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Phosphorus versus nitrogen limitation in the marine environment¹

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Abstract

Limnological and marine geochemical opinion favors phosphorus limitation of organic production in aquatic environments, while marine biological opinion favors nitrogen limitation. Clues in the literature and nutrient budgets for selected marine ecosystems suggest that phosphorus vs. nitrogen limitation is a function of the relative rates of water exchange and internal biochemical processes acting to adjust the ratio of ecosystem N:P availability.

A limiting factor to biological activity is that material available in an amount most closely approaching the critical minimum required to sustain that activity (Odum 1971). This definition can be applied at any scale from cellular metabolism to global biogeochemical cycles. This paper deals with inorganic plant nutrients as limiting factors for the net production of new organic material in marine systems.

Marine geochemists and biologists hold antithetical views about nutrient limitation in the ocean. The view held by most marine geochemists (e.g. Lerman et al. 1975; Meybeck 1982; Broecker and Peng 1982) can apparently be traced to the seminal paper by Redfield (1958). Redfield concluded that phosphorus availability limits net organic production in the sea. He pointed out that any nitrogen deficits can be met by the biological fixation of atmospheric nitrogen, hence nitrogenous compounds can accumulate until the available phosphorus is utilized.

Among marine biologists, Redfield's view has largely been replaced with the view expressed by Ryther and Dunstan (1971) that nitrogen, not phosphorus, is the limiting factor to algal growth in coastal waters. Those workers (p. 1008) accepted the possibility that nitrogen fixation might "be important in regulating the level or balance of nutrients in the ocean as a whole and over geological time," but they concluded: "It (nitrogen fixation) is certainly not effective locally or in the short run."

Similarly, Thomas (1970a,b) and many subsequent workers have relied on experimental cultures of phytoplankton to evaluate nutrient limitation in the marine environment (*see also* Goldman et al. 1979). With a few exceptions (e.g. Myers and Iversen 1981) nitrogen appears to be the nutrient which is most often limiting to the specific growth rate of natural populations of phytoplankton grown in such cultures.

A further antithesis emerges. In contrast to the marine biologists, biological limnologists now generally subscribe to the view that phosphorus availability is ordinarily the primary limit to net organic carbon pro-

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duction in lakes. This view is exemplified by the phosphorus loading models put forth by Vollenweider (1968, 1969, 1976), by the long term monitoring studies conducted by Edmondson and his colleagues on Lake Washington (e.g. Edmondson 1970; Edmondson and Lehman 1981), and by the elegant whole-lake nutrient enrichment experiments summarized by Schindler (1971, 1974, 1977). In some recent analyses of lakes (e.g. Smith 1982) nitrogen is considered to have a significant, but secondary, effect on net production.

Schindler's work is particularly important, because he has explicitly addressed the need to assess questions about ecosystem nutrient limitation at the scale of ecosystems, not just at the scale of individual bottle incubation experiments or other studies of isolated components of the ecosystem. Factors limiting the growth rate of individual organisms should be distinguished from factors limiting the net production rate of entire ecosystems. Conclusions about ecosystems based on single-component studies persist, nevertheless.

We are left with the following questions: Can the geochemical vs. the biological views about nutrient limitation in the ocean be resolved into some kind of single model? What, if anything, is the inherent difference between nutrient limitation in lakes and in the ocean? I will suggest some general clues as to the resolution of these questions, and then I will present some of my own data which I believe further help to resolve these questions.

In a recent summary article on lacustrine nutrient limitation and its contrast with nutrient limitation in estuaries, Schindler (1981, p. 78) stated: "The 'evolution' of optimal ratios for phytoplankton growth . . . may not be able to occur in estuaries due to their short water residence times and domination by physical processes. Nitrogen fixed from the atmosphere or returned from sediments is swept into the open ocean so rapidly that it cannot accumulate to the degree which is common in freshwater lakes."

Schindler's comment is a direct outgrowth of whole-lake models (e.g. Vollenweider 1976; Schindler et al. 1978; Dillon 1975) which consider mass loading rates,

water renewal times, depth, and various parameters of biomass response. The statement clearly implies that the "discrepancy" between phosphorus limitation in lakes and nitrogen limitation in the coastal marine environment lies with the difference between relative rates of biochemical reactions of nitrogen and water exchange in the environment. Water exchange may be fast relative to internal nitrogen fluxes in coastal marine ecosystems.

Broecker and Peng (1982) pointed out that competing, biologically mediated nitrogen fixation and fixed nitrogen loss reactions in the ocean interact with terrestrial nutrient inputs, oceanic circulation, and sedimentation, and tend to push the N:P ratio of dissolved inorganic and particulate organic nutrient cycling between surface and deep water toward a "geochemically balanced" ratio—the Redfield ratio (atomic N:P ratio = 16:1). Because phosphorus is not exchanging between the ocean and an atmospheric reservoir as nitrogen does, the delivery of phosphorus—not nitrogen—limits net production (and sedimentation) of organic material in the ocean as a whole.

