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Marine nitrogen: Phosphorus stoichiometry and the global N:P cycle

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Abstract. Nitrogen supply is often assumed to limit marine primary production. A global analysis of total nitrogen (N) to phosphorus (P) molar ratios shows that total N:P is low (<16:1) in some estuarine and coastal ecosystems, but up to 100:1 in open oceans. This implies that elements other than N may limit marine production, except in human impacted, estuarine or coastal ecosystems. This pattern may reconcile conflicting enrichment studies, because N addition frequently increases phytoplankton growth where total N:P is expected to be low, but P, Fe, or Si augment phytoplankton growth in waters where total N:P is high. Comparison of total N:P stoichiometry between marine and freshwaters yields a model of the form of the aquatic N:P cycle.

Introduction

Marine primary production yields >90 billion kg of food to the world economy each year (FAO 1993). Marine ecosystems store 50-times more inorganic carbon than the earth's atmosphere, so marine primary production may play an important role in establishing global climate (Mackenzie et al. 1993; Ritschard 1992). Factors regulating marine production are therefore of broad societal interest.

There is currently disagreement about the nutrient elements limiting marine primary production (Howarth 1988; Smith 1984). On one hand, some have concluded (e.g. Boynton et al. 1982) that because ratios of dissolved inorganic nitrogen (N) and phosphorus (P) are often lower than the average intracellular N:P ratio of marine organisms (Redfield 1934; Redfield et al. 1963), nitrogen is the element in shortest supply and therefore must limit marine primary production. On the other hand, geochemical budgets suggest that inorganic phosphorus should be in shortest supply (Meybeck 1982) in part because atmospheric N_2 can be fixed (Redfield 1958; Vitousek & Howarth 1991). Experimental additions of inorganic nutrients to seawater samples from various marine ecosystems suggest that several elements may play limiting roles, including N, P, Si and Fe (Boynton et al. 1982; Martin & Fitzwater 1988; Martin et al. 1994).

Although N and P are present in inorganic, organic and particulate forms, much of marine nutrient stoichiometry has been based only upon the relative amounts of dissolved inorganic N and P found in marine ecosystems. Frequently measured NO_2^-, NO_3^-, NH_4^+ and PO_4^{3-} may represent only a fraction of the N and P that can be used by the biotic community, however. Many aquatic organisms, from bacteria to fish, consume and cycle dissolved organic matter (e.g. Amon & Benner 1994; Bentzen et al. 1992; Glibert et al. 1991; Hoegh-Goldberg 1994), although dissolved organic N and P may be cycled at different rates (e.g. Smith et al. 1986). Particulate N and P can also be ingested and rapidly converted to dissolved inorganic and organic forms by zooplankton (e.g. Ikeda et al. 1982). Thus, many analyses of nutrient stoichiometry in marine ecosystems are based on analyses of fragments of the complete N and P pools.

Analyses of total N and P pools are used to distinguish N from P limitation in freshwaters. Phosphorus, usually measured as PO_4^{3-} was initially recognized as the principal limiting nutrient in freshwaters, but limitation by nitrogen has since been reported in many freshwater ecosystems (Elser et al. 1990). Dissolved N and P are cycled so rapidly by living organisms that they are absorbed as fast as they are produced and thus are often difficult to detect in the soluble inorganic state. Because both organic and inorganic N and P can be used by aquatic organisms, analyses of the total amounts of nutrient elements (i.e. the sum of all dissolved, particulate, organic and inorganic nutrients) yield better measurements of freshwater nutrient supply than analyses of soluble, inorganic N and P alone (Sakamoto 1966).

This approach has been successfully applied in the management of freshwater ecosystems. A recent study shows that comparison of the total N:P ratios of whole water samples with the average N and P needs of algal cells is useful in distinguishing freshwater ecosystems limited by N from those limited by P (Downing & McCauley 1992). Ecosystems with N:P molar ratios less than the average required cellular ratio of 16:1 (Hecky & Kilham 1988) are generally N-limited and those with ratios >16:1 are P-limited. Unfortunately, no analysis of marine data on total N and P stoichiometry has been performed due to the scarcity of total N and P data in marine environments. The purpose of this analysis is to summarize existing marine data to find how total inventories of N and P vary in the world's marine ecosystems.

