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Phosphate Depletion in the Western North Atlantic Ocean

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Surface waters of the subtropical Sargasso Sea contain dissolved inorganic phosphate (DIP) concentrations of 0.2 to 1.0 nanomolar, which are sufficiently low to result in phosphorus control of primary production. The DIP concentrations in this area (which receives high inputs of iron-rich dust from arid regions of North Africa) are one to two orders of magnitude lower than surface levels in the North Pacific (where eolian iron inputs are much lower and water column denitrification is much more substantial). These data indicate a severe relative phosphorus depletion in the Atlantic. We hypothesize that nitrogen versus phosphorus limitation of primary production in the present-day ocean may be closely linked to iron supply through control of dinitrogen (N_2) fixation, an iron-intensive metabolic process. Although the oceanic phosphorus inventory may set the upper limit for the total amount of organic matter produced in the ocean over geological time scales, at any instant in geological time, oceanic primary production may fall below this limit because of a persistent insufficient iron supply. By controlling N_2 fixation, iron may control not only nitrogen versus phosphorus limitation but also carbon fixation and export stoichiometry and hence biological sequestration of atmospheric carbon dioxide.

Photosynthetic carbon fixation and subsequent settling of particulate fixed carbon to the ocean's interior represent a biological carbon pump that regulates atmospheric CO_2 concentrations and climate over geological time scales (*1*). This carbon pump is largely controlled by the availability of the major nutrients: nitrogen (N) and phosphorus (P). Nutrient enrichment experiments in the Pacific suggest that phytoplankton growth is limited by available N (*2*). Nutrient distributions in the modern ocean indicate that upward fluxes of inorganic nutrients from the deep ocean are depleted in N relative to P in relation to the elemental requirements of eukaryotic photoautotrophs growing at their maximum rates (*3*). This nitrate deficit has been attributed to a slight imbalance between N_2 fixation and denitrification (*4*, *5*), caused by an iron limitation of N_2 fixation (*6*–*8*). With ample iron, increased N_2 fixation should drive oceanic ecosystems toward phosphorus limitation as occurs in most lakes (*9*) and has been proposed for the ocean during glacial periods (*6*). This conceptual model, however, contradicts the prevailing view of geochemists that net N_2 fixation and the balance between N_2 fixation and denitrification are ultimately set by riverine input of phosphorus, not by eolian iron supply (*10*). To help resolve this controversy, we compared dissolved nitrate plus nitrite (DNN) and dissolved inorganic phosphate (DIP) distributions in iron-replete waters of the western North Atlantic subtropical gyre, where little denitrification exists, with those in iron-poor regions of the subtropical North Pacific, where water column denitrification is substantial, to examine the influence of iron supply on N versus P limitation. Subnanomolar concentrations of DIP in the surface seawater of the western North Atlantic were observed with a highly sensitive MAGIC method for P analysis (*11*).

In a transect from the seasonally stratified Sargasso Sea near Bermuda to permanently stratified waters farther south, we observed no measurable changes in surface concentrations of dissolved organic phosphorus [DOP = total dissolved phosphorous (TDP) − DIP] (Table 1), which accounted for 94 to 99% of the total phosphorus. DIP concentrations in surface waters decreased from 3.9 nM in surface waters near Bermuda to an average value of 0.4 nM in the region of permanent stratification (Fig. 1). This DIP concentration is only ~4% of the mean DIP in nutrient-depleted waters of the North Pacific gyre (Fig. 1, Table 1), indicating a relative DIP depletion in the Sargasso Sea (*12*, *13*).

