

Carbon-controlled nitrogen cycling in a marine 'macrocosm': an ecosystem-scale model for managing cultural eutrophication

S. V. Smith¹, J. T. Hollibaugh²

¹Hawaii Institute of Marine Biology, University of Hawaii, Honolulu, Hawaii 96822, USA

²Tiburon Center, San Francisco State University, Tiburon, California 94920, USA

ABSTRACT: Both data which we present for Tomales Bay (California, USA) and general geochemical reasoning provide evidence to suggest that nearshore marine environments tend to be net heterotrophic by a small margin, and that these systems oxidize on the order of 1 % of their primary production by denitrification. The rate of denitrification can be interpreted to be a simple stoichiometric function of the margin of heterotrophy. Carbon oxidation by denitrification is trivial to the total C budget, but fixed N loss is sufficient to cause apparent N-limitation of primary production in these systems. We suggest that heterotrophic C metabolism causes the apparent N limitation of primary production, and that control of the N cycle by C has important implications for environmental management.

INTRODUCTION

A common paradigm of biological oceanography holds that nitrogen availability ordinarily limits primary production in the marine environment (Ryther & Dunstan 1971). This paradigm has been used to suggest that reducing nitrogen loading is the most important management strategy for controlling cultural eutrophication (Howarth 1988). As commonly interpreted, this paradigm seems at odds with 2 key observations.

The first observation is that, on a global scale, the inorganic N:P loading ratio from land (Meybeck 1982) exceeds either the Redfield ratio for plankton (Redfield 1934) or the N:P ratio of benthic plants (Atkinson & Smith 1983). How, then, might N and P uptake by either phytoplankton or benthic plants drive the global oceanic N:P ratio from excess N loading towards N limitation? There must be an alternative inorganic N sink or inorganic P source.

The second observation is that isolated marine systems receiving only low-nutrient, oligotrophic ocean water with a very low inorganic N:P ratio draw P down to detection limits (Smith 1984). What mechanism allows this drawdown to occur if N is in short supply with respect to organic production? There must, in these systems, be either an alternative N source or an alternative P sink.

We believe that the opposing pathways of denitrification and nitrogen fixation act as negative feedback loops in the N cycle, shunting fixed N to and from gaseous N₂ in response to control by organic C metabolism. The essence of our reasoning is as follows: On some time scale, a system characterized by net organic production (i.e. a net autotrophic system) will exhaust available inorganic P. If inorganic N is not available, it can be fixed from the atmosphere in response to organic production. Thus, over the time scale in question, N fixation is controlled by net production.

Ryther & Dunstan (1971), in their seminal paper on oceanic N limitation, observed that on some time scale N availability might be controlled in just such a manner, as Redfield (1958) had proposed. Our only disagreement with Ryther & Dunstan on this point is that we think that the time scale over which a system can shift from N to P limitation can be relatively short, and hence ecologically significant (Smith 1984).

Similarly, a net heterotrophic system tends to liberate dissolved inorganic N. This N buildup and the presence of additional organic matter to be oxidized should stimulate denitrification, as long as there are anoxic environments where this process can occur. Heterotrophy, of course favors the development of anoxic environments. Therefore on some time scale N liberated during net respiration will tend to be consumed.

We have developed the detail of our reasoning elsewhere (Smith 1984, Smith et al. 1987, Smith et al. 1989). We refer to this paradigm as the carbon-control model for ecosystem nitrogen cycling (Smith et al. 1989), because the difference between N fixation and denitrification appears controlled by the difference between primary production and organic oxidation.

In this paper, we briefly review the data set which has led to our model. We then consider general stoichiometric considerations which arise from it. Finally, we discuss the model as a paradigm with possible implications for environmental management.

RESULTS FROM THE PRIMARY RESEARCH SITE

The research site which led to the development of the model presented here is Tomales Bay, California, USA. Smith et al. (1987) developed a water and salinity budget to define the exchange coefficient for this bay and revised the initial calculations with updated stream flow and evaporation data (Smith et al. in press). The bay is characterized by very slow mixing exchange with the ocean (mixing exchange rate = 0.009 d^{-1}) and, during much of the year, by negligible freshwater inflow (summer advective exchange rate = 0.0001 d^{-1}). Water residence time during the dry season is about 4 mo.

This bay functions as a large incubation chamber, or 'macrocosm', open to the atmosphere but surprisingly well-sealed hydrographically. The water volume entering the bay on flooding tides approaches one third of the bay volume (Smith et al. 1987); despite this large tidal prism and because of the bay hydrography, most of this water exits again. The only significant input during the tidal exchange is likely to be particulate material which can settle out. As a result of the hydrographic isolation, this system develops strong and unambiguous chemical signals from which we can draw inferences about system-scale chemical stoichiometry. We note, however, that other estuaries and coastal lagoons tend to show similar patterns of summer nutrient distributions (e.g. Nixon 1982).