Methods

Marine data on total N and total P are rare because marine studies seldom analyze all fractions of N and P. Some estimates of total N and P concentrations are scattered throughout the world literature, including data from a polluted European estuary, Chesapeake estuary, a North Carolina inlet, several harbors, the Pacific Ocean near Peru, California and New Zealand, the Gulf of Bothnia, the Baltic, the Gulf of Finland, the Strait of Gibraltar, the Indian Ocean, the Adriatic, and the Mediterranean. Several sources of total N and total P data are analyzed here: Ben-Taleb et al. (1987), Black et al. (1981), Coste et al. (1988), Dame et al. (1986), Degobbis & Gilmartin (1990), Jordan et al. (1991), Lahdes & Leppanen (1988) Le Rouzic & Bertru (1992), Perttila et al. (1980), Pietikainen et al. (1978), Pitkanen & Malin (1980), Ramadan et al. (1984), Rydberg & Sundberg (1986), Updegraff et al. (1977), Valderrama (1981), and Williams (1967). Data were restricted to averages for depth strata at sampling stations where analyses of total N and P or all components (inorganic, organic and particulate) were made using accepted standard methods. These methods usually consist of a digestion of samples for TP analysis followed by a colorimetric detection of PO_4^{3-}. Total nitrogen was analyzed by several methods, frequently determining concentrations of N fractions separately then summing, or by digestion to a soluble form, followed by inorganic N determination. Although some of these analyses may underestimate the abundance of dissolved, organic N (Suzuki et al. 1985), such underestimates, if present, would tend toward underestimation of TN:TP ratios (Karl et al. 1993). Standard TP and TN methods employed were those described in: Dal Pont et al. (1974), D'Elia et al. (1977), Grasshoff (1976), Grasshoff (1983), Menzel & Corwin (1965), Strickland & Parsons (1968), Strickland & Parsons (1972), Treguer & Le Corre (1975), and Valderrama (1981).

Results and discussion

We collected published data on total N and P inventories (dissolved inorganic and organic plus particulate forms) for 191 sample series taken at 88 marine sampling stations throughout the world. The total nitrogen concentration in marine ecosystems, ranging from estuaries to oligotrophic seas, only varied by about 30-fold (6–200 μM), whereas total phosphorus varied 650-fold (0.03–20 μM) (Figure 1). Therefore, total N:P ratios varied between about 5 and 310 (in moles), averaging N:P = 37, over all.

The majority of marine data analyzed here show N:P greater than the ratio required by planktonic marine algae (Figure 2). The N:P in living marine organisms varies greatly but averages about 16 (Hecky & Kilham 1988;

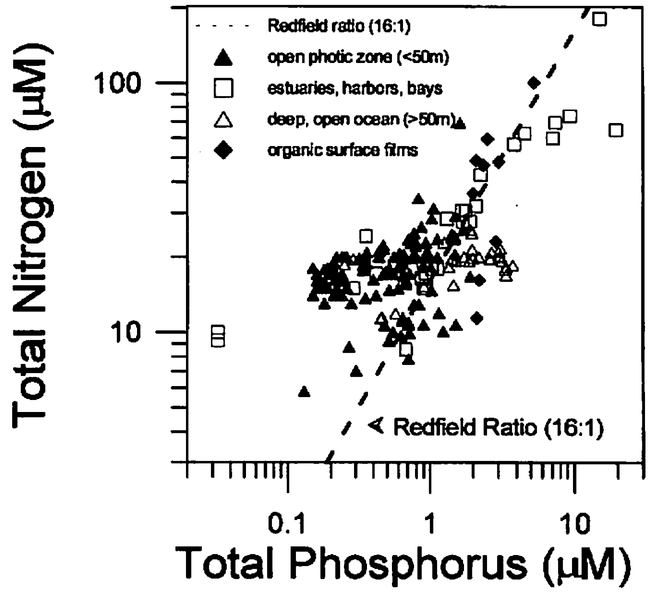

Figure 1. Relationship between total nitrogen and total phosphorus concentrations of marine ecosystems. Total N and P data were usually averages calculated from sets of samples taken at the same site on at least 3 different dates within the same year. Stations in the upper photic zone were defined conservatively as those <50 m in depth (Tett 1990) while nearshore sites were determined from information presented in published studies. The dashed line is the approximate average ratio of N and P in living marine plankton.