Phosphate depletion in Sargasso Sea surface waters can be attributed to the high ratio of DNN to DIP of 20 to 32 in the upper nutricline relative to the planktonic 16 N:1 P ratio (*14*) (Fig. 2). This high nutrient source N:P ratio causes available P to be depleted before N by algal growth after upward nutrient injections into the euphotic zone through advection or diffusion. The scenario is different in the North Pacific where the DNN versus DIP supply ratio from the upper nutricline to the euphotic zone is lower than the N:P ratio of 16 in plankton (Fig. 2), resulting in an N-limited condition with algal growth (*2*). The difference in N:P ratios between the North Pacific and North Atlantic can be further demonstrated by plots of DNN versus DIP measured at Bermuda Atlantic time-series (BATS) and Hawaii Ocean time-series (HOT) stations for the period July 1998 to July 1999 (Fig. 3). A positive intercept on the DNN axis (N excess in the surface water) and a slope of 17.2 indicate a strong P depletion in the North Atlantic. In contrast, the DNN versus DIP plot for the North Pacific shows a negative intercept (excess phosphate in the surface) and a slope of 15.0, suggesting an N depletion.

Although the relative N enrichment in the North Atlantic thermocline is probably due to N_2 fixation, N depletion in the Pacific must result from enhanced levels of denitrification in low oxygen thermocline waters (*15*). However, N depletion in the Pacific should promote the growth of N_2 fixers that would replenish fixed N, driving the system back toward P limitation, as occurs in most lakes (*9*). Contemporary N_2 fixation in the Pacific appears to be restricted by an insufficient supply of iron (*6*–*8*), an important nutrient cofactor for the nitrogenase enzyme.

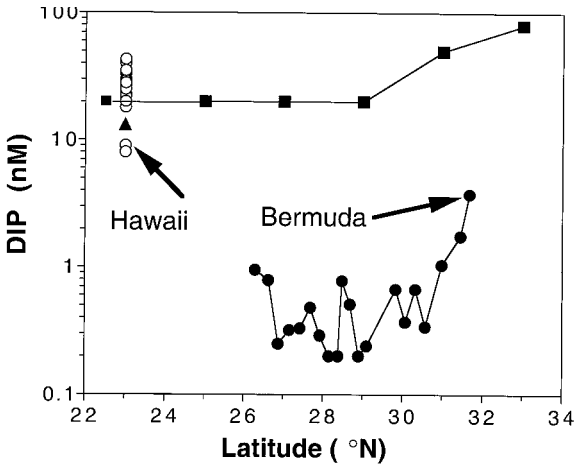

Fig. 1. Surface (~0.5 m) DIP concentrations along a transect from 31.67°N, 64.17°W to 26.10°N, 70.00°W in the Sargasso Sea in March 1998 are compared with those in the North Pacific gyre. –●–, western North Atlantic in March 1998; –■–, North Pacific in November 1997 (*37*); ○, North Pacific near Hawaii in 1991–97 (HOT 11-85) (*35*); ▲, Pacific near Hawaii in November 1998.

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Table 1. A comparison of euphotic zone biogeochemical parameters between North Atlantic and North Pacific gyres.

Parameters (units)	Sargasso Sea	Pacific near Hawaii
DIP (nM)	0.48 ± 0.27*	13 ± 2†; 9–40‡
TDN (nM)	4512 ± 430	5680 ± 620‡
TDP (nM)	75 ± 42	222 ± 14‡
TDN:TDP	60 ± 7	26 ± 3
Eolian Fe flux (μmol Fe m^{-2} day^{-1}) (*20*)	0.2–0.8	0.08–0.16
N_2 fixation rate (mmol N m^{-2} $year^{-1}$)	72§	31–51‖

*Average DIP between 26° and 31°N in the surface waters of the Sargasso Sea in March 1998. †North Pacific near Hawaii (22.9°N, 158.0°W) in November 1998. ‡North Pacific near Hawaii at station ALOHA during 1991–97 (*23*). §Based on isopycnal N* distribution and water age (*21*). ‖Based on a variety of independent estimates including nitrogenase activity by acetylene reduction method, *Trichodesmium* abundance, N:P mass balance, and ^{15}N isotope balance (*23*).