As water ages in the system, its composition changes. Of particular interest to our study are the changes in nutrient concentrations with time and distance from the bay mouth. Phosphate (DIP) increases; $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ (together, DIN) decrease; and dissolved organic N (DON) increases with increasing salinity (Smith et al. 1987, Smith et al. 1989).

Smith et al. (1989) used a steady-state mixing (box) model to calculate the net sources or sinks of dissolved materials within the bay required to explain these nutrient changes. A simple stoichiometric model was used to quantify the most plausible biochemical reac-

tion pathways which are simultaneously consistent with all of the net system fluxes.

Calculated rates are summarized in Table 1. There are 2 important points to note. First, for the dry season represented by both the Smith et al. (1987) and the

Table 1. Non-conservative fluxes of materials in Tomales Bay, California, USA. All rates in $\text{mmol m}^{-2} \text{ d}^{-1}$. Average of rates for October 1985, August and November 1987. The 'local' Redfield C:N:P molar ratio used for these calculations was 99:18:1. Details of calculations, reason for omitting June 1987 data, and adjustments in October 1985 data are discussed in Smith et al. (1989)

Material	Flux (mean \pm SD)	Comments
A. Net non-conservative fluxes, based on box model		
PO_4^{3-}	$+0.060 \pm 0.003$	PO_4^{3-} source
DOP	$+0.004 \pm 0.002$	Insignificant net flux
TDP	$+0.064 \pm 0.001$	
NO_3^-	-0.075 ± 0.057	Minor NO_3^- sink
NH_4^+	-0.016 ± 0.038	Variable NH_4^+ flux
DIN	-0.091 ± 0.086	DIN/DIP imbalance, rel. to Redfield ratio
DON	$+0.063 \pm 0.087$	DON source
TDN	-0.028 ± 0.068	TDN/TDP imbalance, rel. to Redfield ratio
B. Inferred net ecosystem reactions, based on stoichiometry		
DIP release	0.060 ± 0.003	If organic source, implies net heterotrophy
Inferred net respiration	5.91 ± 0.22	Scaled relative to local Redfield ratio
Expected DIN release	1.08 ± 0.05	Scaled relative to local Redfield ratio
Net denitrification	1.18 ± 0.06	Required to balance TDN/TDP flux ratio

Smith et al. (1989) studies, the bay exports DIP; we interpret the regeneration and export of DIP to be the result of organic C oxidation, hence net heterotrophy. Second, consumption of fixed N exceeds DIN release by regeneration from organic matter decomposed in the system, so the standing concentration of DIN tends to be drawn down. This model primarily based on data from P and N fluxes is supported by initial results (Smith et al. 1987) based on C fluxes as well.

We conclude that the consumption of DIN results from net denitrification. In support of this conclusion, we directly measured high rates of potential denitrification by selected substrata during the earlier of the 2 studies cited, but these rates do not give quantitative evidence as to the areal averaged rate of denitrification. The organic C oxidation by denitrification to

balance the N budget against the P budget represents about 20% of the net respiration in excess of organic production (Table 1). Cole (in press) has estimated the primary production of this system to be about $75 \text{ mmol C m}^{-2} \text{ d}^{-1}$, so net denitrification accounts for oxidation of less than 2% of the primary production in this system.

Unlike superficially similar slow-exchange systems described by Smith (1984), Tomales Bay has been net heterotrophic during each of the 4 sampling expeditions used to derive the conclusions presented here. Unlike the other systems studied by Smith (1984), this one receives some organic loading. Only a small fraction (<10%) of detritus produced by upwelling in coastal waters and washed into the bay on a flooding tide need settle out in order to drive the calculated net heterotrophy. As discussed by Smith et al. (1987), that input would be difficult to detect by direct measurement. Alternatively, the heterotrophy may be driven by detrital delivery from land during winter stream flow.

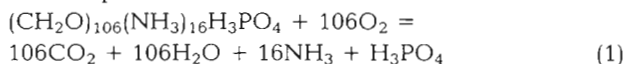
On the basis of qualitative comparison with hydrographically more complex systems (discussed by Smith et al. in press), we believe that the conclusions which we derive for this hydrographically simple system have general relevance. Global budgetary calculations by Smith & Mackenzie (1987) suggest that net heterotrophy, as seen in Tomales Bay, is more characteristic of coastal systems than is net autotrophy.

