INTRODUCTION

Among the major elemental constituents of marine life, N and P are present in seawater in the lowest concentrations. In the warm, sunlit surface waters of the low-latitude ocean, phytoplankton rapidly consume these nutrients during growth, exporting them to depth in sinking particles of organic matter. Equatorward of the peak westerly winds ($\sim 40^\circ$ latitude), the return of these nutrients via oceanic circulation is largely confined to narrow bands of upwelling near the equator and continental margins, and to episodic pulses by mesoscale eddies. The combination of favorable conditions for photosynthesis and physical constraints on nutrient supply subjects most of the low-latitude ocean biosphere to chronic nutrient limitation. The processes that regulate the cyclic transformations of N and P between inorganic nutrients and organic matter, as well as their exchanges with other parts of the Earth system, have been a major focus of ocean biogeochemistry for several decades. The ratios of N to P in seawater and in the metabolic requirements for plankton growth are of particular interest, as these proportions determine which nutrient will limit biological productivity at the base of the food web and may select plankton communities with distinct biogeochemical function.

The oceanic inventories of N and P are governed by different processes and respond to changes in the Earth system on dissimilar timescales (**Figure 1**). The reservoir of oceanic P reflects primarily a balance between river input and sediment burial. These geologically controlled sources

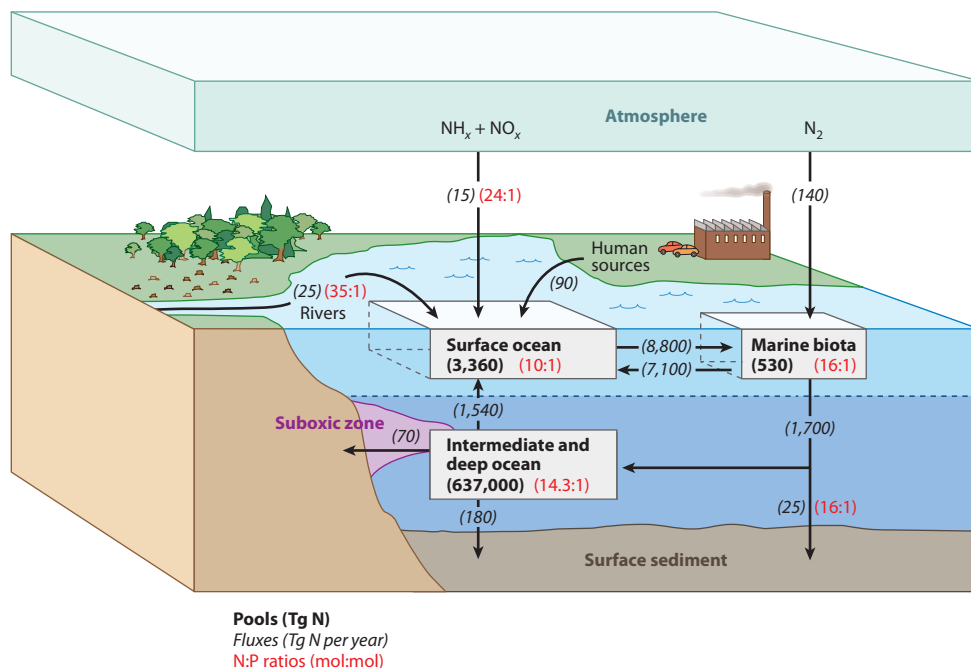


Figure 1

Schematic depiction of major fluxes and reservoirs in the oceanic N and P cycles. Reservoirs [in teragrams (Tg) of N] are shown for NO_3^- only. The rates of biological N_2 fixation (~ 140 Tg per year) and denitrification in the water column (70 Tg per year) and sediments (180 Tg per year) comprise the largest source and sink, respectively, and have no counterpart in the P cycle. Smaller preindustrial N inputs from the atmosphere (Duce & Tindale 1991) and rivers (Meybeck 1982) and their human perturbations also have high N:P ratios. A balanced N budget is not assumed, but is reached (within the large uncertainties) when anthropogenic inputs are included. Adapted from carbon cycle figure by Sarmiento & Gruber (2002).

and sinks are small relative to the size of the P reservoir (primarily phosphate, PO_4^{3-}), so the characteristic timescale of P equilibration (the residence time) is on the order of 50,000 years (Benitez-Nelson 2000, Froelich et al. 1982, Paytan & McLaughlin 2007). In contrast, sources and sinks of bioavailable N (also known as fixed N; all forms except N_2 , primarily nitrate, NO_3^-) are much larger. This is because the ocean contains an inexhaustible inventory of gaseous N_2 , which can be converted to bioavailable N by diazotrophic plankton capable of biological N_2 fixation (Karl et al. 2002). Replenishment of the N inventory is necessitated by the rapid microbial losses of N in anoxic marine environments, where nitrate (as well as NO_2^- and NH_4^+) is reduced to N_2 through a combination of heterotrophic denitrification (Codispoti & Richards 1976, Ward et al. 2009) and anaerobic ammonium oxidation (Kuypers et al. 2005, Lam et al. 2009). These biologically mediated N sources and sinks exceed preindustrial riverine input and atmospheric deposition and sediment burial by roughly an order of magnitude (Brandes & Devol 2002, Codispoti et al. 2001, Gruber 2003). The marine N cycle differs from that of P in that it is biologically rather than geologically controlled and subject to change over correspondingly faster timescales (McElroy 1983).

The global source and sink processes for both N and P account for only a small fraction of overall nutrient transformation within the ocean, which is instead dominated by rapid and nearly balanced rates of net surface nutrient uptake by phytoplankton and subsurface bacterial remineralization (**Figure 1**). Like their sources and sinks (hereafter referred to as budgets) the transformations within marine N and P reservoirs (hereafter referred to as cycles) are also driven by different processes, at least at a physiological level. At the cellular scale, the organic molecules used for resource acquisition (such as proteins and pigments) require substantially more N per atom of P than does the molecular machinery of growth and reproduction (DNA and RNA) (Arrigo 2005, Sterner & Elser 2002). The partition of biomass among these different classes of organic molecules largely determines overall cellular stoichiometry (Geider & La Roche 2002), and reflects both the evolutionary history of plankton lineages (Falkowski 2000, Quigg et al. 2003) and physiological adaptation of organisms to environmental conditions (Finkel et al. 2006, Price 2005). As a result, the N:P ratio of measured phytoplankton species varies by severalfold around its mean value of $\sim 15:1$ (**Figure 2**).

Despite these fundamental differences in the role of N and P in the cycles and budgets of oceanic nutrients, the global distributions of nitrate and phosphate are among the most highly correlated properties of the ocean (**Figure 3**). The strong relationship between these nutrients ($R^2 = 0.98$) has long been taken to imply a universal stoichiometry, at least at the scale of the plankton community. Moreover, the mean oceanic $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio (14.3N:1P) is close to the mean biomass N:P of plankton, a fact first elaborated by Redfield and colleagues (Redfield 1958, Redfield et al. 1963). Thus, the internal cycles of N and P, which maintain a strong large-scale $\text{NO}_3^-:\text{PO}_4^{3-}$ covariation, would appear to be closely connected to their external budgets, which currently sustain an overall inventory of those nutrients in nearly the same ratio. The notion of a constant N:P ratio of plankton, known as the Redfield ratio (hereafter referred to as R_0 , and taken to have a value of 16N:1P), has become a cornerstone of biogeochemistry.

Redfield concluded that this state of affairs must not be a coincidence, but rather the result of coupled dynamics of the P and N cycles (Redfield 1958) (**Figure 4**). He proposed a self-stabilizing feedback, which hinges on a relationship between the $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio of the ocean and the competitive advantage of N_2 -fixing organisms. When N becomes depleted relative to P, organisms capable of using the excess P by fixing new N should find an expanded ecological niche, and the N inventory would rise. As the ocean's N and P approach the ratio needed by phytoplankton, the energetically costly process of N_2 fixation would be discouraged because P would be rapidly consumed by non- N_2 -fixing plankton. The increased N inventory may also initiate alternate feedbacks involving N sinks (Codispoti 1989). With N limitation partly alleviated,

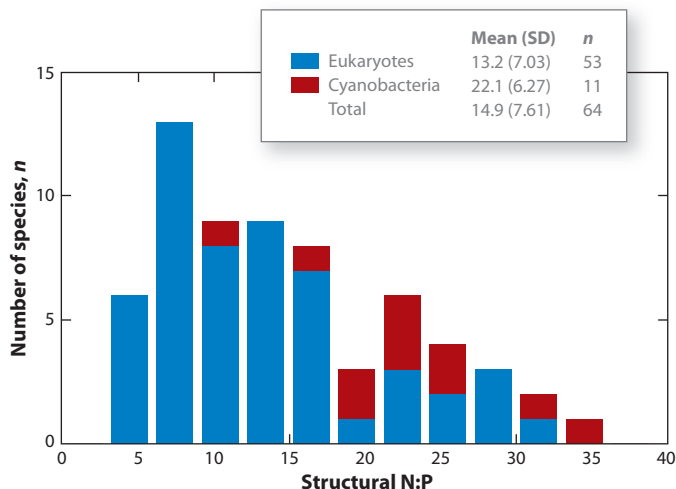


Figure 2

Histogram of cellular N:P ratios for laboratory cultures of marine phytoplankton. Populations were grown in chemostats under optimal growth conditions, so that the biomass N:P ratio can be assumed to reflect allocation to structural components. A total of 64 species are compiled from published studies by Bertilsson et al. (2003), Geider & La Roche (2002), Heldal et al. (2003), Klausmeier et al. (2004), and Quigg et al. (2003).

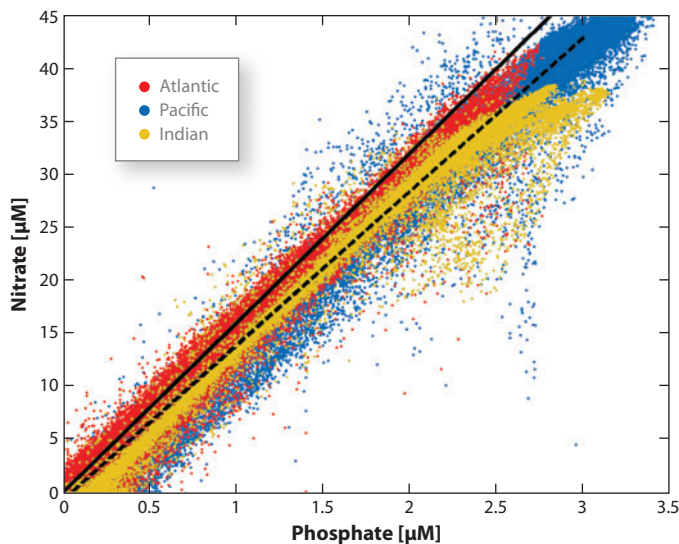


Figure 3

Global relationship between NO_3^- and PO_4^{3-} concentrations based on the Global Ocean Data Analysis Project (GLODAP) (Key et al. 2004). Bottle data were binned onto 33 standard depth intervals and onto a 1° latitude/longitude grid. Colors delineate the Atlantic (*red*), Pacific (*blue*), and Indian (*yellow*) ocean basins. The solid line through the origin has a slope of mean plankton biomass (16:1). The dashed line is the linear regression (slope = 14.5), which is less than the 16:1 ratio of plankton because NO_3^- is removed via denitrification in high-nutrient areas and added via remineralization of N_2 -fixer biomass in low-nutrient areas.