Microorganisms using N_2 as their source of N require at least one order of magnitude more Fe than for growth on nitrate or ammonium (*16*). Iron limitation of N_2 fixation has been demonstrated for natural assemblages of diazotrophs in N-deficient lakes (*17*) and in culture studies with both freshwater cyanobacteria and the dominant marine diazotrophic genus *Trichodesmium* (*8*, *18*). However, there is currently no convincing direct evidence for iron limitation in natural assemblages of marine diazotrophs. In the North Pacific gyre, the iron flux from below the euphotic zone is too low to support observed rates of phytoplankton growth (*19*), and most of the iron in surface waters is derived from eolian deposition (*20*). Areal rates of eolian iron input into surface Pacific waters are 2- to 10-fold lower than in the Sargasso Sea, which receives high inputs of iron-rich dust from northern Africa (*20*). The higher iron inputs to the North Atlantic subtropical gyre are thought to support higher rates of N_2 fixation (*21*, *22*).

Other than available iron, do any other factors limit N_2 fixation in the North Pacific? Although N_2 fixers need P for growth and metabolism, the excess DIP detected in surface waters of the North Pacific suggests that P cannot limit N_2 fixation in the Pacific. Simple box model calculations (*23*) show that in the Pacific gyre near Hawaii, the DIP flux from the upper thermocline to the euphotic zone is ~30% higher than that needed to meet the growth demands of phytoplankton (based on the upward nitrate flux and the 16 N:1 P ratio in plankton). Only about half of this extra phosphate is consumed during N_2 fixation, and the rest (~15% of the total upward flux) remains unused and is mixed downward as inorganic phosphorus. In contrast, the DIP concentration in the North Atlantic is much lower, suggesting that P is an important limiting factor for N_2 fixation as it is in most lakes (*9*). Other potentially controlling factors such as light, temperature, mixed layer depth, and dissolved oxygen (O_2) also cannot explain the lower than expected N_2 fixation in the North Pacific. Sunlight, a warm, calm sea surface, and a shallow mixed layer all favor the growth of N_2-fixing diazotrophs. These factors, however, are not very different in the two oligotrophic gyres. In fact, in the North Pacific near Hawaii (HOT), the annual mean surface temperature is higher and the mixed layer depth is shallower than in the North Atlantic near Bermuda. This should favor a higher N_2 fixation rate at HOT. In contrast, estimated gyre-average N_2 fixation rates are higher in the North Atlantic than in the North Pacific (Table 1). Although O_2 gas is a major inhibitor of nitrogenase activity, *Trichodesmium* can photosynthesize and fix N_2 at the same time (*24*). At present, there is no good evidence to show that O_2 inhibition causes any substantial difference in N_2 fixation between the two oceans. Thus, iron remains the most probable factor limiting N_2 fixation in the North Pacific, although it remains to be proven by more direct evidence such as in situ Fe addition experiments in the future.

Because the DNN:DIP ratio is higher than the Redfield value (N:P = 16:1) in the Atlantic (Fig. 2), the upward flux of N will be in excess of that needed to support algal growth. Thus, if N is not limiting, why should N_2 fixation occur at all in the Atlantic? N_2-fixing diazotrophs should not fix N_2 for biological production if fixed nitrogen is readily available (*25*). The answer to the paradox may lie in the preferential conversion of excess inorganic fixed nitrogen (DIN) into biologically refractory dissolved organic nitrogen (DON) by biological nutrient cycling in the stratified surface waters.