GENERAL STOICHIOMETRIC MODEL

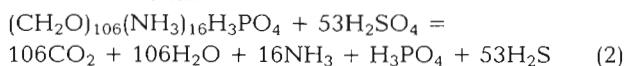
We have briefly developed the basic results of budgeting nutrient fluxes in Tomales Bay. We now discuss some generalities that can be drawn from these site-specific considerations. These generalities arise from consideration of the stoichiometry for various oxidation reactions involving organic material.

Consider 3 processes of organic oxidation in an aquatic environment: oxic respiration, sulfate reduction, and denitrification. Simple 'Redfield stoichiometries' can be written for each; these reactions are summarized by Richards (1965).

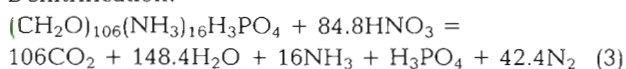
Oxic respiration:



Sulfate reduction:

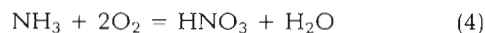


Denitrification:

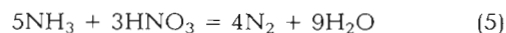


The free energy (ΔG) for the first reaction (aerobic respiration) is $-3190 \text{ kJ mol}^{-1}$ glucose (Krumbein & Swart 1983). For the second reaction (sulfate reduction) ΔG is -380 kJ mol^{-1} , and for the third reaction ΔG is $-2750 \text{ kJ mol}^{-1}$. Thus, even though sulfate is a much more abundant oxidant than nitrate in marine systems, energetic considerations dictate that systems with sufficient biochemical oxidation demand (BOD) proceed from oxic respiration, through denitrification, to sulfate reduction as oxidants are sequentially depleted. Sulfate reduction is common in metabolically active marine systems (Jørgensen 1977), implying that the availability of organic matter is sufficient to drive denitrification, hence that this process is usually likely to be limited by NO_3^- availability.

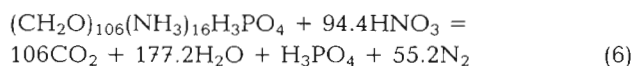
Nitrate is the major form of land-derived DIN supplied by runoff. As in the case of Tomales Bay, some NO_3^- may be supplied from the ocean by tidal mixing. However, it is clear that the most significant source of NO_3^- in coastal systems is nitrification of NH_3 released by any of the above oxidation processes. Although much of the NH_3 released ('regenerated nitrogen'; Dugdale & Goering 1967) may be reincorporated into organic matter, at least some fraction of the released NH_3 will be oxidized by nitrifying bacteria (Richards 1965, Kaplan 1983):



Of course, the actual nitrification process is more complex than represented by this net reaction, passing through intermediate production of NH_2OH and HNO_2 (Kaplan 1983). That complexity is biochemically interesting and important, but of no direct relevance to system-level stoichiometry. The oxidation of NH_3 through intermediate products to N_2 can also be represented by a simple net reaction (Richards 1965):



The biochemical reactions represented by Eqs. (3) and (5) are not necessarily coupled, as long as an external source of HNO_3 is available to drive denitrification or an external source of NH_3 is available to support nitrification. However, the reactions clearly are often coupled in nature, at oxic-suboxic interfaces such as the sediment water interface. Therefore Richards (1965) combined Eqs. (3) and (5); we define 'complete denitrification' as the reaction coupling denitrification with nitrification:



ΔG for the complete denitrification reaction is $-3030 \text{ kJ mol}^{-1}$, as glucose (Krumbein & Swart 1983). Allowing for considerations of activation energy and the existence of appropriate enzymatic pathways, denitrifi-

cation should proceed virtually as readily as aerobic respiration and far more readily than sulfate reduction, as long as fixed N is available.

The dissolved inorganic C (DIC) to fixed dissolved inorganic N (DIN) release ratio by either Eq. (1) or (2), or other reactions not using fixed N as the oxidant, is the familiar Redfield plankton oxidation-reduction ratio (r_o) of 6.63. By contrast, the DIC:DIN reaction ratio for complete denitrification (r_d) by Eq. (6) is -1.12 , negative because DIN is consumed while DIC is released. It follows that 6 moles (r_o/r_d) of organic matter must be oxidized (by equations like (1) or (2)) in order to provide the NO_3^- required for each mole of organic matter oxidized by denitrification (Eq. 6). Any denitrification in excess of this proportion must rely directly on ambient watercolumn DIN, ordinarily a minor DIN source.