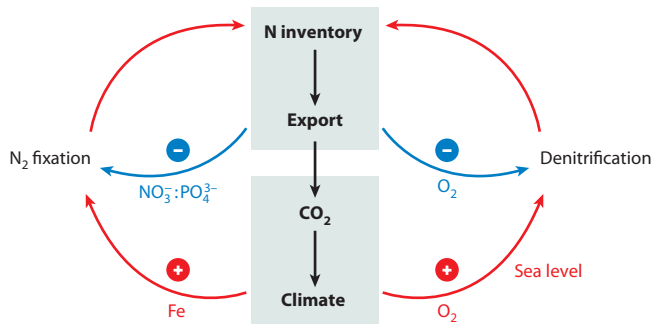


Figure 4

Schematic depiction of forcings and feedbacks in the N budget. Each step in the feedback mechanism involves a direct proportionality (arrow with plus sign) or an inverse proportionality (arrow with minus sign). Warm climates may reduce oxygenation of the ocean interior (e.g., via solubility and/or stratification), expanding the suboxic habitat for denitrifying bacteria; at the same time, these climates also reduce delivery of Fe-bearing dust to the surface ocean (e.g., via atmospheric moistening), decreasing the viable areas for diazotrophic plankton. Both perturbations decrease the N inventory, weakening the biological C pump and amplifying the climate perturbation. This positive climate feedback may function only if negative feedbacks are not initiated by the changes in N sources or sinks. The reduced productivity should allow suboxic zones to shrink, counteracting the climate-driven increase in denitrification. Meanwhile, the reduction of the N:P ratio of the nutrient supply to the surface ocean expands the potential niche of N_2 -fixing organisms, counteracting the supposed climate-driven increase in Fe supply. Adapted from Deutsch et al. (2004).

organic C export and its respiration in the deep ocean would increase, causing denitrification rates to rise within expanded anoxic regions of the water column, and to a lesser degree in sediments, counteracting the initial rise in nitrate. Together, these restorative feedbacks will act like a nutrient thermostat, stabilizing the N inventory by linking it to the inertia of the P reservoir, at a ratio slightly below the mean plankton quota.

The efficacy of the ocean's nutrient thermostat depends on the sensitivity of N_2 fixation and denitrification to changes in the severity of N limitation, and thus the global $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio. However, these processes are also influenced by other environmental factors, so that climate forcing can in principle overwhelm the stabilizing feedbacks. Climatic changes in anoxic extent have been shown to induce large changes in denitrification rates across glacial–interglacial transitions (Altabet et al. 1995, Ganeshram et al. 1995) and on decadal timescales (Deutsch et al. 2011). The supply of Fe has also been hypothesized to exert overriding control on diazotrophs owing to the high Fe quota for the nitrogenase enzyme system (Berman–Frank et al 2001, Kustka et al 2003). This would promote N_2 fixation during dustier glacial climates (Broecker & Henderson 1998, Falkowski 1997), and may also modulate N_2 fixation rates on decadal timescales (Moore & Doney 2007, Moore et al. 2006). In contrast to the nutrient thermostat, these dynamics would operate collectively as a climate amplifier by adding N and increasing C storage during cold and dusty climates when O_2 and Fe are high, and removing it in warm climate epochs. Other physiological sensitivities of diazotrophs may have the opposite influence, however, favoring N_2 fixation during warm climates with strong stratification (Karl et al 2001a) and higher $p\text{CO}_2$ (Hutchins et al 2007).

The role of climate forcing and biological feedbacks in governing the ocean's $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio can be illustrated with a simple conceptual model (Tyrrell 1999) (**Figure 5**). For relatively slow-growing diazotrophs to coexist with other plankton, the mean ocean $\text{NO}_3^-:\text{PO}_4^{3-}$ must fall below the average plankton N:P quota. The magnitude of the NO_3^- deficit depends on both the growth-rate handicap for diazotrophs (which may vary, e.g., because of Fe) and the rate of denitrification (which will vary with ocean oxygenation). Over a wide range of these parameters, the presence

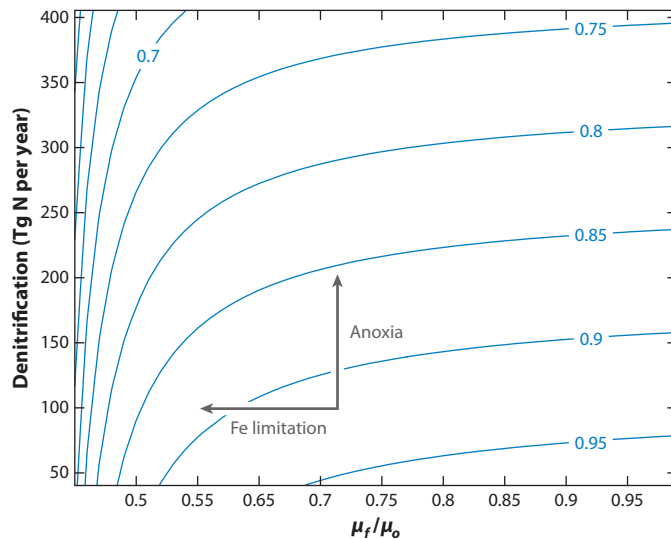


Figure 5

Steady-state mean ocean $\text{NO}_3^-:\text{PO}_4^{3-}$ and its dependency on the total denitrification rate (in teragrams of N per year) and the growth rate of diazotrophs relative to other plankton (μ_f/μ_o), according to a box model (Tyrrell 1999). The $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio is normalized by the biomass N:P ratio of non- N_2 -fixing plankton, which is $\sim 16:1$ in the modern ocean but may take other values. The ocean N inventory cannot exceed the N:P ratio of mean plankton, but approaches that value either when diazotrophs experience little growth-rate handicap or when denitrification is slow.

of negative feedbacks restricts the range of $\text{NO}_3^-:\text{PO}_4^{3-}$ ratios to $\pm 30\%$. However, these factors determine the ocean's nutrient ratio only in relation to the biomass N:P of non- N_2 -fixing plankton, which provides the only means by which the upper bound on deep ocean $\text{NO}_3^-:\text{PO}_4^{3-}$ may be lifted above R_o , allowing productivity to exceed the limit imposed by a fixed ocean P reservoir (Broecker 1982). The mean biomass N:P of plankton therefore acts as the set point of the ocean's nutrient thermostat, a fundamental determinant of ocean fertility that is independent of the N budget and for which no theory currently exists.

The close coupling of both the cycles and budgets of N and P suggests that the myriad actions of ocean microbes with flexible stoichiometries, some with complex metabolisms that add or remove fixed N, produce a seemingly coordinated effect on global nutrient dynamics. The fundamental basis for such organized outcomes might be that as life transforms its chemical environment, it is in turn constrained by those very transformations. However, the apparent coupling at large scales and the flexibility of N:P stoichiometry at biological scales has not been reconciled, and poses major questions about the operation of nutrient cycles in the Earth system:

- What determines the mean N:P ratio of the ocean's plankton ecosystems?
- At what spatial and temporal scales does it vary?
- How do these variations affect the feedbacks that couple the N and P cycles and regulate ocean fertility?
- To what degree can these regulatory feedbacks be overwhelmed by climatic forcing?

Naturally, the nutrient distributions themselves contain numerous clues to these questions. In this review, we take up the current status of understanding the distributions of key processes that maintain the coupling of the N and P cycles. We do this by summarizing what is known about deviations from a constant $\text{NO}_3^-:\text{PO}_4^{3-}$ relationship. Comprehensive discussion of some of the

individual processes can be found in other reviews (Brandes et al. 2007, Gruber 2003, Karl et al. 2002, Zehr & Kudela 2011).

2. STOICHIOMETRIC TRACERS OF NUTRIENT CYCLES AND BUDGETS

The composition, function, and material fluxes of plankton ecosystems vary on spatial scales of kilometers and evolve over timescales of days. Understanding variations at these scales is necessary to achieve a mechanistic understanding of oceanic nutrient stoichiometry. However, an assessment of their integrated effect on the ocean's stoichiometric balance relies on geochemical tracers that naturally integrate the short-term and small-scale fluctuations in biological processes. The integrative nature of tracer constraints is a double-edged sword, however: Extracting quantitative information from chemical distributions requires detailed knowledge about physical circulation and mixing, often resulting in rather coarse-grained views of the processes of interest. And over large scales, tracers are more likely to integrate (in a confounding sense) multiple processes. Still, some of the major revisions to the understanding of N budget processes have come from these approaches, although large uncertainties remain.

2.1. Measures and Patterns of N:P Variation

Variations in nutrient stoichiometry of seawater can be quantified with either of two metrics (**Figure 6**). Perhaps the most natural is the $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio, because it can be easily compared against the cellular quota of phytoplankton to determine whether plankton growth in a given water mass will become N or P limited. However, it is a poor indicator of biological stoichiometry for two reasons. First, the analytical errors in the determination of $\text{NO}_3^-:\text{PO}_4^{3-}$ ratios become quite large as nutrient concentrations become small (Fanning 1992). Second, the $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio is not conserved by two of the most pervasive processes in the upper ocean—physical mixing and uptake/remineralization at the ratio R_0 (**Figure 6a**). These difficulties can be circumvented by using a linear combination of NO_3^- and PO_4^{3-} that is conserved by both these processes (Deutsch et al.