Based on estimates of the rate of N_2O production from NO_3^- , Broecker and Peng argued that the upper limit on the time needed to balance the N:P ratio in the oceans as a whole is about 10^6 yr; they further pointed out that the real adjustment time is likely to be $\ll 10^6$ yr and is unknown. They did not attempt to assess global nitrogen fixation and fixed nitrogen loss rates in order to resolve the adjustment time any more precisely. Because a million years is relatively short geologically, an uncertainty of this magnitude is not entirely unsatisfactory to geochemists. However, most ecologists or environmental managers have trouble dealing seriously with 10^6 yr, and water exchange rates in shoal-water marine ecosystems are obviously very much shorter than that.

The caution with which these turnover times are given by Broecker and Peng is appropriate. The loss of fixed nitrogen back to gaseous nitrogen (N_2 , N_2O) may arise from either denitrification or nitrification, each with its own particular biochemical pathways and constraints (Cohen and Gordon

1978; Hashimoto et al. 1983; Webb 1981; Hattori 1982). The constraints involve availability of nitrogen species, oxygen, and light, each of which can show microenvironmental variations not readily amenable to large-scale budgets. From the vantage of such budgets, the pathways do not really matter, but these alternate pathways can affect calculation of turnover times from N_2O data. Unless I am specifically referring to a particular biochemical pathway, I will use the noncommittal term "fixed nitrogen loss."

Ecologists turn by default to the statement by Ryther and Dunstan (1971) that nitrogen fixation is not really of local relevance in the marine environment on an ecologically meaningful time scale. That conclusion is certainly not disproven by the estimates of Broecker and Peng (1982), and Schindler's (1981) comments further help to put the subject into the perspective of one class of marine environments—estuaries.

If direct data are not available, then nutrient (usually nitrogen) limitation is often inferred from a deviation of N:P concentration or loading ratios from the composition of primary producers in the system (see e.g. Jaworski 1981). Is there any suggestion that the rate of internal N:P adjustment in the marine environment relative to N:P delivery and export ratios might ever be sufficiently rapid to be directly relevant to the understanding of individual ecosystems in the ocean?

Myers and Iverson (1981) implicated phosphorus, rather than nitrogen, as the nutrient most limiting to phytoplankton growth in estuaries along the northeastern margin of the Gulf of Mexico. McComb et al. (1981) have suggested that an estuarine system in Western Australia may shift seasonally between nitrogen and phosphorus limitation. Are these localized anomalies, or can we find some more general clues as to the rate of N:P adjustment in marine systems?

Martinez et al. (1983) argued that nitrogen fixation in the open ocean has been seriously underestimated because of experimental artifacts associated with incubation procedures. Moreover, there is evidence (reviewed by Doremus 1982) that the metabolism of nitrogen-fixing organisms can itself

be limited by the availability of phosphorus. Dominance by nitrogen-fixing organisms in lakes with low N:P ratios has been well documented (Schindler 1977; Flett et al. 1980; V. H. Smith 1983). These observations suggest that nitrogen fixation—hence nitrogen availability—in the marine environment can be high but that it can be regulated by the availability of phosphorus.

Phosphorus and nitrogen budgets for three ecosystems which I have investigated provide further insight into this subject. These studies were not initially designed to test hypotheses about nitrogen vs. phosphorus limitation. Rather, the ideas have arisen from retrospective analyses of available data sets. Consequently, the analyses presented here do not constitute clean, well designed, repeated experiments. In a sense, these shortcomings are also a major value of the data sets. Despite the fact that these studies were not initially designed to test hypotheses about phosphorus vs. nitrogen limitation of net ecosystem production of organic material, the general conclusions that emerge seem inescapable.

Ecosystem nutrient budgets

The three sites discussed here can all be loosely described as "embayments" with one relatively restricted passage through which water and material exchange with the ocean occurs. These sites differ from "positive estuaries" in having no significant input of water or other materials from land, hence no advective throughput of materials. All three sets of nutrient budgets are tied to water, salt, and carbon budgets discussed in the references cited. Three kinds of data enter into the calculations of nutrient flux: the net oceanic delivery of materials, the immediate molar uptake ratio of N:P in primary producers, and the long term net molar uptake ratio of the sediments.