A variety of DON and DOP compounds are released into the water column by a number of processes: viral cell lysis, cell disruption during grazing, excretion of digestion waste products, and excretion of oxidatively damaged biomolecules. Many of these compounds, such as amino acids and phospholipids, are biologically labile and are readily reassimilated by microorganisms. However, many others, such as partially oxidized and polymerized biomolecules (humic acids), have complex and varied structures that are not amenable to biological utilization. The N and P in the labile compounds are reassimilated (either directly or after enzymatic degradation, e.g., by phosphatases or deaminases), whereas N and P in the refractory compounds remain in the water. With continued nutrient cycling (*26*), there is a

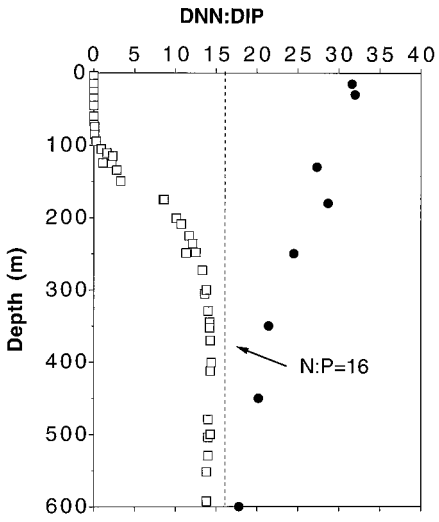

Fig. 2. Vertical profiles of N:P molar ratios in the Sargasso Sea near Bermuda (31.67°N, 64.17°W) (●) and in the Pacific near Hawaii (HOT USJGOFS Web site at hahana.soest.hawaii.edu) (□).

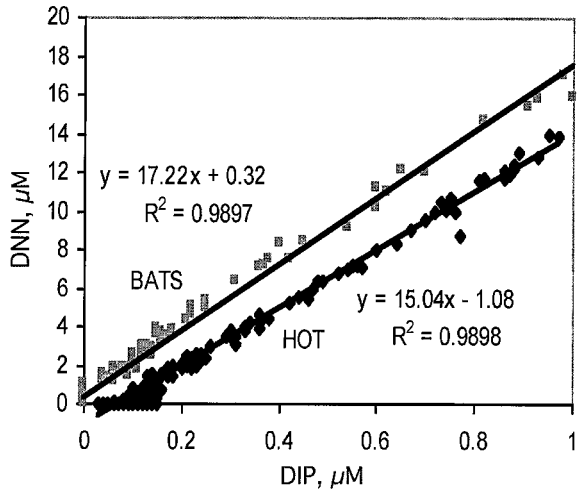

Fig. 3. The plot of phosphate versus nitrate measured from BATS (www.bbsr.edu/users/ctd/batscast.html) and HOT (hahana.soest.hawaii.edu/hot/hot.html) time series for the period July 1998 to July 1999 (*38*).

progressive transfer of N and P from biologically available inorganic pools to increasingly biologically refractory organic ones. There is evidence that the DON in seawater is relatively more "resistant" to microbial assimilation and decomposition than is the DOP (*27*). Consequently, biological nutrient cycling would cause a greater percentage of DIN than DIP to be converted to refractory organic forms. Thus, although excess DIN is upwelled from below the euphotic zone, the intense nutrient cycling in stratified surface waters could decrease the concentrations of available fixed nitrogen to limiting levels, promoting N_2 fixation by diazotrophs.

The cycling of phosphorus from the more biologically labile DOP pool ultimately provides much of the excess P required for N_2 fixation even when the N:P ratio in the nutrient flux to the surface is much higher than that found in plankton (*28*). In addition, some species of N_2 fixers such as *Trichodesmium* can migrate vertically to acquire phosphate from below the mixed layer (*29*), providing an additional phosphate source for diazotrophic growth. The continued input of recently fixed N by N_2 fixation (without an extra P supply from the deep ocean) increases the total dissolved nitrogen to total dissolved phosphorus ratio (TDN:TDP) in the upper ocean of the western North Atlantic to values well above the Redfield ratio (*30*), as observed in our present data (Table 1).