Meybeck 1982; *cf* Elser & Hassett 1994), therefore ambient N:P < 16 would indicate N limitation, while N:P > 16 would suggest P limitation of production. N:P is especially high in the upper photic zone where most of the ocean's planktonic production occurs and where nutrient limitation of production is most acute (Tett 1990). Only 12% of the open ocean photic zone sites had total N:P < 16:1. Only 3% had N:P indicating strong nitrogen deficiency (N:P < 10), 19% had N:P near to biological requirements (10 < N:P < 20), while 78% of open, photic zone sites had N:P indicating a deficiency of phosphorus or some element other than nitrogen (Figure 2). Both parametric and nonparametric statistical analyses show that the average total N:P ratio ($\overline{N:P}$ = 43) for open ocean photic zone sites (conservatively estimated as <50 m depth) was significantly ($p < 0.0001$) greater than 16:1. Oligotrophic sites have highest total N:P illustrated by the negative correlation between the logarithm of N:P and the logarithm of total P (Figure 3; $p < 0.00001$, $r^2 = 0.81$). The significant tendency for oligotrophic, open seas to have N:P greater than 16, indicates that P or some nutrient other than N limits production in open seas. Ratios of N:P are frequently >50:1 in the nutrient poor sites examined (Figure 3), often as great as 100:1. Total N:P > 16 occurred at 61

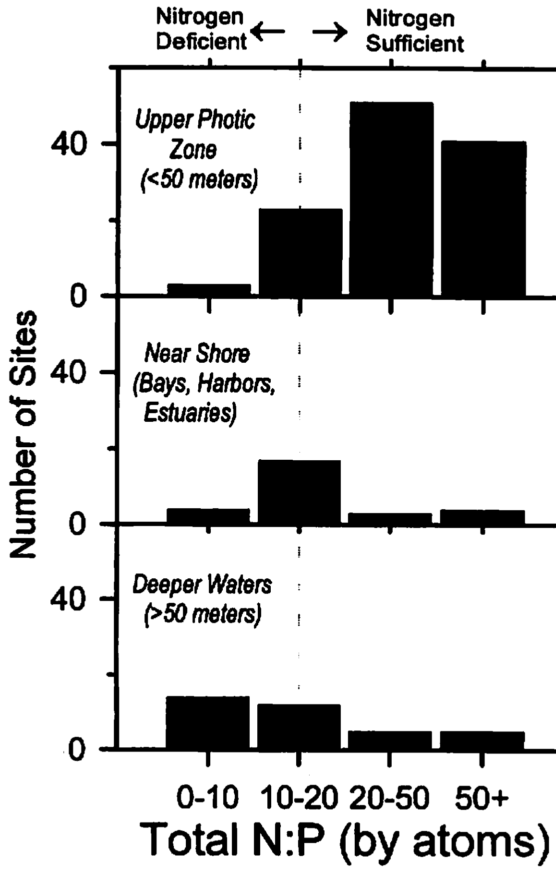

Figure 2. Nitrogen deficiency in marine waters relative to the usual N:P of living organisms. Shown are total N:P calculated from inventories of dissolved and particulate inorganic and organic N and P at several marine sampling stations. Environments include a broad variety of conditions and represent station-depth averages. Stations in the upper photic zone were defined conservatively as those <50 m in depth (Tett 1990) while nearshore sites were determined from information presented in published studies.

sites in 34 ecosystems, analyzed independently in 13 different studies, using several different standard methods. Provided that there is not a great divergence in the fraction of total N and P that are biologically labile, total N and P stoichiometry suggests that phosphorus or other factors limit production in the open oceans.