Oceanic delivery is established by assuming that salinity and water volume in each system remain constant through time: salt advection, driven by net water flow to or from the system (the direct result of rainfall minus evaporation), is balanced by salt diffusion down the concentration gradient. As developed by Atkinson and Smith (1983), the deviation of any material from a strict

Table 1. Generalized procedure for calculating nutrient fluxes. Details for each system are discussed in the text.

Flux	Symbol	Procedure
Phosphorus		
Oceanic delivery	$O_p = f(\text{salt, water budgets})$	
Net uptake	$P = O_p$	
Nitrogen		
Oceanic inorganic N delivery	$O_{din} = f(\text{salt, water budgets})$	
Oceanic organic N export	$O_{don} = f(\text{salt, water budgets})$	
Immediate uptake	$N_i = P \times \text{biotic N:P}$	
Long term uptake	$N_l = P \times \text{sediment N:P}$	
N fixation		
Lower limit	$F_l = N_i - (O_{din} - O_{don})$	
Upper limit	$F_u = N_l - (O_{din} - O_{don})$	
Fixed N loss	$D < F_u - F_l$	

proportional relationship with salinity is a quantitative measure of net uptake or release of that material within the system. This uptake or release is scaled to a rate function with the water budget. Ecosystem net organic production must equal or slightly exceed 0 for the biomass of an isolated ecosystem to be maintained (Smith and Atkinson 1984). Hence, we are considering only net nutrient uptake for all of these systems.

Table 1 presents the generalized procedure used for calculating nutrient fluxes. The details differ for each system and are discussed in the text. An oceanic delivery budget entirely describes net ecosystem phosphorus uptake, because there are no significant additional sources of phosphorus. The sediments and organisms are important to the internal cycling of phosphorus, but neither of these reservoirs can constitute a long term phosphorus source in a steady state system. Nor, by the choice of systems examined, is there a significant terrestrial phosphorus source.

Such oceanic budgets provide only partial records of nitrogen uptake or release within the system because of the additional pathways of gas (N_2 or N_2O) transfer across the air-water interface coupled with N_2 fixation

or fixed nitrogen losses from the water column or sediments back to gaseous form. As described below, insight into these additional, nonoceanic deliveries can be derived from the discrepancies between budgetary derivations of net nitrogen and phosphorus fluxes and the N:P uptake ratios of the organisms and sediments.

The minimum amount of nitrogen that must be available for net metabolism in these isolated ecosystems is established as the net phosphorus uptake (from the oceanic delivery budget) multiplied by the molar N:P ratio in the sediments (the long term net uptake ratio of the systems). The systems in question have no significant input of fixed nitrogen from terrestrial sources, so some fraction of this minimum net nitrogen requirement must be met by the oceanic delivery budget (adjusted in two of the systems for DON export), the remainder by nitrogen fixation. This calculation defines the minimum nitrogen fixation rate which must occur. Maximum nitrogen fixation would occur if there were no internal nitrogen recycling and would be represented by the difference between the oceanic delivery and the immediate uptake requirements (from the plant molar N:P ratios multiplied by the oceanic phosphorus uptake). Maximum fixed nitrogen loss back to N_2 or N_2O is the difference between the maximum and minimum rates of nitrogen fixation.

Shark Bay—The first location under consideration is Shark Bay, a large (13,000 km²), hypersaline embayment in Western Australia. As discussed by Smith and Atkinson (1983, 1984), organic metabolism in that ecosystem is dominated by seagrass communities and by extensive soft-bottom infaunal communities. Rates of plankton production are not known but appear to be low. Net ecosystem production of organic carbon has been estimated to be 1.2 mmol C·m⁻²·d⁻¹ (Smith and Atkinson 1983).

Smith and Atkinson (1983) developed a detailed phosphorus budget for the bay from a salt and water budget, and Smith and Atkinson (1984) inferred a nitrogen budget from the salt, water, and phosphorus budgets, plant composition, and sediment composition. Because of the very slow water turnover in the bay (average residence time

Table 2. Material budgets of the three study sites. Relevant references are discussed in the text.