Our comparison of the nutrient cycles in North Pacific and North Atlantic gyres is consistent with the hypothesis that N versus P limitation in the contemporary ocean is closely linked to eolian Fe supply. Although we cannot directly prove this hypothesis with the currently available data, our results do indicate that the ocean N and P cycles are more complex than predicted by simple models (*10*). Although enhanced N_2 fixation causes P depletion in the more iron-rich North Atlantic, a lack of Fe appears to limit N_2 fixation in the N-depleted North Pacific gyre. If indeed N_2 fixation in the Pacific is limited by bioavailable Fe, and if inefficient nutrient cycling between DON and DIN promotes N_2 fixation in an N-replete condition (N:P $>$ 16), these conditions have important implications for oceanic carbon fixation and export and biological sequestration of atmospheric CO_2 over geological time scales.

It has long been argued that because the oceanic residence time for P (~50,000 years) is much longer than that for N (~3000 years), P inventory would set the upper limit for the amount of organic matter produced in the ocean over long time scales (*10*, *31*). But, if N_2 fixation is controlled by Fe supply, a dearth of iron could lower total primary production below this limit (*32*). The effect may occur on various time scales. A persistently low iron input could result in an imbalance between N_2 fixation and denitrification over long time scales. If this imbalance is small, the oceanic N inventory can vary over time scales much longer than the N residence time. If the imbalance is large, one would expect changes to a new steady state over much shorter time scales (*6*). In this situation, steady state oceanic N inventory and productivity would be limited by insufficient iron, not by phosphorus. Only when there is enough iron would nitrogen inventory in the ocean be controlled by phosphorus (*10*, *31*).

Although exact information on the oceanic P inventory in the geological past is not known, its long residence time implies that a large (over 30%) change in P inventory on glacial-interglacial time scales is unlikely. However, P control of the N inventory could be affected to some extent by the ability of N_2 fixation to adjust oceanic N:P ratio to values exceeding 16 as occurs in the contemporary western North Atlantic Ocean. Although information on the N:P ratio in the ocean over geological time is lacking and the limit for P control of N inventory remains to be understood, it is likely that by controlling N_2 fixation, iron has exerted an important role on N inventories and hence biological sequestration of CO_2 into the ocean between the present and the Last Glacial Maximum. It has been argued that increased inputs of iron-rich dust to the ocean during drier and windier glacial periods should have increased N_2 fixation rates (*6*, *22*). This effect, in combination with decreased denitrification (*4*, *33*), would increase the global oceanic N inventory, resulting in a decrease in atmospheric CO_2 from the atmosphere by a stronger oceanic biological pump (*7*, *34*). In such a situation, the interrelationships between iron supply, N_2 fixation, and phosphate limitation in much of the ocean may have resembled the current situation in the western North Atlantic. Investigating iron versus phosphate limitation of N_2 fixation and its role in nutrient cycling in this region may provide a better understanding of oceanic carbon fixation and export during glacial periods and the interrelationship between this interaction and global climate variations.