In most shallow water systems, organic matter cycles with a system-level gross production to respiration ratio (p/r) near 1.0. In the absence of nitrogen fixation and denitrification, if that ratio were exactly 1.0, DIC, DIP, and DIN would turn over without net loss or gain and the hydrographic import and export of inorganic nutrients would balance. If, as we suppose, nitrogen fixation and denitrification act as negative feedback loops in the nitrogen cycle, then any DIN buildup should shut off nitrogen fixation (Head & Carpenter 1975), while denitrification clearly cannot take place in the absence of fixed N.

Consider, for the moment, a system with very slow hydrographic exchange, such as Tomales Bay. Nitrogen fixation and denitrification might occur in such a system, but the fixed N fluxes by these processes should balance one another. It becomes the system net organic production minus oxidation (i.e. the net trophic status) which either uses or supplies fixed N, hence is of immediate interest here. If the system is not isolated, as we have initially considered, the mechanisms which we advance should simply work with lesser efficiency.

If we take 0.95 to be a typical p/r ratio in coastal systems (Smith & Mackenzie 1987, Smith et al. 1989), then the net denitrification required to consume all DIN released by the 5% net excess of respiration over production is 0.8% of the total system production and respiration. Primary production in bays and estuaries is typically on the order of $100 \text{ mmol C m}^{-2}\text{d}^{-1}$ (Nixon et al. 1986); 0.8% oxidation by denitrification would be $0.8 \text{ mmol C m}^{-2}\text{d}^{-1}$. By r_d from Eq. (6), this C oxidation rate is equivalent to a denitrification rate of $0.7 \text{ mmol N m}^{-2}\text{d}^{-1}$ – modest by comparison with available data (Seitzinger 1988).

Three important points emerge from this analysis. First, excess of organic oxidation over organic production has the potential to draw DIN towards 0 with high efficiency. Second if most coastal systems are hetero-

trophic (Smith & Mackenzie 1987), then denitrification should exceed N fixation (as is apparently true; Seitzinger 1988). Third, an amount of net denitrification forced by the net oxidation of C but trivial to the total system C turnover is sufficient in many situations to control N availability.

Denitrification has, at least since Nixon (1981) discussed it, been recognized as likely to be important in nearshore marine and estuarine systems. In that sense, our results from Tomales Bay are not at odds with the results from other researchers. We interpret the significance of denitrification somewhat differently, however, than do other researchers. Instead of concluding that this net denitrification causes N-limited primary production, we contend that the amount of denitrification is controlled by the characteristics of C oxidation. Hence, we interpret the apparent N limitation of primary production to be a consequence of the characteristics of the C cycle, rather than a control on it.

MANAGEMENT IMPLICATIONS

What are the environmental management implications of this model? The management issue with respect to eutrophication is really control of biomass and BOD, not control of N, P, or primary production. According to this model, the reason for apparent N limitation of primary production is a reflection of the opposing negative feedback loops in the N cycle. DIN deficits can be met by N fixation. Excess DIN not sequestered into biomass is used as a minor oxidant by denitrification, a process which is likely to be DIN (actually NO_3^-) limited. In fact, as suggested by our calculations, as well as the arguments of Seitzinger (1988), this consumption of ambient DIN is likely to represent a small fraction of the total fixed N loss to denitrification.

Jones (1985) recognized N fixation to be a 'universal negative feedback loop' within the N cycle of ecological and agricultural systems characterized by high primary production. The systems which she considered (seagrass beds, in specific numerical models; crops, more general discussion) are characterized not only by high primary production but also by net system production.

Net heterotrophy in systems with high primary production adds an important complexity to system N dynamics. We argue that denitrification is a second negative feedback loop within the N cycle, of generally greater (Seitzinger 1988) quantitative importance than N fixation within the nearshore zone because of a tendency towards net heterotrophy (Smith & Mackenzie 1987). The 2 loops respond to organic production and oxidation. The summed response of these 2 feed-

back loops is controlled by the difference between organic production and oxidation within the system and favors net denitrification in most bays and estuaries.

A consequence of having 2 negative feedback loops in the N cycle responding to C metabolism should be that altering external DIN loading will have only a temporary, local, and minor quantitative impact on the much larger, internally driven N cycle, and a trivial long-term impact on the C cycle. In fact, one might expect that severely restricting external N supply alone in the presence of excess P would stimulate blooms of N-fixing cyanobacteria without having much impact on nutrient cycling and net production. There is some evidence (Smith 1983, Jansson et al. 1984, Larsson et al. 1985, Horstmann 1988) that supports this expectation, and that severely eutrophic systems can have rapid, spatially separated rates of both N fixation and denitrification. The dominance of organic production versus oxidation will determine the dominance of N fixation versus denitrification.