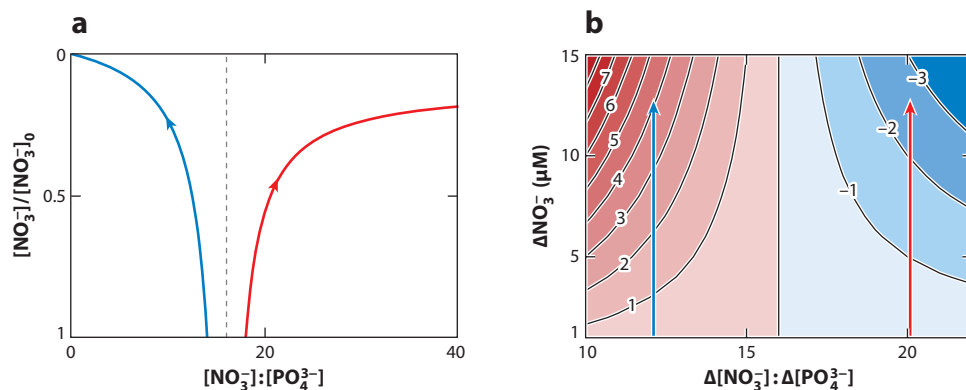


Figure 6

Effects of nutrient consumption on (a) the $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio and (b) N^* . In panel a, for a water parcel with $N^* > 0$, nutrient consumption at the Redfield ratio (R_0) leads to an increase in the residual $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio (red arrow), whereas an initial $N^* < 0$ leads to the opposite trend (blue arrow). In panel b, nutrient consumption decreases N^* (contours $\Delta N^* < 0$) when it occurs at a ratio above R_0 ($= 20:1$) and increases N^* (contours $\Delta N^* > 0$) when consumption ratios are low (blue arrow = 12:1), regardless of the initial N^* value.

2001, Gruber & Sarmiento 1997, Hansell et al. 2004, Michaels et al. 1996). Among the various expressions that have been used, we adopt the simplest: $N^* = [\text{NO}_3^-] - 16[\text{PO}_4^{3-}]$. This quantity has a concrete interpretation—namely, the excess of NO_3^- relative to PO_4^{3-} , for the growth of average plankton. Its value reflects the net effect of N_2 fixation (which increases N^*) and denitrification (which decreases N^*), but can also be significantly altered by uptake and remineralization of N and P by plankton with an N:P ratio above or below R_0 (Figure 6b).

The mean N^* among global measurements (Figure 3) is approximately $-3.5 \mu\text{M}$, indicating that for average phytoplankton, mean ocean water is deficient in NO_3^- by $\sim 10\%$ relative to PO_4^{3-} . An excess of NO_3^- (i.e., $N^* > 0$) is rare, occurring in only $\sim 3\%$ of global measurements, similar to the frequency of N^* values below $-10 \mu\text{M}$. Most of this range of N^* variation is evident at time-series stations in the subtropical North Pacific [Hawaii Ocean Time-Series (HOT)] and North Atlantic [Bermuda Atlantic Time-Series (BATS)] (Figure 7). In the Pacific, the $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio decreases upward from $\sim 13:1$ at 400 m to near zero at the surface. In contrast, Atlantic $\text{NO}_3^-:\text{PO}_4^{3-}$ ratios increase upward, reaching values of $\sim 30:1$ in the photic zone (Wu et al 2000). In the Pacific,

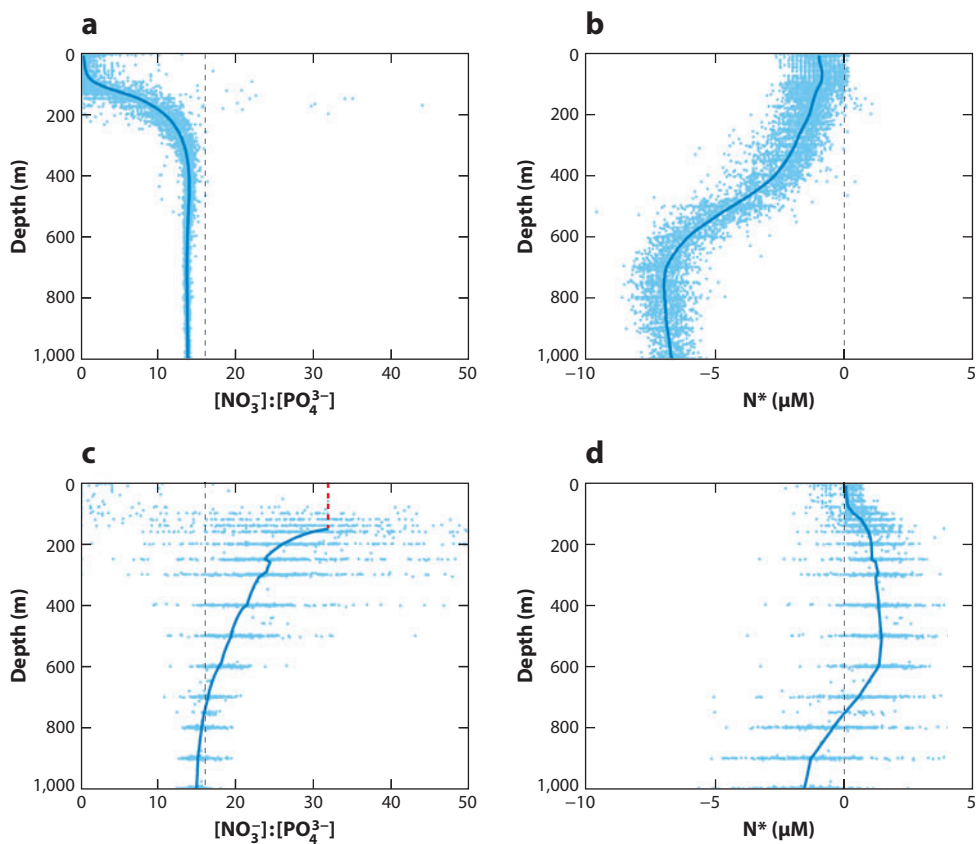


Figure 7

Depth profiles of $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio (panels *a* and *c*), and N^* (*b* and *d*) from ocean time-series stations near Hawaii (*a* and *b*) and Bermuda (*c* and *d*). Light blue points are values binned into regular depth intervals for each month since the program inception. Blue lines are average profiles from the entire time period. The red dashed line indicates the approximate surface value from high-precision measurements reported by Wu et al. (2000). Grey dashed lines are shown for $\text{NO}_3^-:\text{PO}_4^{3-} = 16:1$ and $N^* = 0$.

N^* is negative throughout the water column and decreases with depth, while the Atlantic has an excess of nitrate ($N^* > 1 \mu\text{M}$) throughout much of the thermocline (100–800 m) but returns toward global mean values in the deep water and toward zero at the surface, where both nutrients are strongly depleted. The antisymmetry of $\text{NO}_3^-:\text{PO}_4^{3-}$ ratios at these sites resembles the effect of Redfield uptake (Figure 6), but thermocline N:P differences are generally attributed to N budget processes, N_2 fixation, and denitrification.

2.2. Dissolved Organic Matter

Dissolved organic matter (DOM) is a major reservoir of surface N and P, typically exceeding the concentration of inorganic nutrients in oligotrophic regions by an order of magnitude (Church et al. 2002). It therefore plays an important role in the nutrient supply that sustains phytoplankton growth (Williams & Follows 1998). Although DOM represents a complex mixture of compounds whose chemical characterization is far from complete, it is clear that the elemental stoichiometry of DOM differs dramatically from canonical ratios. And although these pools remain sparsely sampled, oceanic transects indicate that the deviations from R_0 exhibit coherent large-scale structure.

In general, studies of the elemental stoichiometry of DOM and sinking organic matter suggest that dissolved organic P (DOP) is more reactive than dissolved organic N (DON) and has substantially faster turnover (Clark et al. 1998). Transects in both the Pacific (Abell et al. 2000) and Atlantic (Torres-Valdes et al. 2009) show less variation in DON than in DOP, both in vertical and meridional gradients. In both basins, DOP undergoes a marked drop from the tropics, where it is produced, to the subtropical gyre, where it is consumed. Over the same distance, DON is much less variable. This suggests that differential production and degradation of DON and DOP among components of DOM with lifetimes comparable to the gyre circulation have a significant effect on overall stoichiometry of nutrient supply and utilization in the surface ocean.

The apparent reactivity of DOP relative to DON stems in part from the relative ease with which plankton can use it as a substrate for growth (Bjorkman & Karl 2003). The well-studied diazotrophs *Trichodesmium* spp. can directly access DOP (Dyhrman et al. 2006), whereas picocyanobacteria have the capacity to replace P-based membrane lipids with ones based on sulfur (Van Mooy et al. 2009). These metabolic switches likely represent critical adaptations of plankton to the low- PO_4^{3-} environments in which they are dominant. At the same time, many diazotrophs release a substantial fraction of the newly fixed N to the surrounding environment as DON (Mulholland 2007). These and other factors likely contribute to the observed gradients of the surface DON:DOP ratio and enhance the effective supply of P in oligotrophic regions relative to N.

2.3. Tracing N Sources and Sinks

The spatial heterogeneity, episodic nature, and taxonomic diversity of N fixation and denitrification/anammox (Capone et al. 2005, Lam et al. 2009, Moisander et al. 2010, Montoya et al. 2004, Needoba et al. 2007, Ward et al. 2009, Zehr et al. 2001) motivate the use of geochemical tracers to infer spatial distributions and rates that can be considered representative of time-mean conditions. Geochemical estimates of both N_2 fixation and denitrification have relied heavily on the distributions of the major macronutrients, NO_3^- and PO_4^{3-} . Assuming that N_2 fixation and denitrification are the sole source of non-Redfield N and P fluxes (but see Section 2.4), the physical transport and mixing of N^* can be related to the net rate of N_2 fixation (F) and denitrification (D):

$$\frac{dN^*}{dt} - \nabla \cdot (\kappa \nabla N^*) = a_1 F - a_2 D, \quad (1)$$

where the left side is the time derivative following a water parcel and the diffusive transport, and a_1 and a_2 are constants of order one whose precise values depend on the stoichiometric ratios

of the source/sink processes. Because the broad distribution of N^* is known from observations (**Figure 8**), the pattern of N_2 fixation or denitrification can in theory be estimated by computing the physical fluxes of N^* , whose steady-state convergence (divergence) must equal the rate of N_2 fixation (denitrification).

The global extremes of N^* are contained within the oceanic thermocline (**Figure 8a**). Along a surface of constant potential density, $\sigma_\theta = 26.5$ at depths of 200–600 m, waters are shallow enough to bear the regional signatures of high N:P remineralization from diazotrophic organic matter and N loss from denitrification in suboxic zones and shallow sediments.