	Location		
	Shark Bay	Christmas Island	Canton Atoll
Incoming water composition (all measured)			
Salinity (‰)	36	35	36
Reactive P ($\text{mmol} \cdot \text{m}^{-3}$)	0.2	0.3	0.6
Inorganic N ($\text{mmol} \cdot \text{m}^{-3}$)	0.5	2.7	3.6
Average embayment composition (all measured)			
Salinity (‰)	46	32	38
Reactive P ($\text{mmol} \cdot \text{m}^{-3}$)	0.05	0.1	0.2
Inorganic N ($\text{mmol} \cdot \text{m}^{-3}$)	0.5	0.9	0.7
Mean water residence time (all calculated)			
Days	400	50	50
Average biotic composition			
Plankton molar N:P	16:1*	—	—
Benthos molar N:P	30:1*	27:1†	30:1‡
Average sediment composition (measured, except as noted)			
Organic C ($\text{mmol} \cdot \text{g}^{-1}$)	2.1	0.5	0.7
Total N ($\text{mmol} \cdot \text{g}^{-1}$)	0.05	0.02	0.02‡
Total P ($\text{mmol} \cdot \text{g}^{-1}$)	0.007	0.006	0.006‡
Sediment molar N:P	7:1	3:1	3:1‡
Net oceanic nutrient export or import (all calculated, $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$)			
P import	4	17	52
Dissolved inorganic N import	2	100	380
Dissolved organic N export	?	220	708
Internal nitrogen reactions (all calculated, $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$)			
Immediate N uptake	64–120	467	1,560
Long term net N uptake	28	51	156
N fixation	62–118	171–587	484–1,888
Fixed N loss	<92	<416	<1,404

* Measured.

† Calculated.

‡ Assumed.

is about 400 days), we assumed that virtually all particulate material produced in the system is sedimented there rather than exported; the sediments therefore provide a reliable record of net nitrogen and phosphorus accumulation by the system. In the case of nitrogen, this net accumulation reflects uptake of nitrogen supplied via water exchange with the ocean, plus nitrogen fixation, minus fixed nitrogen loss. The bay is surrounded by desert, and there are no significant terrestrial inputs to this system.

Table 2 summarizes the nutrient budgets, both known and inferred. Several important points emerge: Net metabolism of Shark Bay must be almost entirely dependent on internally fixed nitrogen, rather than on the delivery of nitrogen from the ocean. More than half of the gaseous nitrogen fixed into

organic materials within the bay may be subsequently lost back to the gaseous phase.

The ratio of dissolved inorganic nitrogen to phosphorus concentration in water entering Shark Bay is about 2.5:1, immediately suggesting nitrogen limitation. Phosphorus concentration decreases as salinity increases with increasing net evaporation and water residence time in the bay (Fig. 1), while nitrogen concentration remains at a low (but constant) level. The steep negative slope of phosphorus as a function of salinity indicates that there will be diffusive, as well as advective, input of phosphorus (Smith and Atkinson 1983). The zero slope for nitrogen indicates that there is advective, but not diffusive, nitrogen import. Hence, the oceanic import N:P ratio (0.5:1) is lower than the concentration ratio (Table 2).

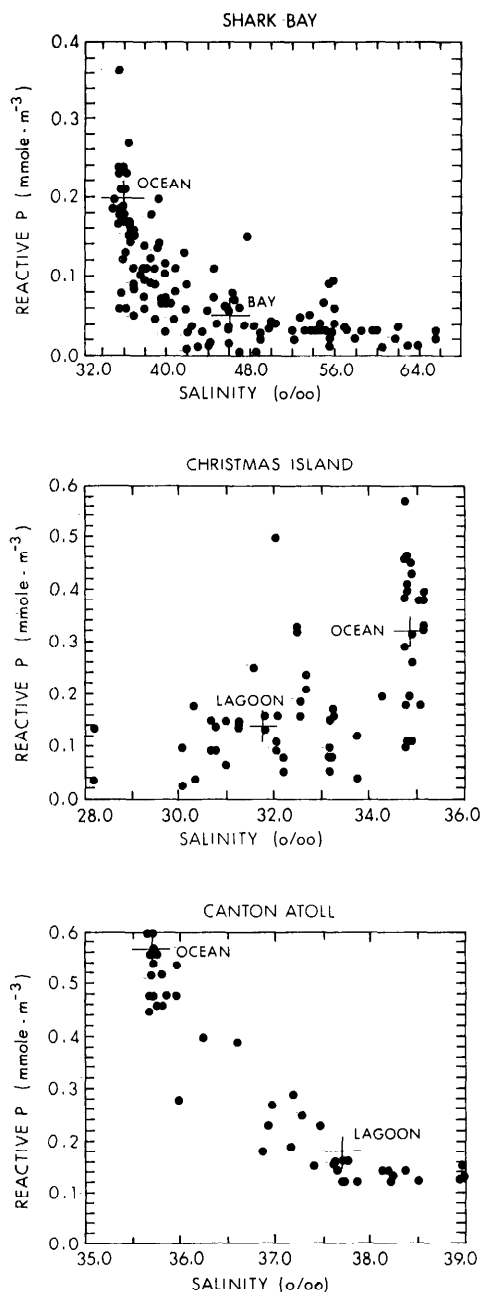


Fig. 1. Reactive phosphorus vs. salinity at Shark Bay, Christmas Island lagoon, and Canton Atoll lagoon. In all cases, ocean water enters these embayments with a salinity of 35–36‰. As water ages in Shark Bay and the Canton lagoon, it becomes more saline via net evaporation. As water ages in the Christmas lagoon, it becomes less saline through net rainfall.