The data analyzed here suggest that N:P is very high in oligotrophic, open seas but often very low in estuaries and coastal ecosystems (Table 1). Estuarine, coastal, or enclosed parts of the sea had N:P ratios less than the required cellular ratio of 16:1 significantly more frequently (χ^2-test, p = 0.005) than samples taken from the surface waters of the open ocean (Figures

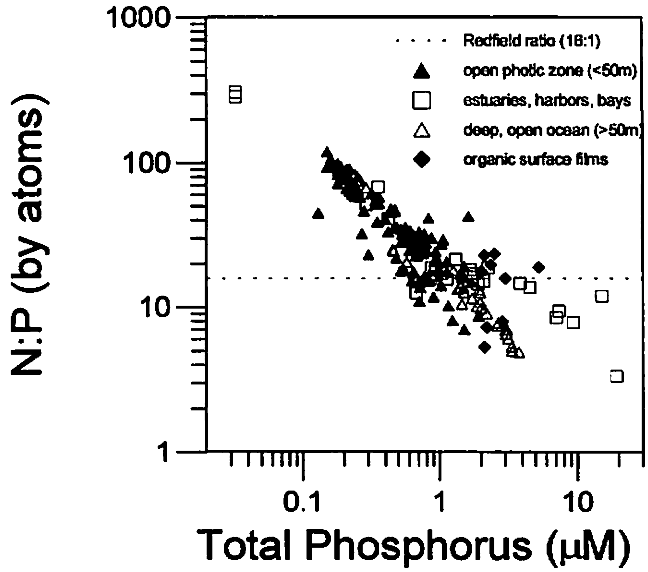

Figure 3. Total N:P ratios of data plotted in Figure 1 distinguishing types of marine environments. Deep and shallow sites were determined as in Figure 2. Data obtained from estuaries, harbors and bays were differentiated as such by the authors of studies. The dashed line is the approximate average ratio of N and P in living marine plankton.

Table 1. Frequency of total N:P molar ratios (Figure 3) that are greater than the approximate average ratio of N and P in living marine plankton (16:1). Ratios >16 imply that nitrogen is probably not the principal limiting nutrient.

Environment	Frequency of total N:P molar ratios: <16	≥16
Open oceans, <50m depth	14	104
Open oceans, surface films	3	6
Estuaries, harbors, bays	11	17
Deep, open oceans, >50m depth	23	13
Total	51	140

2–3; Table 1). Nitrogen is therefore probably the primary limiting nutrient in estuarine and coastal ecosystems, especially those heavily loaded by human influence (Howarth et al. 1995).

The unexpectedly great frequency of high N:P in open oceans is surprising because, except for a few cases (e.g. Kron et al. 1991), most analyses have concluded that N:P is usually <16 in marine ecosystems. This pattern has probably been missed because measurements of dissolved organic, particulate or whole N and P fractions have lagged behind measurements of NO_2^-, NO_3^-, NH_4^+ and PO_4^{3-}.

Some modern studies measuring several N and P pools at oligotrophic, open ocean sites also indicate total N:P frequently >16 in the photic zone. For example, the fractionation of N and P at an oligotrophic station in the open Pacific can be approximated from data collected under the Hawaii Ocean Time-series project of the Joint Global Ocean Flux Study (Winn et al. 1993). Water samples, collected in February, March, April, May, June, July, August, September, October, and December of 1991, were analyzed for several N and P fractions. N and P in different fractions and depths can be estimated from averaged N and P profiles in different sample series. Averaging over all cruises during the year, the approximate average total nitrogen concentration in the upper 200 m was 9.7 μM and total phosphorus was 0.4 μM. The annual average N:P of the photic zone was therefore about 24, but average N:P of the photic zone during individual cruises was as high as 120 and was >16 on 8 out of 10 dates. Karl et al. (1995) have also discussed the lack of evidence for N limitation shown in these samples. Although Karl et al. (1993) suggest that the average N:P (considering dissolved forms alone) does not depart from the Redfield ratio, more recent work shows that photic zone TDN:TDP ratios in the photic zone are stongly skewed toward high, non-Redfield ratios (David M. Karl, pers. comm.).

In spite of the high total N:P found at this site, traditional analyses of dissolved inorganic N:P would have suggested N limitation. The average dissolved inorganic N:P in the upper 200 m was usually <5. The particulate and dissolved organic fractions, however, had N:P as high as 200:1 in many samples. The fact that N:P was very high in particulate matter further counter-indicates N-limitation at this open-ocean site since much of the particulate matter may be living plankton.