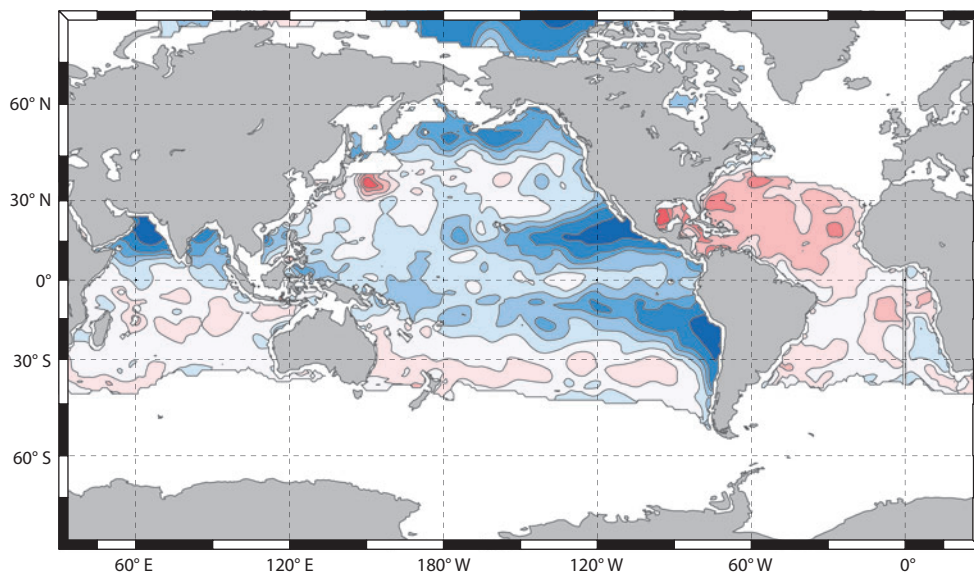
Global N^* minima are found in the Eastern Tropical Pacific and in the Arabian Sea associated with anoxia. Although the process of denitrification is confined to anoxic zones, its signature is transported well beyond them. In the Pacific, the extreme nitrate deficits ($N^* < -20 \mu\text{M}$) along the coasts of North and South America are transported westward by the North and South Equatorial Currents (Deutsch et al. 2001), poleward in coastal undercurrents (Castro et al. 2001, Silva et al. 2009), and toward the surface by upwelling. The earliest tracer-based estimates of denitrification rates used concurrent estimates of the NO_3^- deficit and geostrophic velocities along transects surrounding the anoxic zone of the Eastern Tropical North Pacific (Codispoti & Richards 1976). Subsequent studies used N^* distributions together with transient tracers of water mass residence time to estimate N loss rates in the Arabian Sea (Howell et al. 1997) and in the Eastern Tropical South Pacific and Eastern Tropical North Pacific (Deutsch et al. 2001) at a collective rate of 60–90 Tg N per year (**Figure 1**).

Large regions of low N^* can also be seen in waters that are not anoxic but are overlying expansive continental shelf sediments where rates of organic C deposition are high, and denitrification in sedimentary pore waters extracts nitrate from bottom water. This is particularly evident in the subarctic North Pacific and in the Arctic waters entering the North Atlantic (Devol et al. 1997, Yamamoto-Kawai et al. 2006). Although sedimentary denitrification is thought to be the largest sink for fixed N (Brandes & Devol 2002), its clear signature in N^* has never been used to estimate global rates, likely owing to the complex circulations among heterogeneous continental margin environments.

A broad global N^* maximum stretches across much of the tropical and subtropical North Atlantic thermocline, indicating N inputs to the basin. Numerous studies have estimated its rate of accumulation, differing significantly on its rate and causal origin (Bates & Hansell 2004; Gruber & Sarmiento 1997; Hansell et al. 2004, 2007; Landolfi et al. 2008; Michaels et al. 1996; Zamora et al. 2010). The earlier work attributed most of the signal to the remineralization of diazotrophs that sink from the surface ocean and are remineralized with a high biomass N:P ratio (R_f) (Gruber & Sarmiento 1997, Michaels et al. 1996). The inferred rate of N_2 fixation is sensitive to R_f (entering into the coefficient a_1 in Equation 1), which is probably highly variable within and between species (White et al. 2006). More recent estimates have highlighted the role of atmospheric N deposition and the differential decomposition of DON and DOP in generating the thermocline N^* maximum. These contributions are difficult to assess because they are largely determined by surface processes where airborne nutrients are deposited and the initial DON:DOP ratio of water masses is set. The rates at which newly fixed N is released by diazotrophs into surface waters (as NH_4 or DON) is also not estimable from thermocline N^* , yet may be substantial given the high degree of nutrient recycling in the oligotrophic ocean.

Surface distributions of N^* provide additional constraints on the stoichiometry of surface biological processes, including N_2 fixation. The climatological distribution of N^* in global surface waters (**Figure 8b**) includes larger-than-average NO_3^- deficits ($N^* < -4 \mu\text{M}$) in much of the tropical and subpolar Pacific, in the northern Indian Ocean, and in the northwest and southeast Atlantic. Elsewhere, NO_3^- has no significant deficit or surplus ($N^* \sim 0$). The rate at which NO_3^-

a Isopycnal surface ($\sigma_\theta = 26.5$)



b Surface waters (0–75 m)

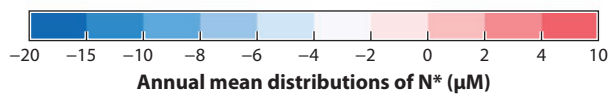
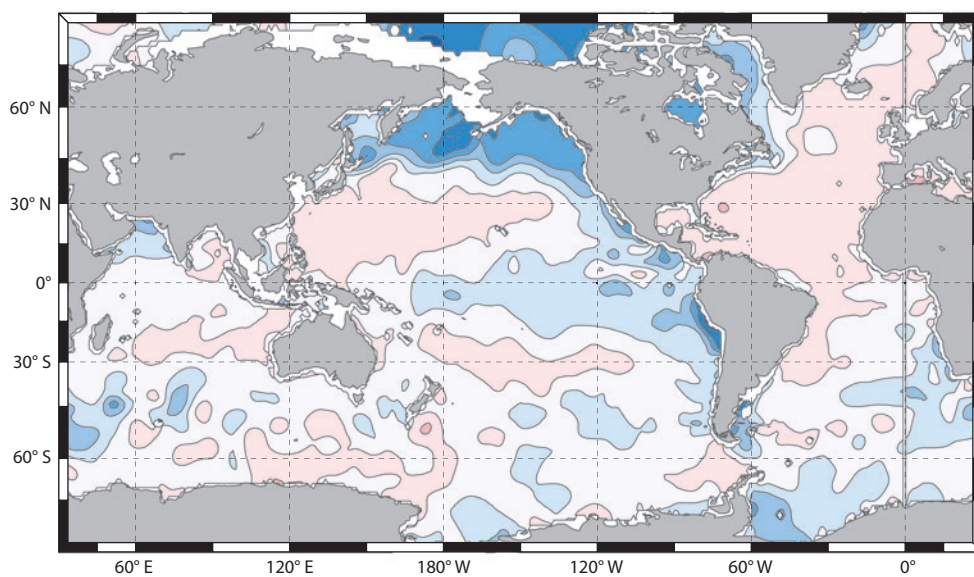


Figure 8

Annual mean distributions of N^* (in micromolar) (*a*) along the isopycnal surface ($\sigma_\theta = 26.5$) and (*b*) in surface waters (0–75 m), based on Garcia et al. (2005).

deficits disappear as waters circulate through the oceanic surface layer is a reflection of non-Redfield nutrient uptake and can be directly related to N_2 fixation, assuming all other plankton follow the canonical 16:1 ratio. Deutsch et al. (2007) computed N:P ratios of nutrient uptake by assimilating global distributions of NO_3^- and PO_4^{3-} (along with sparse DON and DOP data; see Section 2.2) into an ocean general circulation model to derive geographical patterns and rates of N_2 fixation. In contrast to the impression given by distributions of N^* in the thermocline, the rates of N_2 fixation diagnosed from surface nutrients are larger in the Pacific than in the Atlantic. Similar basin-scale differences are inferred using remote sensing of *Trichodesmium* (Westberry & Siegel 2006). The patterns suggest that waters with a recent history of denitrification help stimulate N_2 fixation by conferring an ecological advantage to diazotrophs. To the degree that other factors such as airborne Fe supply might restrict this niche, they do not prevent diazotrophs from erasing most of the NO_3^- deficit in the basins where it is created by denitrification.

Direct observations of N_2 fixation rates have shown significant correlations between atmospheric Fe supply and/or in situ Fe concentration in the Atlantic (Moore et al. 2009) and Pacific (Moutin et al. 2008), although periods with no correspondence have also been reported (Tyrrell et al. 2003). P limitation may limit N inputs by *Trichodesmium* in the Atlantic (Sañudo-Wilhelmy et al. 2001), where Fe is relatively abundant; in the oligotrophic South Pacific, diazotrophs responded only weakly to both P and Fe (Bonnet et al. 2008). The lack of a clear connection between N_2 fixation rates and either Fe or P may reflect a more complex situation of Fe/P colimitation (Mills et al. 2004) as well as factors beyond this simple dichotomy. Ideally, the distribution of N_2 fixation derived from direct measurements and tracer-based approaches would converge on a consensus about the relative influence of all the environmental constraints and stimuli. Inherent differences in temporal and spatial scales represented in these two approaches complicate direct geographic comparisons, and a global analysis of statistical relationships to environmental factors has not been conducted. To the degree that robust in situ rate measurements of N_2 fixation cannot be reconciled with geochemical rates, it highlights the need to relax the assumption of a universal stoichiometry upon which the latter are based (Mills & Arrigo 2010, Zamora et al. 2010).

2.4. Tracing Deviations from Redfield Cycling

Nutrient-based tracers of N sources and sinks assume that the faster internal cycles of N and P are connected in fixed Redfield proportions, so that their influence on seawater chemistry can be removed using N^* . The relationship between deep NO_3^- and deep PO_4^{3-} offers prima facie support for this assumption, but it has not been reconciled with the wide spectrum of N:P variation at biological levels. Some mechanism by which organism-scale N:P variations are averaged out at larger scales is clearly required. First, the local balance and temporal succession of phytoplankton species and phenotypes could reduce the deviation from R_0 in the assemblage as a whole, whereas processing by heterotrophs with a narrower range of N:P ratios could further homogenize the composition of sinking particles (Sterner & Elser 2002). Following Weber & Deutsch (2010), we will refer to such local processes as ecosystem averaging. Second, large-scale circulation and mixing by ocean currents may act to integrate subsurface nutrients between regions with different planktonic N:P ratios, further reducing the apparent stoichiometric flexibility, a process we will refer to as circulation averaging. To assess the stoichiometric averaging mechanisms described above, we review the evidence for N:P flexibility across multiple scales, from plankton culture experiments to the formation and export of organic matter in near-surface waters to its remineralization in the heterotrophic deep ocean.