Both of these ratios are very low relative to the net N:P uptake ratio indicated by plant composition. The immediate biotic uptake in the system is adjusted to a net N:P uptake ratio between about 16 and 30:1 (i.e. between the average N:P compositional ratio of plankton or benthic plants; Atkinson and Smith 1983, confirmed for Shark Bay). This adjustment occurs over an average water residence time of about 1 year, and the nitrogen made available by the adjustment is sufficient to account for the uptake of virtually all reactive phosphorus supplied to the system (Fig. 1).

The system-wide nitrogen fixation rate being invoked in this budget is reasonable in comparison with estimates of nitrogen fixation rates in seagrass communities and estuaries elsewhere. We estimated that nitrogen fixation provides $<120 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$; Capone and Carpenter (1982) summarized data which indicate that estuaries and seagrass communities fix nitrogen at rates between 20 and $1,000 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$.

Billen (1982) summarized available experimental data for shoal-water denitrification rates; the median value in his tabulation is about $1,000 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. Seitzinger et al. (1984) derived a denitrification rate of about $1,400 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ for Narragansett Bay, Rhode Island. That system has a relatively high organic loading (Nixon 1981), so it is not surprising that its rate of fixed nitrogen loss substantially exceeds that of Shark Bay ($<90 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$).

Christmas Island—The second nutrient budget presented here is for the main lagoon of Christmas Island, a coral atoll in the central Pacific Ocean (Univ. Hawaii Coop. Rep. UNIHI-SEAGRANT-CR-84-02). Typical quiet-water coral reef communities and interreef soft-bottom infaunal communities dominate the organic metabolism of the system. The area of this lagoon is about 200 km^2 , and water residence time averages about 50 days. Net ecosystem production of organic carbon has been estimated to be about $6 \text{ mmol C} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (Univ. Hawaii Coop. Rep. UNIHI-SEAGRANT-CR-84-02). Results of the nutrient budgets are summarized in Table 2.

Estimates of dissolved inorganic nitrogen

and phosphorus and organic phosphorus import and dissolved organic nitrogen export were derived from salt and water budgets. Again any significant terrestrial nutrient source can be dismissed. Dissolved organic nitrogen export exceeds inorganic nitrogen import, so there must be an internal nitrogen source.

As a minimum, internal nitrogen fixation must offset the export of dissolved organic nitrogen. Based on the following argument, we concluded that it was somewhat larger than this minimum. From Webb et al. (1975), we estimated that about $\frac{3}{8}$ of the nitrogen fixed on coral reef flats is exported from the flats as dissolved organic nitrogen, and the remainder is exported as dissolved inorganic nitrogen. In the case of a relatively enclosed lagoon like Christmas Island, we assumed that any inorganic nitrogen fixed on the lagoonal reef flats and exported from them is taken up elsewhere in the lagoon, while the apparently less labile organic nitrogen is largely exported from the entire system.

Water enters the lagoon with an inorganic N:P ratio of about 9:1, perhaps suggesting nitrogen limitation. The oceanic delivery ratio adjusted for advection and diffusion is about 6:1 (Table 2). From the inferred flux pathways, the calculated N:P uptake ratio is 27:1, virtually identical with the 30:1 average compositional N:P ratio of benthic marine plants (Atkinson and Smith 1983). These budgetary calculations indicate that about 60–85% of the nitrogen being incorporated into organic material by this system is made available from internal fixation. Reactive phosphorus in the Christmas Island lagoon is depleted substantially below oceanic levels (Fig. 1), although not to the dramatic extent that occurs in Shark Bay.

Again, the nitrogen fixation rate being invoked for this system is modest in comparison with accepted rates of nitrogen fixation in similar environments elsewhere. The estimated nitrogen fixation rate is $<600 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, in comparison with rates of up to 13,000 estimated for other coral reef flats (Wiebe et al. 1975).

Previously unpublished data on sediment nitrogen and phosphorus for the Christmas

Island lagoon have been included in the calculations. These calculations suggest a fixed nitrogen loss of up to about $400 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. From both water turbidity and sediment composition it is obvious that a large fraction of the organic material produced in that lagoon is exported rather than being sedimented there. It is therefore entirely possible that the N:P ratio of the sedimentary materials yields a substantial overestimate of the denitrification rate of the entire system. Nevertheless I offer these preliminary estimates for eventual comparison with other system-wide fixed nitrogen loss rates. The maximum fixed nitrogen loss rate is about 70% of the estimated nitrogen fixation rate for the system.