Other studies also show that particulate and dissolved organic N:P can be very high at a variety of oligotrophic sites in the open sea (Copin-Montégut & Copin-Montégut 1983; Jackson & Williams 1985). The organic N and P pools are therefore essential to our understanding of N and P cycling in the seas but measurements of the size of these pools and their dynamics have been beyond the reach of standard marine chemical methodology. We therefore need much more extensive knowledge of the total stoichiometry of marine ecosystems.

Differences in the total N:P stoichiometry among marine ecosystems may reconcile the conflicting results obtained in nutrient bioassays. Many such analyses have experimentally enriched nutrients in natural seawater samples to see which nutrients lead to increased phytoplankton growth (Table 2). In polluted estuaries and bays, where total N:P ratios are frequently low (Figure 3), such bioassays usually find that N addition leads to greatest increases in algal activity (Granéli 1987; Le Rouzic & Bertru 1992; Ryther & Dunstan 1971), although some coastal systems may vary seasonally from N to P limitation (D'Elia et al. 1986; D'Elia et al. 1992; Fisher et al. 1992; Rinne & Tarkiainen 1975) depending upon the N:P of inflowing waters. Less polluted coastal waters also show N limitation (Edmondson 1956; Smayda 1974; Tarkiainen et al. 1974) but addition of both N and P together often results in greater phytoplankton growth than addition of N alone (Granéli 1984; Rudek et al. 1991; Vince & Valiela 1973). The N:P supply ratio may therefore be very close to 16:1 in some less polluted coastal systems. In the open ocean, however, where I found total N:P generally >16 (Figure 3), nitrogen is rarely the principal nutrient limiting phytoplankton abundance or activity (Table 2). Instead, nutrient bioassays usually find that production is limited by phosphorus (Berland et al. 1980; Berland et al. 1987; Bonin et al. 1989; Lapointe 1986), iron (DiTullio et al. 1993; Martin & Fitzwater 1988; Menzel & Ryther 1961; Menzel et al. 1963; Ryther & Guillard 1959; Tranter & Newell 1963), or silica (Smayda 1971). Nitrogen is probably rarely the principal element limiting phytoplankton in the open oceans because its supply appears to be ample relative to phosphorus.

Global N:P model

The combined patterns of variation of total N:P ratios in marine and freshwater environments provides a model of the global N:P cycle. In upstream freshwaters, where input is mostly derived from high N:P precipitation and high N:P run-off from undisturbed soils (Downing & McCauley 1992), P concentrations are low, N:P is high (Figure 4) and production is strongly P-limited. As water moves downstream, it is enriched by high P, low N:P run-off from terrestrial systems, P increases and N:P declines, resulting in frequent N-limitation of primary production (Elser et al. 1990) and blooms of N-fixing cyanobacteria (Smith 1983). This enrichment may proceed to a varying degree, depending upon the size, land use, and human inhabitation in the drainage system (Peierls et al. 1991).

When nutrient laden rivers flow into coastal marshes and estuaries, anoxic sediments and organic matter are usually abundant, leading to rapid denitrification (Seitzinger 1988), which may explain the drop in N:P as freshwater discharge passes through estuarine environments (Figure 4). As coastal waters move out into open seas, P may be sedimented more rapidly than N, as evidenced by low N:P in deep waters (Figures 2–3), marine sediments and sedimentary rocks (Downing & McCauley 1992). Phosphorus concentrations decline more rapidly than N concentrations in open seas, perhaps because atmospheric N_2 can be fixed in surface waters (Capone & Carpenter 1982;

Table 2. Examples of nutrient enrichment studies arranged in approximately increasing order of expected total N:P, based on the pattern observed in Figure 3. Elements that increased algal growth, production or biomass are listed in decreasing order of their importance (most important first), as perceived by the authors of the studies. "N+P" indicates that adding N and P together increased biomass over addition of N or P alone.