The stoichiometry of nutrient assimilation by phytoplankton at the base of the marine food web has been extensively investigated in laboratory experiments (Goldman et al. 1979), field studies

(Geider & La Roche 2002), and models (Klausmeier et al. 2004). Although broad syntheses tend to find a mean elemental composition similar to R_0 , variations in N:P between taxa and growth conditions span at least an order of magnitude (**Supplemental Figure 1**; follow the **Supplemental Material link** from the Annual Reviews home page at <http://www.annualreviews.org>). Growth limitation by either NO_3^- or PO_4^{3-} promotes luxury uptake and storage of the nonlimiting nutrient, drawing cellular N:P quotas toward that of the growth medium (Rhee 1978). Extended exposure to a particular environmental forcing can stimulate physiological acclimation, whereby an organism changes its cellular allocation among different classes of structural biomolecules, each with distinct N and P requirements. The production of N-rich protein-pigment complexes is favored under light-limited growth, increasing cellular N:P (Finkel et al. 2006). Phosphoglycerides are replaced by other lipids as a P-sparing measure under chronic P starvation (Van Mooy et al. 2009), and allocation to P-rich RNA increases so that high reproductive rates are sustained during bloom growth. In resource-replete cultures, plankton should assimilate nutrients at the optimal ratio for reproduction—an evolutionary trait that varies significantly between plankton families (Quigg et al. 2003). Diatoms and other members of the red plastid superfamily generally exhibit the lowest N:P (<10:1) under such conditions, whereas the abundant marine cyanobacteria *Prochlorococcus* and *Synechococcus* exhibit particularly high ratios (>20:1) (Bertilsson et al. 2003, Heldal et al. 2003).

Little is known about how organism-scale stoichiometry propagates through the food web and is ultimately transmitted to the deep ocean. The stoichiometry of the marine ecosystem as a whole can be estimated from the N and P in surface organic particles, although these measurements can include detritus and adsorbed P as well as intracellular pools (Fu et al. 2005). We compiled particulate N:P observations from numerous sources in the published literature (**Figure 9**). A wide range of N:P ratios (5–33.5) are represented, around a mean value (16.11) close to R_0 , but the sparse nature of these data precludes the identification of systematic spatial patterns. A more fundamental limitation is that most data points represent only a single observation or a brief observational period. At the few stations with longer time series, particle composition was found to vary widely over seasonal, interannual, and decadal timescales (see Section 3), so a single snapshot is unlikely to be representative of mean conditions.

A more integrated view of N and P export fluxes can be obtained from the ratio between NO_3^- and PO_4^{3-} removed from surface waters by the net effect of all ecosystem processes. Several studies have examined local nutrient removal based on time-series data in high-latitude areas with a strong seasonal cycle (Arrigo et al. 1999, De Baar et al. 1997, Green & Sambrotto 2006, Rubin et al. 1998). Throughout the Antarctic Zone of the Southern Ocean (55°–70°S), seasonal NO_3^- and PO_4^{3-} drawdown yields a relatively consistent view of N:P stoichiometry (**Figure 9**). The polar waters are largely characterized by drawdown ratios significantly lower than 16:1, with the exception of a region of deep-water formation in the coastal Ross Sea (Arrigo et al. 2002). Non-Redfield cycling also leaves its signature in the large-scale, time-mean nutrient distributions. Combining NO_3^- and PO_4^{3-} climatologies with an ocean circulation model, Weber & Deutsch (2010) diagnosed nutrient removal ratios in the Southern Ocean along the flow path of upwelling circumpolar deep water. They found a systematic latitudinal trend in N:P drawdown, increasing from 12:1 in the Antarctic Zone to 20:1 in the Subantarctic Zone (35°–50°S) (**Figure 10**).

These diagnostic approaches reveal consistent spatial patterns of exported N:P variability, but not their causes, which may include nutrient storage, phytoplankton community composition, and processing at high trophic levels. In the Antarctic Zone of the Southern Ocean, periods of particularly low N:P nutrient drawdown were associated with blooms of diatoms (Arrigo et al. 1999, De Baar et al. 1997, Green & Sambrotto 2006, Rubin et al. 1998). In the coastal waters of the Ross Sea, Arrigo et al. (1999) found a regional separation between low N:P (~10:1)

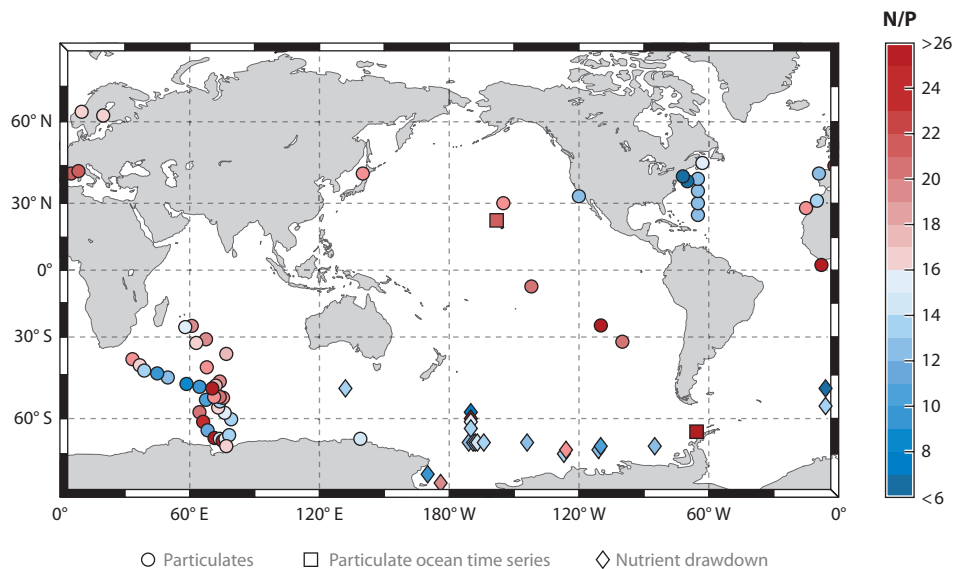


Figure 9

Global distribution of N:P stoichiometry observed in organic particles and nutrient drawdown over seasonal timescales. For time series, the temporal mean is taken across the duration of the study. Particulate data are taken from Geider & La Roche (2002) and references therein (Ducklow 2008, Haug et al. 1973, Raimbault et al. 2008, Yanada & Maita 1978); drawdown data are taken from Arrigo et al. (1999), De Baar et al. (1997), Green & Sambrotto (2006), Rubin et al. (1998), Turner & Owens (1995), and Wang et al. (2003).

drawdown in diatom-dominated waters and high N:P ($\sim 20:1$) in adjacent waters dominated by the prymnesiophyte *Phaeocystis antarctica*. Weber & Deutsch (2010) diagnosed the contribution of diatoms to total organic export across the Southern Ocean from SiO_3 fluxes in an ocean circulation model and found that it could account for 98% of the latitudinal gradient in export stoichiometry, implying a mean diatom N:P of $\sim 11:1$ and a mean N:P for the remaining plankton of $\sim 20:1$.

Following export from the surface layer, the ratio between N and P released from sinking organic particles reflects both their initial composition and any preferential remineralization of either nutrient by heterotrophic bacteria. Both direct (particle-based) and geochemical (nutrient-based) methods have been used to constrain the stoichiometry of remineralization. Particle-based estimates of N:P ratios in sinking flux (Honjo & Manganini 1993) are sparse and may contain significant biases in capture efficiency, especially for P (Antia 2005). Numerous studies of nutrient regeneration ratios in the deep ocean have been made, using estimates of regenerated NO_3^- and PO_4^{3-} along isopycnal surfaces. Nutrients regenerated from sinking organic matter are estimated by subtracting the contribution of preformed nutrients derived from simple end-member mixing models common in water mass analysis (Anderson & Sarmiento 1994, Minster & Boulahdid 1987, Takahashi et al. 1985).

Figure 11 shows the qualitative findings common to most of these studies. Along individual isopycnal surfaces, the correlations between regenerated NO_3^- and PO_4^{3-} are strong, indicating a relatively constant N:P ratio of remineralization. However, a general decrease in N:P is observed with depth toward values significantly lower than 16:1. This trend is opposite to the increase that might be expected from the relative lability of organic P versus organic N (see Section 2.2), and has been interpreted as an additional N removal via sedimentary denitrification, which overprints

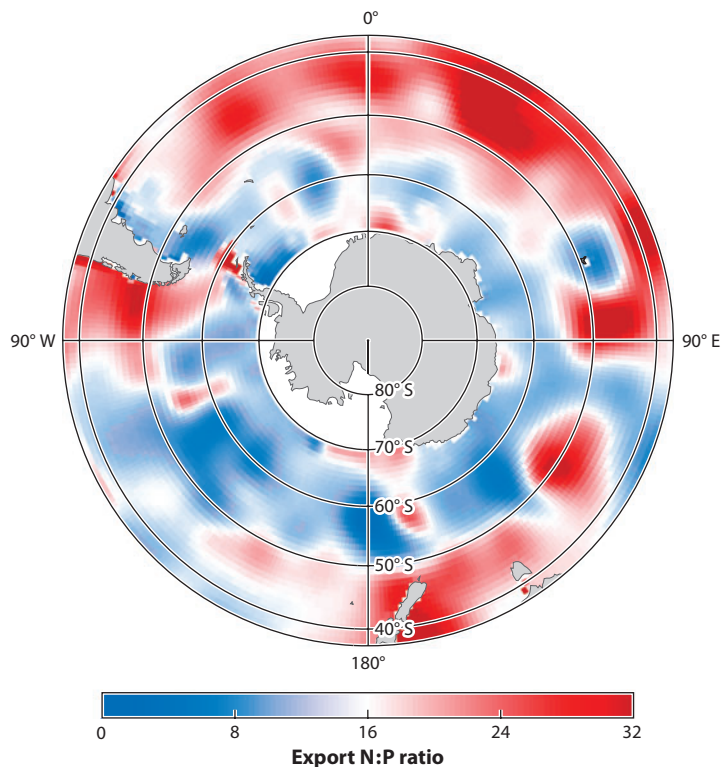


Figure 10

Export N:P ratio diagnosed from climatological nutrient distributions assimilated into an ocean circulation model using a transport matrix from the Estimation of the Circulation and Climate of the Ocean (ECCO) project (Khatiwala 2007). Figure modeled after Weber & Deutsch (2010).

the particle remineralization stoichiometry. Whether the rates of sedimentary denitrification can actually account for the vertical structure of inferred N:P remineralization ratios has not been demonstrated. The variations in these ratios and their methodological uncertainties (Schneider et al. 2005) leave ample room for deviations from a 16:1 ratio at regional and larger scales.