Canton Atoll—The third site for these nutrient budgets is the lagoon of Canton Atoll, also in the central Pacific Ocean (Smith and Jokiel 1978). This reef-dominated lagoon has an area of about 40 km², and the average water residence time is about 50 days. After correcting the original carbon budget with a more precise estimate than that first used for net CO₂ gas flux across the air–water interface, I have estimated the net organic carbon production rate of the Canton lagoon to be $14 \text{ mmol C} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (S. V. Smith 1983; Univ. Hawaii Coop. Rep. UNIH-SEAGRANT-CR-84-02).

We lack data on sediment nitrogen or phosphorus or dissolved organic nitrogen for Canton. Nevertheless, the somewhat more complete budget for Christmas Island suggests that a great deal can be inferred from the expected N:P uptake ratio of benthic marine plants. These results are also summarized in Table 2.

Water enters the Canton lagoon with an inorganic N:P concentration ratio of 6:1, again perhaps suggesting nitrogen limitation. The oceanic delivery ratio is 7:1. In order that an immediate N:P uptake ratio approximating the average composition of benthic marine plants be achieved (30:1; Atkinson and Smith 1983), $1,180 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ of gaseous nitrogen must be fixed and incorporated with the phosphorus. As for Christmas Island, this fixation is estimated to represent $\frac{5}{8}$ of the total fixation, the remainder being exported from the lagoon as dissolved organic nitrogen. The es-

timated fixation rate is still very low in comparison with rates found on coral reefs elsewhere. Reactive phosphorus in the ecosystem is largely consumed (Fig. 1), even though the input rate is much higher than it is for the other two systems.

I do not have sediment nutrient data for Canton, but I would predict that the sediment N:P ratio would again be low, reflecting fixed nitrogen loss largely balancing this higher rate of nitrogen fixation. Such an interpretation is entirely consistent with the assessment by Nixon (1981) for Narragansett Bay. If the sediment N:P ratio at Canton is assumed to equal that at Christmas, then the calculated maximum fixed nitrogen loss rate is about 70% of the calculated maximum nitrogen fixation rate.

Discussion

What has been learned from these budgets that cannot be readily derived from other ecosystem nutrient budgets? Many nutrient budgets for estuaries are dominated by advective input and output (e.g. Jaworski 1981; Monbet et al. 1981). Jaworski summarized estuarine nutrient loading rates of up to about $200 \text{ mmol N} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ and $20 \text{ mmol P} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$; most of that loading is exported. In systems with high advective throughput, nutrient concentrations are likely to be nearly conservative with respect to nonreactive tracers such as salinity (Boyle et al. 1974; Biggs and Cronin 1981; Schindler 1981), and details of internal fluxes are not easily deciphered. The rate of N:P adjustment under such circumstances is—as previously discussed—slow compared to the rate of advective nutrient throughputs via water exchange.

Near-conservative behavior of nitrogen and phosphorus with respect to salinity indicates that nutrient composition is controlled primarily by the physical processes of advection and mixing, not by net biological uptake; uptake and release may introduce scatter into the data set but roughly balance one another (Imberger et al. 1983). If the net flux of both nitrogen and phosphorus is approximately conservative with respect to salinity, then neither nutrient limits net ecosystem production in any operational sense. The specific growth rate of

individual organisms in the system may be limited by the local concentration of nitrogen or phosphorus, but net ecosystem production must be limited by some other factor (e.g. another nutrient, light, temperature, grazing pressure, or biomass washout).

It is also misleading to interpret low N:P concentration or loading ratios as indicative of nitrogen limitation. There may, for example, be substantial gaseous nitrogen transformation reactions (nitrogen fixation and fixed nitrogen loss) which are coupled with rapid internal turnover of nitrogen (e.g. see Imberger et al. 1983), effectively obscuring any net ecosystem nitrogen gains by the scatter which is ordinarily interpreted as “analytical noise.” Net gains in nitrogen availability may be sufficient to deplete available phosphorus without being statistically detectable in data sets derived from such advectively dominated systems.

Isolated measurements of low (or no, or high) nitrogen fixation or denitrification in incubation chambers also do not address the question of nitrogen fixation at the scale of the ecosystem. In order to evaluate the environmental significance of nitrogen fixation and fixed nitrogen loss, we need to reconstruct what must be occurring at the scale of the ecosystem. As demonstrated here, these reconstructions become more easily achieved as advective throughputs diminish.

The confined ecosystems examined here have very slow advective throughput; water residence time in these systems ranges from almost 2 months to >1 year. Clearly the rate for adjustment of the N:P availability ratio is fast compared to these exchange rates, and these systems have become phosphorus-limited. The minimum time scale for phosphorus limitation in the marine environment remains unclear, but it is short enough to be significant to the understanding and management of marine ecosystems.