Place	Reference	Limiting elements
Polluted, enclosed estuary: Gulf of Morbihan, France	Le Rouzic & Bertru (1992)	N, N+P
Shallow, polluted Long Island Bays	Ryther & Dunstan (1971)	N
Brackish Laholm Bay	Granéli (1987)	N
Chesapeake Bay	Fisher et al. (1992)	N, P*
Chesapeake Bay	D'Elia et al. (1986; 1992)	N, P†
Neuse River Estuary, North Carolina.	Rudek et al. (1991)	N, N+P
New York Harbor, polluted Long Island Sound	Ryther & Dunstan (1971)	N
Lower Narragansett Bay	Smayda (1974)	N
Polluted Baltic near Helsinki	Rinne & Tarkiainen (1975)	N, P*
Baltic near Helsinki	Tarkiainen et al. (1974)	N, P‡
Woods Hole Harbor	Edmondson (1956)	N, P
Woods Hole Harbor	Vince & Valiela (1973)	N, N+P
Oresund narrows near Copenhagen	Granéli (1984)	N, N+P
Ocean between Bermuda and Puerto Rico	Smayda (1971)	N, P, Si
Open Ocean between Montauk Pt. and Bermuda	Ryther & Guillard (1959)	Fe, N+P
Indian Ocean	Tranter & Newell (1963)	Fe, N+P
Sargasso Sea	Menzel & Ryther (1961)	Fe, N+P
Sargasso Sea	Ryther & Guillard (1959)	Fe, N+P
Sargasso Sea	Menzel et al. (1963)	Fe, N+P
Sargasso Sea, Sargassum	Lapointe (1986)	P
Subarctic Pacific	Martin & Fitzwater (1988)	Fe
Mediterranean Sea	Bonin et al. (1989)	P
Mediterranean Sea	Berland et al. (1977)	P
Mediterranean Sea	Berland et al. (1987)	P, N+P

* changes seasonally. † changes according to N:P of inflowing waters. ‡ usually N limited.

Smith & Veeh 1989) and aeolian N deposition can be substantial (Fanning 1989). Surface N:P ratios can increase dramatically in offshore marine environments, leading to frequent limitation of production by P or nutrients other than N.

Taken together, the results of this study and those of Downing & McCauley (1992) suggest the form of general longitudinal N:P profiles of temperate zone rivers in developed countries (Figure 5A). Upland, headwater streams should have high N:P that largely reflect nutrient ratios in precipitation. Thus, in pristine areas, N:P ratios should be very high because N in rain is enriched by atmospheric fixation and there should be little P in aeolian deposition. N:P in precipitation is sometimes lower in urbanized or agricultural areas, and may alter headwater N:P (Loehr 1974). Downstream freshwaters will usually be

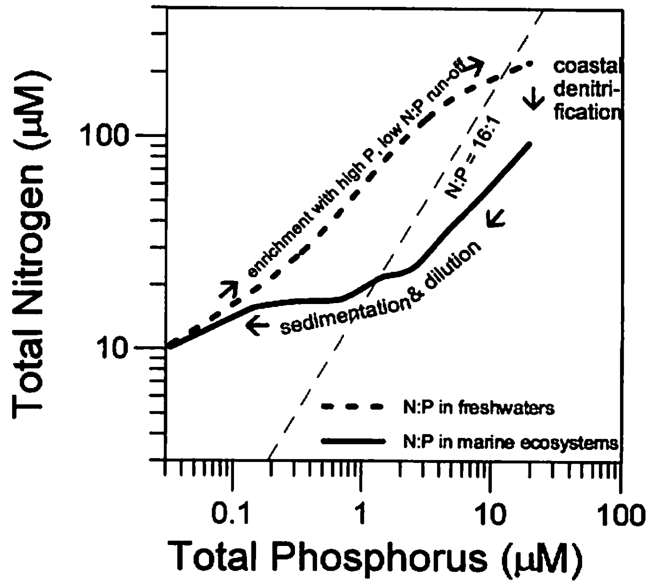

Figure 4. Observed global aquatic N:P cycle. Average trends shown are locally weighted sequentially smoothed fits to the actual observations. Trends were determined using LOWESS, a model-free, unbiased method for finding average trends in data (Cleveland & McGill 1985). LOWESS parameters were $\Delta = 0$, n-steps = 2, $f = 0.5$. The freshwater line is from Downing & McCauley (1992) and the marine line is fitted to the data in Figure 1.

richer in both N and P but have lowered N:P unless P is selectively removed or N is enriched.