References and Notes

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11. N and P methods: Seawater samples were collected from ~0.5-m depth with an underway all plastic ultraclean sampling system and from greater depths with Niskin sampling bottles. Samples were filtered through 0.4-μm pore size Nucleopore membranes and stored frozen until analysis. The filtration eliminates DIP contamination from particulates (>0.4 μm), which can be as high as 0.5 to 1.0 nM. DIP was measured on thawed samples with the modified MAGIC method [D. M. Karl and G. Tien, *Limnol. Oceanogr* **37**, 105 (1992); (*35*)]. DIP was preconcentrated 100-fold onto $Mg(OH)_2$, precipitated from 50 ml of seawater by addition of 150 μl of 1 M NaOH. The $Mg(OH)_2$ was dissolved in 450 μl of dilute HCl to release DIP, which was then measured by the molybdenum blue method [J. Murphy and J. P. Riley, *Anal. Chim. Acta* **27**, 31 (1962)] after correcting for arsenate interferences [D. L. Johnson, *Environ. Sci. Technol.* **5**, 411 (1971)]. The detection limit is ~0.2 nM and precision is ~10% at the 2 nM level. DNN was measured with an auto analyzer by standard methods [J. D. H. Strickland and T. R. Parsons, *A Practical Handbook of Seawater Analysis* (*Fish. Res. Board Can. Bull.*, Fisheries Research Board of Canada, Ottawa, Canada, ed. 2, 1972)]. Total N and P were analyzed on sample replicates irradiated with 1 kW of ultraviolet light for 24 hours to photooxidize organic matter [F. A. J. Armstrong, C. R. Stearns, J. D. H. Strickland, *Deep Sea Res.* **14**, 381 (1967)].
12. To grow in the Sargasso Sea, larger cells may have to use the much larger, but more biologically refractory DOP pool through the zinc enzyme alkaline phosphatase [G. Y. Rhee, *J. Phycol.* **9**, 495 (1973)] and other enzymes such as nuclease, pyrophosphatase, and nucleotidase. In this situation, larger cells may become colimited by phosphorus and zinc because dissolved zinc concentrations (0.06 ± 0.02 nM) in surface waters of Sargasso Sea [K. W. Bruland and R. P. Franks, in *Trace Metals in Sea Water*, C. S. Wong *et al.*, Eds. (Plenum, New York, 1983), pp. 395–414] are the lowest measured anywhere in the ocean and free Zn^{2+} concentrations are sufficiently low [~1 pM (K. Bruland, personal communication)] for their diffusion to limit algal zinc uptake [W. G. Sunda and S. A. Huntsman, *Limnol. Oceanogr.* **37**, 25 (1992)]. In addition, under low phosphate concentrations, autotrophs must have evolved uptake mechanisms to differentiate between arsenate and phosphate or to detoxify intracellular arsenate to avoid poisoning by arsenic, which is found at 10 to 20 nM in oligotrophic surface waters.
13. Although increased stratification associated with El Niño events over the past two to three decades has led to a two- to threefold decrease of soluble reactive phosphate (SRP) concentrations in the surface water of the North Pacific near Hawaii [D. M. Karl and G. Tien, *Mar. Chem.* **56**, 77 (1997); (*36*)], DIP levels at station ALOHA in 1998 are still an order of magnitude higher than those in the stratified surface water of Sargasso

Sea (Fig. 1, Table 1). A simple box model calculation suggests that the decreased surface water DIP from 1989 to 1998 at HOT can be caused both by decreased mixing rate between the surface and upper thermocline and by increased N_2 fixation rate. The observed decreasing SRP with increasing stratification in the Pacific is also consistent with the hypothesis that the accumulation of eolian Fe deposition in the shallow mixed layer enhances N_2 fixation, which then draws down surface water SRP.