Sediment data for two of the systems that I have examined in detail and water composition data for all of them indicate that relatively little nitrogen above the oceanically imported nitrogen actually accumulates in these systems. Rather, the locally fixed nitrogen is held up in the systems long enough for fixed nitrogen loss largely to off-

set nitrogen fixation. Sediment data consistently suggest that most nitrogen available for community metabolic needs is subsequently lost from the sediments. Differential rates of nitrogen and phosphorus regeneration might partially account for this loss, but N:P sediment regeneration ratios that are near or below plant uptake ratios, even though particulate fallout ratios approximate that of plant uptake (Nixon 1981; Smith et al. 1981), suggest that sediment denitrification, nitrification, or both are significant loss pathways.

We thus return to the bases on which nitrogen, not phosphorus, has come to be considered the nutrient most limiting to metabolism in the marine environment. Ryther and Dunstan (1971) concluded from ambient nitrogen and phosphorus concentration data and from bottle enrichment experiments that nitrogen fixation in the ocean is not effective locally or in the short run. On the basis of the composition of phytoplankton grown experimentally under various conditions of nutrient limitation, Goldman et al. (1979, p. 215) concluded that "severe phosphorus limitation probably does not occur in the world's oceans." These arguments are reminiscent of bottle-based arguments for lacustrine nutrient limitation (e.g. the work by Lange 1970 on carbon limitation; see Schindler 1971 for a detailed critique).

At a global scale, these arguments are unlikely to be correct. Nutrient availability, not concentration, is most relevant to limitation of net ecosystem production. From Hattori (1982) and Capone and Carpenter (1982), I estimate that at least 1×10^{12} mol of nitrogen are fixed annually in surface ocean waters. This rate seems likely to be low (Martinez et al. 1983). Dissolved inorganic nitrogen import from streams apparently totals about 8×10^{11} mol·yr⁻¹ (Meybeck 1982), so total fixed inorganic nitrogen availability apparently is at least 2×10^{12} mol·yr⁻¹. From Lerman et al. (1975), Meybeck (1982), and Froelich et al. (1982), I estimate that dissolved phosphorus input from land totals about 4×10^{10} mol·yr⁻¹. We see that the N:P availability ratio (>50:1) substantially exceeds the Redfield ratio (16:1). The net oceanic nitrogen bud-

get is clearly dominated by internal biochemical reactions, not by inputs from land.

Arguments which have been presented to substantiate nitrogen limitation are also unconvincing at the scale of ecosystems. The bottle experiments which "demonstrate" nitrogen limitation in the marine environment can obviously exclude or deactivate major nitrogen-fixing organisms (Martinez et al. 1983), so the interpretation from these experiments of nitrogen limitation should be restricted to the limitation of the specific growth rate of the plankton most actively growing in those bottles. This aspect of nitrogen limitation does not appear particularly relevant to the understanding and management of net production in the marine environment, although it is clearly of great physiological interest.

Although apparently unproven as a phenomenon at the scale of marine ecosystems, nitrogen limitation may nevertheless occur in the ocean. If the nitrogen and phosphorus budgets for a particular ecosystem were to demonstrate system-wide nitrogen limitation, then one might look to rapid throughput of locally fixed nitrogen or perhaps to large losses of relatively refractory dissolved organic nitrogen as the most obvious explanations.

There is not an inherent difference in the characteristics of nutrient limitation between lakes and the ocean. The apparent difference lies in part with the relative rates for material exchange via the physical processes of advection and eddy diffusion and the biochemical processes of nitrogen fixation and fixed nitrogen loss. If the exchange rates are faster, then net ecosystem production of organic material may be nitrogen-limited; if the biochemical rates are faster, then the net production will tend toward phosphorus limitation.

Different analytical approaches applied to lakes and the ocean also appear to have contributed to this perceived environmental difference between lakes and the ocean. As clearly demonstrated by the various limnological studies cited (Vollenweider 1968, 1969, 1976; Schindler 1971, 1974, 1977; Schindler et al. 1978; Flett et al. 1980; Dillon 1975; Smith 1982; Edmondson 1970; Edmondson and Lehman 1981), firm con-