The preceding observations, summarized in **Figure 12**, illustrate the role of both ecosystem averaging and circulation averaging in reconciling the relative constancy of deep-ocean nutrient ratios with the wide-ranging N:P values among plankton species. Species N:P ratios vary broadly between phytoplankton, with taxonomic variations appearing dominant. Because plankton assemblages contain numerous species, part of the organism-scale variability is averaged out locally within the ecosystem, and is not reflected in aggregate particle ratios or net nutrient fluxes from the surface. However, each assemblage does not contain the same balance of species: plankton biogeography is organized by physical properties of the ocean into biomes (Longhurst 1995) with distinct species composition and N:P stoichiometry. It is ocean circulation that must average across these vast spatial scales, homogenizing regenerated nutrients to give the impression of nutrient cycles with a universal stoichiometry. This has been demonstrated in the Southern Ocean, where physical mixing in the subsurface efficiently integrates and homogenizes remineralized nutrients along flow lines, erasing the signature of variable stoichiometry carried by sinking particles (Weber & Deutsch 2010). Thus, the canonical correlation between NO_3^- and PO_4^{3-} only weakly constrains large-scale patterns in the N:P stoichiometry of biological production.

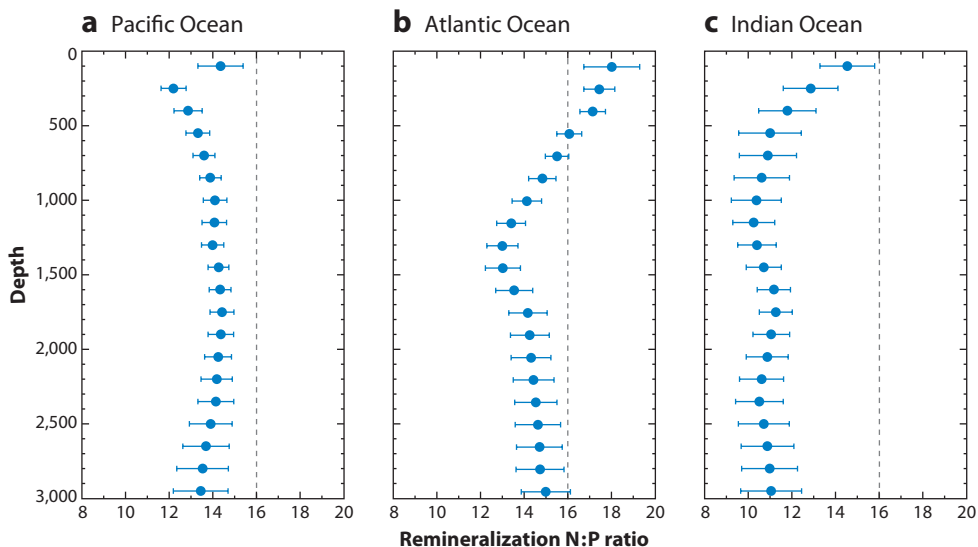


Figure 11

Tracer-derived estimate of relative N and P release from sinking organic particles in the (a) Pacific, (b) Atlantic, and (c) Indian Oceans. Remineralized nutrients (defined as the difference between observed and preformed distributions) are correlated along isopycnal surfaces (plotted versus mean depth for visualization purposes), similar to the technique of Anderson & Sarmiento (1994) and Minster & Boulaïhid (1987). Here, preformed distributions are computed in a coarse-resolution, observationally constrained general circulation model (T. DeVries & F. Primeau, manuscript submitted). The lower N:P ratios along deeper isopycnals (~2,000 m) are interpreted as the signal of sedimentary denitrification.

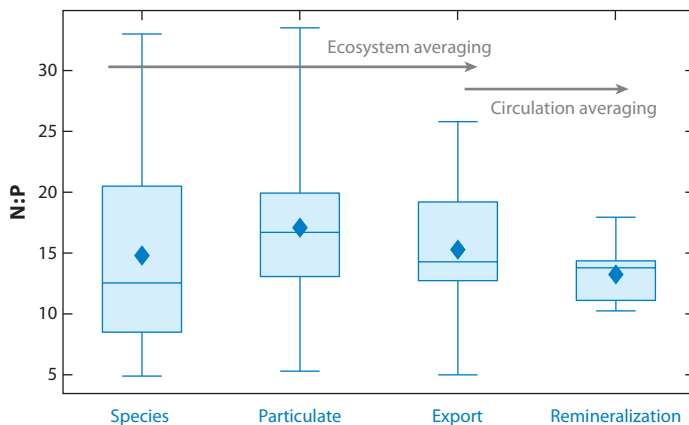


Figure 12

Range of N:P stoichiometry at different levels of the biogeochemical cycle. The reduction in N:P variance between individual species of phytoplankton, organic particles, and nutrient drawdown ratios represents the effects of local ecosystem averaging. The further reduction in N:P variability at the remineralization level reflects the physical mixing of remineralized nutrients between biomes, referred to as circulation averaging in Weber & Deutsch (2010). Box-whisker plots indicate median (*center line*), interquartile range (*box*), and total range (*whiskers*). Blue diamonds indicate the mean.

3. VARIABILITY OVER TIME

The time-mean patterns of N:P stoichiometry (**Figure 8**) provide a critical (albeit foggy) window into the factors that differentiate the metabolic demands of ocean biomes and that promote or constrain the N sources and sinks in the full complexity of natural environments. Changes in N:P stoichiometry over time are potentially even more telling, because they are the only direct source of information about the sensitivity of nutrient stoichiometry to physical and chemical forcings. Our empirical knowledge of temporal variability is limited, but variations in N^* have been observed at a small number of time-series sites, giving important but unresolved clues to the dynamics of nutrient cycles in a changing climate.

3.1. Decadal Variability

Ocean time series have revealed large variations in nutrient stoichiometry on interannual and decadal timescales. In the North Atlantic thermocline at the density of subtropical mode water (STMW, $\sigma_\theta \sim 26.5$) where N^* reaches its maximum value, interannual variations are large, $\sim 3 \mu\text{M}$ (**Figure 13**). Bates & Hansell (2004) hypothesized changes in STMW formation rate as

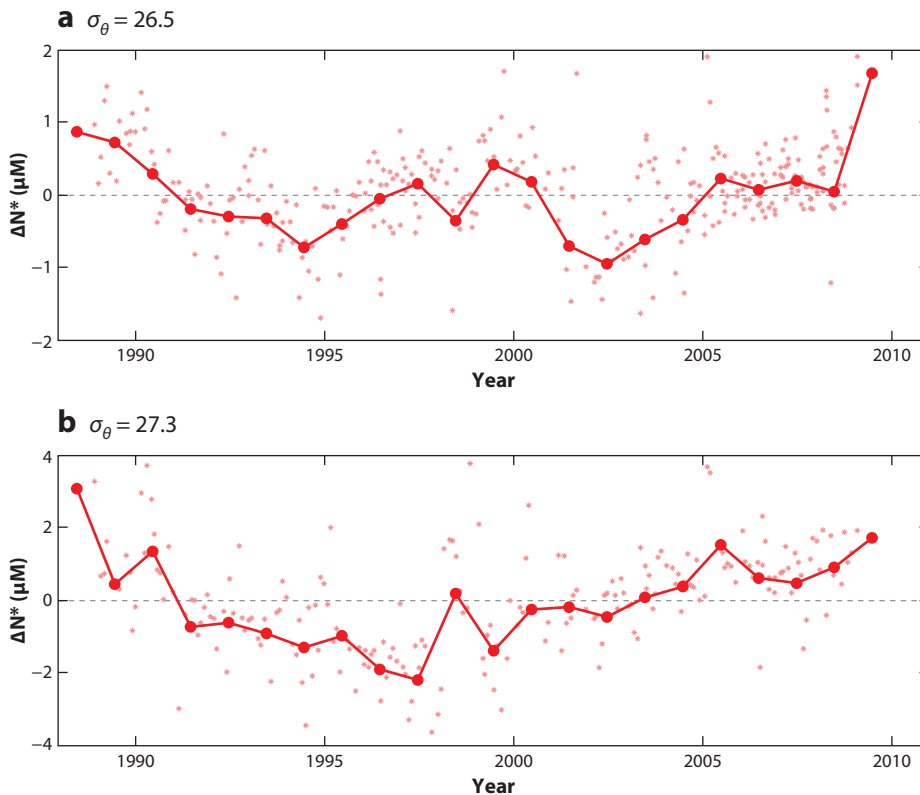


Figure 13

Variability in N^* (in micromolar) from (a) the Bermuda Atlantic Time-Series (BATS) site on constant potential densities of subtropical mode water ($\sigma_\theta = 26.5$) and (b) the upper portion of the Labrador Sea Water ($\sigma_\theta = 27.3$). The low-frequency variation exhibits significant vertical coherence, but its amplitude increases with depth. Updated from Bates & Hansell (2004).

a likely cause, because the rate at which STMW circulates determines the amount of excess NO_3^- (i.e., N^*) that can accumulate before the waters arrive at the BATS site. This interpretation was supported by a correlation between N^* and the North Atlantic Oscillation, which influences the strength of winter cooling and subduction rates in the formation region of STMW. Correlations were also reported between N^* and dust deposition, suggesting that the N_2 fixation rates might vary on decadal timescales. However, the input rate of newly fixed N should decrease with depth, yet the magnitude of variance in N^* increases steadily downward, reaching a maximum at densities of $\sigma_\theta \sim 27.3$ ($\sim 1,000$ m). This suggests that the source of low-frequency variation in STMW may in fact lie partly in the deeper, low- N^* waters ventilating the intermediate depths of the subtropical North Atlantic from high latitudes.

Further indications of the dynamic nature of surface nutrient stoichiometry are found in the N-limited North Pacific Gyre (Church et al. 2002, Karl et al. 2001b) (**Figure 14**). At the HOT site, surface PO_4^{3-} (0–100 m) has declined by roughly half since 1988, from an average PO_4^{3-} value of ~ 0.1 μM before 2001 to ~ 0.05 μM in the period since. In contrast, NO_3^- increased over the same period, leading to a decrease in the N deficit of ~ 1 μM . At the same time, the N:P ratio of suspended particulate organic matter has risen and the stable isotope ratio of organic N collected in sediment traps has declined. Together, these trends indicate an increase in the importance of N_2 fixation as a source of the N fueling export production (Karl et al. 1997, 2001a).