14. Alternatively, the relative phosphate depletion in the Sargasso Sea may also be due to dominant species of phototrophs and community structure that are fundamentally different from those in the North Pacific. Although *Procholorococcus* is the dominant picoplankton genus at station ALOHA in the North Pacific, *Synechococcus* is more abundant in the North Atlantic near Bermuda. But one may argue that this phytoplankton species difference is largely due to the fact that Bermuda is located at a higher latitude than Hawaii and that community structure is not fundamentally different between the two oligotrophic gyres. The hypothesis that community structure controls DIP levels in the ocean will remain untested until information on the threshold P concentrations needed to support growth of both picoplankton genera is available.
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23. In the North Pacific near Hawaii, DIP concentrations in the upper thermocline [0.5 ± 0.2 μM at 250 m from 1989 to 1998; HOT U.S. Joint Global Ocean Flux Study (JGOFS) web site at hahana.soest.hawaii.edu] are ~30% higher than that needed to meet the growth demand of phytoplankton as calculated from nitrate concentrations at the same depth (6.0 ± 2.5 μM). The average surface water DIP concentrations (which decreased from ~100 nM in 1989 to ~40 nM in 1998) are ~15% of those in the upper thermocline. If horizontal mixing and advection are assumed to be negligible, mixing between surface mixed layer and upper thermocline would lead to ~15% of upward phosphate flux returning downward to the thermocline as bioavailable inorganic phosphate. This result does not contradict the observation that N_2 fixation is ~50% of particulate organic N export at HOT (*36*). Because upward nutrient flux has an N:P ratio of 12 and downward export flux has an N:P ratio of >16 (due to DOM N:P ratio of 25 at HOT), ~15% excess P in upward flux would be sufficient to support 50% extra N from N_2 fixation.
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26. Export production in subtropical gyres is often only a small portion of gross primary production [R. W. Eppley and B. J. Peterson, *Nature* **282**, 677 (1991)], suggesting that the majority of N and P needed to support primary production come from in situ nutrient cycling through the microbial loop [F. Azam *et al.*, *Mar. Ecol. Prog. Ser.* **10**, 257 (1983); F. Azam, *Science* **280**, 694 (1998)].
27. G. A. Jackson and P. M. Williams, *Deep Sea Res.* **32**, 223 (1985); S. V. Smith, W. J. Kimmerer, T. W. Walsh, *Limnol. Oceanogr.* **31**, 161 (1986). Although there is no direct evidence for an enhanced biological and chemical lability of DOP relative to DON compounds in seawater, vertical profiles of DON and DOP in the Pacific (*37*) show that DOP decreases much faster than DON with increasing depth, which results in an increase in the N:P ratio of organic matter. This behavior suggests that when organic matter is mixed downward, DON is relatively more resistant to decomposition than is DOP.
28. If nutrients with an N:P ratio of 25 are supplied to the surface water (DNN = 3.8 μM and DIP = 0.15 μM) and 80% of the upwelled DNN is converted to unavailable DON and the DIP is converted to refractory DOP, the net ratio of available N to P in the upward flux would be 6, well below the N:P ratio in plankton.
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30. As dissolved organic matter in the surface mixed layer has a high N:P ratio, when these dissolved organic materials mix downward and decompose in the upper thermocline, the N:P ratio in thermocline water increases. This process can raise upper ocean DIN:DIP ratios to over 16, even if organic matter produced by N_2-fixing *Trichodesmium* and non–N_2-fixing algae has an N:P ratio of 16.
31. If an N:P ratio of 16 is assumed for organic matter produced in the euphotic zone, a 50% decrease in oceanic P inventory without a concurrent decrease in N inventory would result in an N:P ratio of 32:1 in the deep ocean, and the growth of both N_2-fixing and non–N_2-fixing phototrophs will be limited by available P. The initial decreased N_2 fixation would cause an imbalance between N_2 fixation and denitrification, which would then decrease oceanic N inventory.
32. When an insufficient Fe supply decreases N_2 fixation in the presence of ample P, the rate of N_2 fixation would decline to below that of denitrification, and the ocean would start to lose fixed N. The decreased oceanic N inventory causes N limitation to primary production, which in turn would decrease water column denitrification by increasing O_2 content in the deep water until denitrification balances N_2 fixation at a new steady state. In this situation, oceanic N inventory would be set by Fe supply, not by P.
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The Response of Two Contrasting Limestone Grasslands to Simulated Climate Change

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Two different UK limestone grasslands were exposed to simulated climate change with the use of nonintrusive techniques to manipulate local climate over 5 years. Resistance to climate change, defined as the ability of a community to maintain its composition and biomass in response to environmental stress, could be explained by reference to the functional composition and successional status of the grasslands. The more fertile, early-successional grassland was much more responsive to climate change. Resistance could not be explained by the particular climates experienced by the two grasslands. Productive, disturbed landscapes created by modern human activity may prove more vulnerable to climate change than older, traditional landscapes.

The impact of climate change on the structure, composition, and function of grassland ecosystems is a topic of current concern. Climate-driven changes in grassland productivity could have serious consequences for the distribution and profitability of pastoral agriculture (*1*, *2*). Climate change will also affect the conservation value of limestone grasslands, which are among the most species-rich plant communities in Europe (*3*, *4*). Different plant communities, when exposed to changes in temperature and precipitation,