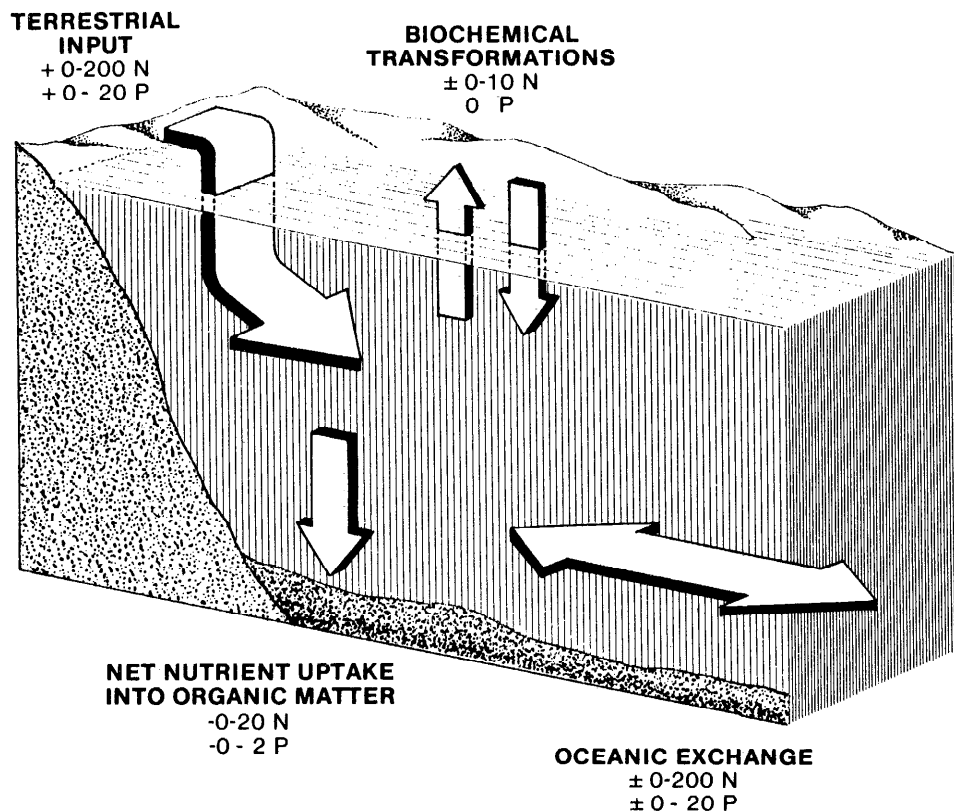


Fig. 2. Schematic diagram to illustrate the approximate ranges of nutrient fluxes (in $\text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) contributing to the net production of organic matter in aquatic environments.

clusions about nutrient limitation of total-system organic carbon production should be derived at the scale of whole ecosystems rather than bottles. Each ecosystem of interest should be examined on the basis of its characteristics of nutrient supply, internal metabolic cycles, and export, in order that phosphorus vs. nitrogen limitation be assessed at this scale. The insights gained from budgeting nitrogen and phosphorus together greatly exceed those gained from single-nutrient budgets. The budgets should address the characteristics of internal biological and sedimentary nutrient pools, as well as advective and diffusive inputs and outputs. The kind of limitation being discussed—specific growth rate of taxa, primary production of communities, or net production of systems—should be carefully specified.

“Availability” is clearly a key aspect of the definition of limiting factors. Availability extends beyond the concentration and loading of materials. In the case of nutrient limitation of net ecosystem production, availability must include the ability of the ecosystem to supply materials by internal biochemical cycles.

Conclusions

I summarize my conclusions from these budgets with a general figure (Fig. 2) and equation:

$$\begin{aligned} \text{Net ecosystem production of} \\ \text{organic matter} = \\ R \times \text{net nutrient uptake} = \\ R \times [(\text{hydrographic nutrient} \\ \text{additions} - \text{losses}) + \\ (\text{biochemical nutrient} \\ \text{additions} - \text{losses})]. \end{aligned}$$

R is the scaling ratio between the uptake of any nutrient and the desired measure of net production. Hydrographic gains and losses, via terrestrial inputs and oceanic exchange, can span a wide dynamic range; for discussion I suggest a range of $0\text{--}20\text{ mmol P}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ and $0\text{--}200\text{ mmol N}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. By contrast, net biochemical fluxes for phosphorus apparently do not occur and, for nitrogen, reach only about $10\text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. Net ecosystem uptake of phosphorus and nitrogen is a response to nutrient availability and is constrained to equal the sum of these fluxes; but nutrient uptake is also constrained by other factors limiting net organic production. From data on net organic production rate, I estimate that the upper limit of nutrient uptake in aquatic systems is of the order of $2\text{ mmol P}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ and $20\text{ mmol N}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$.

If hydrographic fluxes are small, then biochemical fluxes of nitrogen are likely to obviate nitrogen limitation while phosphorus is exhausted. If hydrographic fluxes are large, then neither biochemical fluxes nor hydrographic supply of either nitrogen or phosphorus is likely to limit net ecosystem production of organic matter. Other limiting factors must be sought.

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