To explain these trends, most studies have focused on the physical mechanisms that supply nutrients to the photic zone and constrain the net productivity of its biota (Bidigare et al. 2009, Corno et al. 2007). Enhanced stratification across the nutricline (200–500-m depth) imposes a higher energetic barrier to the vertical displacements required to supply nutrients from below, producing a more strongly oligotrophic habitat. It is hypothesized that this transition has expanded the relative abundance of diazotrophs, which are not reliant on the NO_3^- supplied by mixing, leading to the observed shift toward a P-limited system (Karl et al. 1997, 2001b). Although this simple physical mechanism is conceptually appealing and compatible with long-term trends in nutrient stoichiometry at the HOT site, significant cyclical variations over shorter timescales have yet to be explained. A comprehensive statistical analysis of physical properties, climate variability, and biological parameters at the HOT site found that stratification of the upper water column explained little of the variance in biological productivity and nutrient export (Dave & Lozier 2010). Among climate indices, El Niño/La Niña and the Pacific Decadal Oscillation were not well correlated with stratification, productivity, or N_2 fixation, although stronger correlations were found for the North Pacific Gyre Oscillation (Di Lorenzo et al. 2008). Similar trends in N^* have been observed in the subpolar North Pacific, but also lack a clear causal mechanism (Watanabe et al. 2008). Identifying the links between climate and the striking changes in nutrient stoichiometry in the North Pacific remains a major challenge.

Time-series stations established in the subtropical gyres are ideally situated to examine long-term changes in N_2 fixation. The major denitrification zones, being more spatially confined, do not benefit from a similar time series. Some indication of the variability of denitrification can be gleaned from the California Cooperative Oceanic Fisheries Investigations (CalCOFI) program, which began nutrient analyses along several transects off the coast of Southern California in the early 1970s. The spatially averaged anomalies in N^* reveal an increase in the nitrate deficit of thermocline waters since the early to mid-1980s (**Figure 14b**). The phasing and sign of the N^* anomalies are consistent with model-predicted changes in the scale and intensity of suboxic conditions in the Eastern Tropical North Pacific since 1960, which are driven by a basin-scale mode of low-frequency thermocline depth variations closely related to the Pacific Decadal Oscillation (Deutsch et al. 2011). The large amplitude of decadal changes in denitrification rates (\sim fourfold)

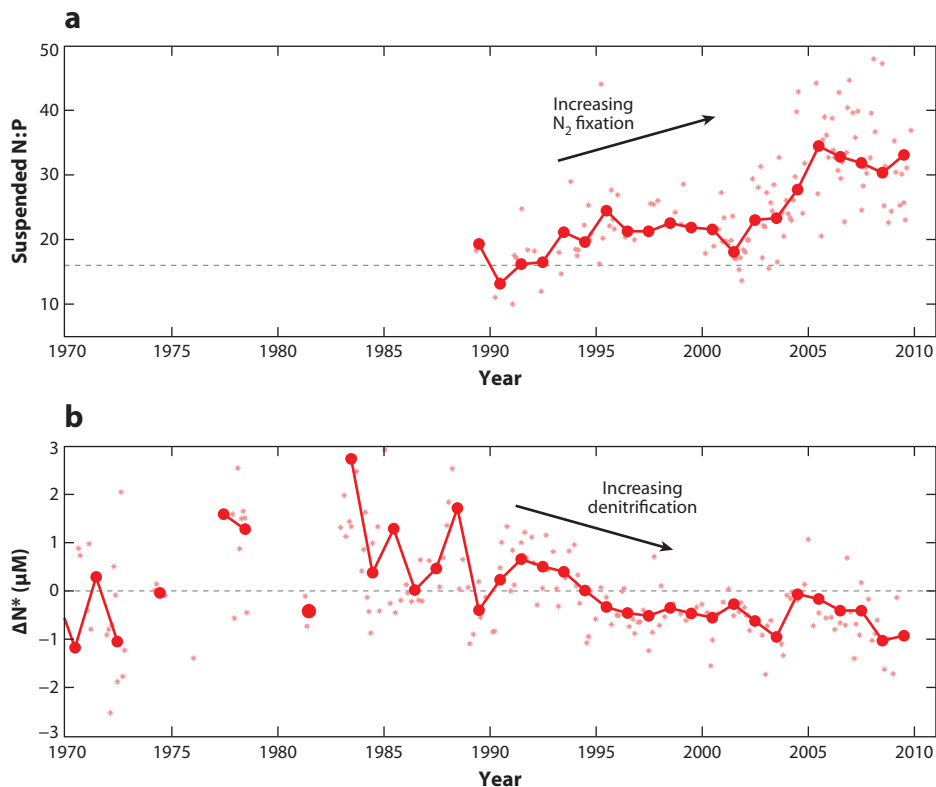


Figure 14

Time series of stoichiometric anomalies in the Pacific Ocean from the (a) Hawaii Ocean Time-Series (HOT) and (b) California Cooperative Oceanic Fisheries Investigations (CalCOFI) programs. At the HOT site, the N:P ratio of suspended particles (0–100 m) has increased dramatically along with N* (not shown). In the CalCOFI region, N* anomalies at 250–300 m have declined over the same period. Nitrate and phosphate data are independently binned into a 0.5° latitude/longitude grid at standard depth levels and monthly frequency. Deviations from the time-averaged value are then spatially averaged throughout the region sampled by the CalCOFI program.

and the observed propagation of its stoichiometric signature away from tropical suboxic waters may modulate the strength of N limitation at a basin scale.

The preceding observations suggest that nutrient stoichiometry can be quite dynamic even on a decadal timescale. In each instance, the amplitude of changes in N* that are evident on interannual to decadal timescales is comparable to the large-scale spatial gradients on which most geochemical rates have been based. Given the high degree of variability, the time rate of change terms (Equation 1) may need to be included in tracer-based rate estimates (Bates & Hansell 2004). More important, the trends point to increases in both N₂ fixation and denitrification over the past couple decades in the Pacific Ocean. If the current interpretations are correct, then these changes are being simultaneously forced by relatively small shifts in the thermal structure of the upper ocean. Whether basin-scale modes of climate variability will generally lead to counteracting changes in the N budget is unclear. The role of biologically mediated feedbacks described above (Figure 4) cannot be ruled out, although the likely time lags involved will make detecting them difficult given the short observation record.

3.2. Glacial/Interglacial Cycles

The feedbacks that maintain coupling between the N and P cycles must contend with much larger forcings at geological timescales. Glacial/interglacial cycles represent an important test case for probing the strength of these feedbacks because the climate forcings are strong and the geological records are well resolved. Although the nutrient stoichiometry cannot be directly inferred for past oceanic states, some of the major processes of interest are recorded in the $\delta^{15}\text{N}$ of sedimentary organic matter (Sigman & Casciotti 2001). In regions of complete surface nutrient utilization, the $\delta^{15}\text{N}$ of sinking particulate flux reflects that of source water NO_3^- , often of thermocline origin. In turn, these source waters bear the isotopic signature of the major source/sink processes, denitrification and N_2 fixation. At the coarsest level, the distribution of N isotopes is the mirror image of N^* . N_2 fixation increases N^* by adding nitrate with a low $\delta^{15}\text{N}$, whereas denitrification reduces N^* by removing isotopically light NO_3^- , raising the $\delta^{15}\text{N}$ of the remaining NO_3^- (Sigman & Casciotti 2001). An important exception is that sedimentary denitrification, which stands out in N^* distributions, does not strongly fractionate the N isotopes and so is largely invisible in $\delta^{15}\text{N}$.

N isotope records recovered from sediment cores reveal a general fluctuation between low $\delta^{15}\text{N}$ during glacial periods and high $\delta^{15}\text{N}$ during warm interglacial periods in each of the major anoxic zones of the global ocean: the Arabian Sea (Altabet et al. 1995), the Eastern Tropical North Pacific (Ganeshram et al. 1995, Pride et al. 1999), and the Eastern Tropical South Pacific (De Pol-Holz et al. 2009). Together with evidence for deglacial expansion of water column suboxia from faunal assemblages (Cannariato & Kennett 1999), bioturbation, and trace metals (van Geen et al. 2003), the geologic record demonstrates a coherent climatically driven increase in denitrification at the end of the last ice age (**Figure 15a**). The subsequent reduction of $\delta^{15}\text{N}$ suggests that rates did not remain high, possibly owing to either the negative feedback on denitrification in anoxic zones or a slower global increase in sediment denitrification driven by sea level rise (Deutsch et al. 2004). In this case, a compensatory response from N_2 fixation would be required to avoid a near collapse of biological productivity. The glacial rates of N_2 fixation were recently assessed by Ren et al. (2009) by reconstructing the glacial $\delta^{15}\text{N}$ signature associated with N_2 fixation (**Figure 15b**). In the modern ocean, $\delta^{15}\text{N}$ reaches its lowest values of $\sim 2\text{‰}$ in the North Atlantic in the high- N^* waters (Knapp et al. 2008). In the glacial North Atlantic, foraminiferal N had an isotope ratio closer to the background mean ocean value (5‰), suggesting that N_2 fixation at that time was much weaker (see also Haug et al. 1998).

Taken together, the sediment records are consistent with a sequence of events that support an ocean N budget with both strong environmental sensitivities and compensatory responses (see **Figure 4**): (a) an expansion of suboxic conditions and a coincident increase in denitrification, (b) a subsequent increase in N_2 fixation in the Atlantic, and (c) a relaxation of denitrification in the water column and/or an increase in denitrification in newly submerged continental shelf sediments. A quantitative constraint on the strength of the feedbacks that takes into account both the rise and fall of $\delta^{15}\text{N}$ in suboxic regions, and the apparent similarity of the global mean $\delta^{15}\text{N}$ of ocean nitrate in glacial and interglacial states, place an upper bound on nitrate losses of $\sim 30\%$ (Deutsch et al. 2004), comparable to the range admitted by simple conceptual models (**Figure 5**). As the quantity of isotopic data increases and its systematics are developed, such quantitative interpretations are certain to improve.

4. SYNTHESIS AND OUTLOOK

We are now in a position to revisit the questions posed in the introduction, outlining our current perspective on how the emerging understanding of N:P variations in oceanic nutrient distributions reinforces and/or alters current paradigms.