A conservative mixing of two solutions that have different relative concentrations of two elements results in a linear relationship between the concentrations of the two elements in all possible admixtures of the two solutions. Therefore, if the variations in observed N:P are simply due to conservative enrichment of rainwater by polluted waters or the dilution of river water by dilute oceanic waters, relationships between N and P should be approximately linear across marine and freshwater systems. In freshwater systems, there is a clear change in mechanism of relative N and P enrichment as one moves from headwaters to downstream systems (Figure 5B). Since the slope of the relationship is directly related to the N:P of the enriching solution, this pattern is suggestive of a progressive decrease in the N:P of effluents. In marine systems however, the decline in N concentration with decreasing P in open oceans is nearly linear, suggesting that variations in marine N:P may be related to the conservative dilution of freshwater effluent by oceanic waters.

This study adds to the mounting evidence that productivity is limited by elements other than N in many of the world's open oceans (Martin & Fitzwater 1988; Martin et al. 1994). These data imply that N:P > 16 is found

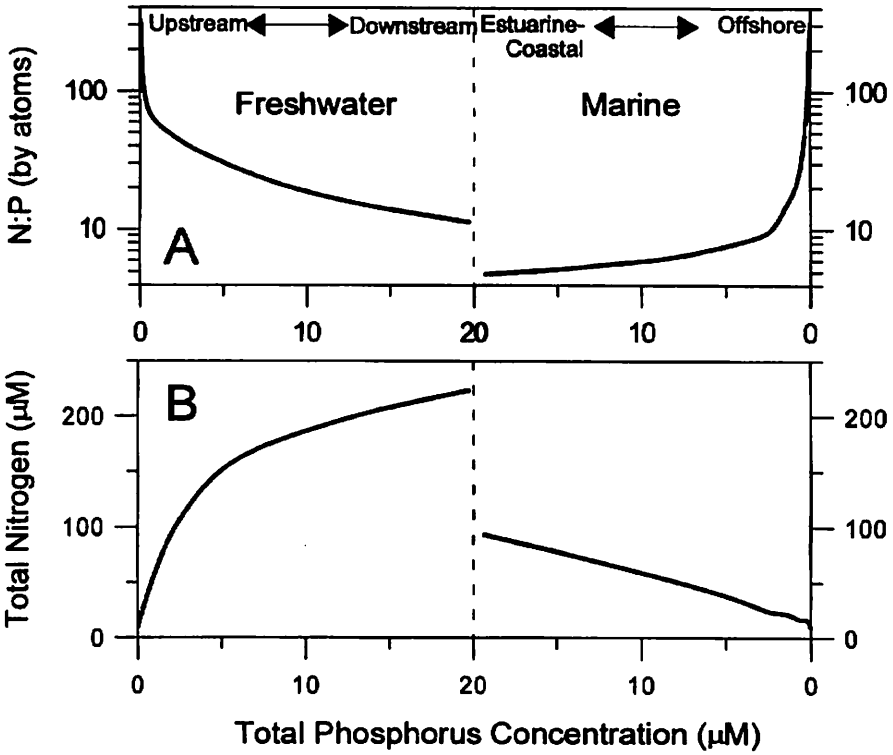

Figure 5. Predicted gradient in total N and P along the axis of rivers in temperate zone developed countries. Trends are actual LOWESS relationships (*see* Figure 4) in data from upstream and downstream lakes (Downing & McCauley 1992) and inshore vs. offshore marine ecosystems. (A) shows trends in N:P while (B) shows trends in N concentration. Data are arranged in order of increasing enrichment (0–20 μM P) in freshwaters and in order of decreasing enrichment (20–0 μM P) in marine systems.

most frequently below total P concentrations of 1 μM. Broad-scale surveys of total P in marine environments suggest that concentrations >1 μM may be rare away from shore or upwellings (Gibbs et al. 1986; Rochford 1958). The concept of nitrogen limitation of marine productivity and carbon cycling may therefore have its principal relevance to the shallow and coastal areas of the world's oceans where waters are polluted by low N:P freshwaters.

One might correctly suggest that <200 sets of observations of total N and total P can scarcely be expected to represent all of the world's oceans. However, it is significant that these data are all of the total N and P inventories that I could discover in an extensive literature review and letter writing campaign. This is the most extensive collection of data on total N and P stoichiometry in marine waters. It strongly suggests that open ocean nutrient ratios do not support the marine nitrogen limitation model.

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