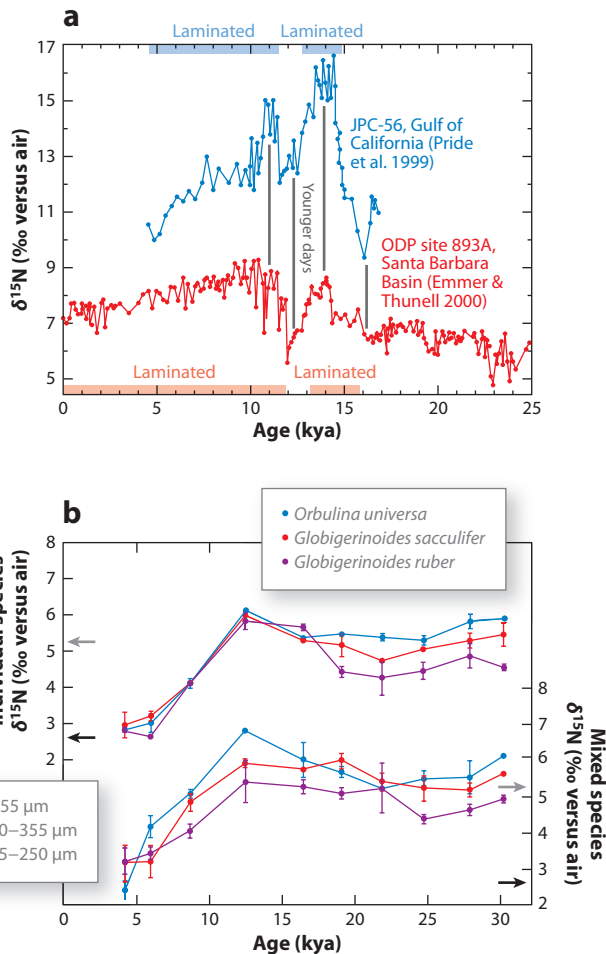


Figure 15

Sediment records of $\delta^{15}\text{N}$ since the last glacial maximum from (a) the Eastern Tropical North Pacific (Emmer & Thunell 2000, Pride et al. 1999) and (b) the subtropical North Atlantic (Ren et al. 2009). The rise in $\delta^{15}\text{N}$ in the Eastern Pacific indicates a deglacial increase in denitrification rates, while the decline of $\delta^{15}\text{N}$ in the Atlantic implies a subsequent increase in N_2 fixation rates. Arrows represent radiocarbon dates. Abbreviations: JPC, jumbo piston core; ODP, Ocean Drilling Program.

In elaborating the foundational observation that the N:P ratio of marine phytoplankton is well matched to the oceanic $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio, Redfield stressed that the observed organic matter was an average among species certain to vary in their cellular stoichiometry. However, when positing an ecosystem dynamic that would maintain such a state, the average N:P of biomass ceases to be a mere statistic and takes on both ecological significance (as the ecological threshold that triggers N_2 fixation) and geochemical significance (as the set point of the ocean's nutrient thermostat). The assumption of a single ratio in this context is not without merit—the diversity of plankton is everywhere high enough that averaging biomass over small scales could conceivably yield nutrient cycles that are, for all practical purposes, driven by the global average plankton. Current evidence points toward biotic N:P variation across multiple scales, from plankton communities to ocean

biomes. These two extremes also provide a useful starting point to highlight where relevant lines of inquiry begin and end.


If variation in the N:P of plankton ecosystems were confined to the small spatial scales of plankton communities, then nutrient cycles would conform to the universal stoichiometry paradigm, and the mean N:P of plankton biomass and thus of the ocean nutrient reservoirs could be said to arise from ecosystem dynamics described by Redfield. In this case, the nontrivial question would be why those dynamics lead to a value of 16:1 and not, say, 10:1 or 20:1. The solution to this must account for not only the processes by which plankton assemblages maintain a balanced stoichiometry, but also how evolution has produced the spectrum of species N:P ratios from which local environmental fluctuations and ecological interactions assemble such balanced communities. This question is central regardless of the scale of biomass N:P variation.

If, instead, the spatial scales of variation in community N:P approach those of distinct oceanographic biomes, then ocean circulation and climate must also play an important role in setting the global mean N:P ratio of plankton production. Assuming that taxonomic variation is the primary determinant of community N:P, the question boils down to understanding what sets the oceanic balance among the major ocean biomes housing plankton groups with different nutrient metabolisms. The prominence of diatoms takes on a special significance, because they appear to anchor the low end of the N:P spectrum. Classical theories posit a major role for upper-ocean mixing, via its effect on light (Margalef 1997), but their unique Si requirement grants additional leverage to wind-driven upwelling (Anderson et al. 2009). To the degree that phenotypic variation in N:P contributes to the large-scale structure and/or mean value of plankton N:P, we must also consider effects of temperature as well as light and nutrient limitation, including Fe.

Stoichiometric variability at the scale of marine biomes has immediate implications for understanding the processes constituting the N budget. The magnitude and spatial pattern of N_2 fixation inferred from surface and thermocline N^* distributions will be greatly influenced by deviations from 16N:1P in the biomass of nondiazotrophic phytoplankton, which account for most of the nutrient gradient in the ocean. Mills & Arrigo (2010) argued that if low-N:P diatoms are responsible for most of the excess PO_4^{3-} uptake in upwelling zones, then global N_2 fixation would be greatly reduced. However, the apparent global mean export ratio of 16:1 requires regions of high N:P export ratios as well, and these imply a counteracting increase in N_2 fixation somewhere, presumably in the subtropical gyres. This in turn requires revising the assumptions underlying the accumulation of excess NO_3^- in the subtropical thermocline (Zamora et al. 2010). Given the mounting evidence for large-scale patterns in plankton N:P ratios, a quantitative reassessment of the major fluxes in the N budget is clearly needed.

The prospect of an ocean with large-scale structure in N:P requirements poses deeper questions. How does the N homeostasis imagined by Redfield operate in an ocean in which diazotrophs compete primarily with the plankton who are (like the children of Lake Wobegon) “all above average” in their N:P quota? And how does this affect our understanding of the strength of feedbacks in the N budget that maintain N:P coupling near the current mean biomass ratio of 16:1? Preliminary answers can be derived from the N-cycle box model of Tyrrell (1999), which we modify to give high-latitude plankton a low N:P requirement characteristic of diatoms, while the low-latitude domain is dominated by high-N:P plankton with whom N_2 fixers interact (**Supplemental Figure 2**).

In the absence of a circulation pathway to connect the upper ocean in high and low latitudes, the ratio between ocean N and P inventories closely tracks variations in the N:P of plankton in low latitudes, allowing global $NO_3^-:PO_4^{3-}$ to exceed the global mean plankton biomass of 16:1 (**Figure 16**). This is because the excess P available to diazotrophs is set only by two factors: the deep-ocean nutrient reservoirs and the N:P ratio of their local competitors. Thus, if the N:P ratio

 Supplemental Material

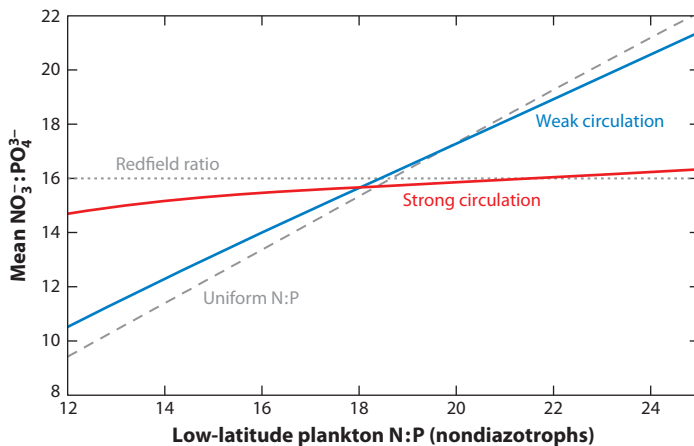


Figure 16

Influence of large-scale N:P variability on the regulation of the ocean fixed-N inventory. The gray dashed line (uniform N:P) is derived from a two-box model (deep ocean and surface ocean) modified from Tyrrell (1999), in which the ratio of ocean N and P inventories closely tracks the N:P of a single plankton type. The solid lines are derived from an extended version of the model (Lenton & Klausmeier 2007) with the surface split into high- and low-latitude regions (50% each), and diazotrophs present in low latitudes only. The model is run with a range of nondiazotroph N:P ratios in low latitudes; in high latitudes, biomass N:P is adjusted to ensure a global mean export ratio of 16:1. When surface transport from low to high latitudes is weak (*blue line*), mean ocean $\text{NO}_3^-:\text{PO}_4^{3-}$ primarily tracks the algal N:P in low latitudes. As the circulation of high-latitude water into the low latitudes is strengthened (*red line*), mean $\text{NO}_3^-:\text{PO}_4^{3-}$ becomes less sensitive to low-latitude plankton N:P and more closely reflects that of a global biomass with a constant mean value of 16N:1P.

of nondiazotrophic plankton in oligotrophic regions is significantly higher than 16:1 (as observed), then the mean ocean $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio should also be higher than 16:1.

However, when high-latitude surface waters are allowed to flow directly into the upper ocean of low latitudes (Sarmiento et al. 2004a), the stoichiometry of export in the high latitudes also has a direct influence on the relative supply of NO_3^- and PO_4^{3-} to low-latitude plankton. In this case, the ecological niche of diazotrophs is determined by remote communities as well as local competitors. As this shallow overturning circulation becomes stronger, deep-ocean $\text{NO}_3^-:\text{PO}_4^{3-}$ increasingly reflects the global mean composition of plankton, independent of the spatial separation between high- and low-N:P end-member communities.

Thus, at least in this simplified depiction, the homeostasis Redfield proposed may still be achieved in an ocean with large-scale differences in biotic N:P demands, provided the differences in regenerated nutrient ratios are transmitted from one region to another, allowing plankton communities to communicate their nutrient requirements even without directly interacting or competing. In the Southern Ocean, it appears that subsurface mixing is an efficient homogenizer across stoichiometric gradients, but the mechanism might be less effective in regions with less vigorous circulation features than the Antarctic Circumpolar Current. Clearly, further progress in understanding these mechanisms will require models that account for stoichiometric differences among marine biomes and the communication of their resource constraints through realistic depictions of ocean circulation processes.

Anthropogenic climate change promises to shift the physical boundaries that define the large-scale patterns of marine productivity (Sarmiento et al. 2004b) and the planktonic communities that inhabit them. At the same time, the human acceleration of the global N cycle is likely to

impinge ever more strongly on the ocean (Gruber & Galloway 2008), as has long been evident in many coastal areas (Ryther & Dunstan 1971), potentially altering both N losses (Codispoti 2010) and the ecological niche for N₂-fixing plankton (Krishnamurthy et al. 2007). A mechanistic understanding of nutrient stoichiometry and models that account for it will be needed to assess how these interacting effects will drive responses by the marine biosphere.

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