There may, of course, be a temporal or spatial lag between reduced DIN loading and ecosystem N fixation response. Thus local DIN reduction without reducing other contributors to eutrophication (DIP, organic matter) may well limit local plant growth (e.g. D'Elia et al. 1986), but at the same time transfer a eutrophication problem away (downstream, in a flow-through system such as most estuaries) from the immediate site of DIN reduction.

If our reasoning is correct, then a more generally useful management strategy is reducing organic matter in the system, either by reducing organic loading or indirectly, by reducing DIP loading. Denitrification in response to lowered fixed N demand to support primary production will ultimately reduce the pool of N available for biomass and return the plankton growth to N limitation. This approach is currently used for managing eutrophication in freshwater systems (Schindler 1977).

SYSTEM RESPONSE CHARACTERISTICS

Having presented the stoichiometric basis for this model, we now present simple equations which formalize the C control of N cycling and allow some evaluation of the time scales over which the N feedback processes act.

Consider the change in dissolved fixed N with time in a system of volume (V):

$$V \frac{dN}{dt} = \text{import} - \text{export} + \text{mineralization} - \text{uptake} \\ + \text{N fixation} - \text{denitrification} = 0 \quad (7a) \\ \text{(at steady state)}$$

Restating the equation symbolically:

$$V \frac{dN}{dt} = i - e + m - u + f - d = 0 \quad (7b)$$

The terms i and e represent hydrographic processes with a wide dynamic range; the remaining terms are internally controlled biochemical processes with a much narrower dynamic range (Smith 1984). Let us consider the biochemical processes. The system-level rate (s) of any biochemical process can be considered to be the product of the biomass-specific rate (v) and the biomass (b):

$$s = v \cdot b \quad (8)$$

integrated between the system boundaries. The biomass-specific rate (v) is, of course, subject to short-term (physiological) modifications by local environmental factors. Net system trophic status, production - respiration ($p - r$), can be expressed as the difference between 2 such rates:

$$p - r = (v_p \cdot b_p) - (v_r \cdot b_r) \quad (9)$$

In the absence of an external DIN source (i.e. i in Eq. (7b) = 0), the difference between p and r is the initial control on availability of DIN. If we scale from the C-based processes of p and r to N uptake (u) and mineralization (m) by the Redfield oxidation-reduction ratio (r_o):

$$((v_p \cdot b_p) - (v_r \cdot b_r)) / r_o = u - m \quad (10)$$

The remaining 2 biochemical processes, N fixation (f) and denitrification (d) adjust Eq. (7b) to reflect the export of N (e). In a system with long water residence time, e is small so:

$$f - d \approx u - m \quad (11)$$

Available data (Nixon 1982) suggest that system-level p (and, by implication, total system r) is strongly correlated with b . In that same reference it is explicitly observed that p is not well correlated with DIN. Moreover, it is clear that benthic plant communities such as coral reefs and tropical seagrass beds achieve high primary production in the face of low DIN concentration. Such high primary production is achieved by the accumulation of locally fixed N and maintenance of a high (and probably largely P-limited) biomass (Smith 1984, Jones 1985, Kinsey 1985).

The turnover time (t) over which N would adjust to N fixation and denitrification can be estimated from N concentration in the water column ($[N]$) and the water depth (z):

$$t = [N] \cdot z / |(f - d)| \quad (12)$$

Consider an estuary with $z = 5$ m and $|(f - d)| = 1 \text{ mmol m}^{-2}\text{d}^{-1}$. It is not entirely clear what fixed N pool is the most relevant to the role of denitrification in

environmental management. If we consider a DIN pool of 2 mmol m^{-3} , then $t = 10 \text{ d}$; if we consider a total fixed N pool of 20 mmol m^{-3} , then $t = 100 \text{ d}$. The ecological and biogeochemical relevance of these scaling arguments is that they give some sense of system response times to altered N loading.

If information about net water flow is available, then relevant space scales can also be inferred. We leave it as a management decision whether N reduction within this range of turnover time scales and an equivalent range of space scales is of importance in controlling eutrophication. If these scales are judged to be important, then controls on b_p and b_r (from Eq. 9) seem more important management options than manipulation of DIN loading in order to control v_p and v_r .

In nature, the importance of each term in Eq. (7) is, to some extent, scale-dependent. In a relatively small system, water exchange is often large relative to system volume and relative to the various biochemical terms (Smith 1984); hence the terms import and export tend to dominate the equation. Experimentally, these hydrographic terms can be eliminated or controlled by the use of incubation chambers. The experiments, however, tend to reduce the scale to the point that the natural sites of the various biochemical terms are also decoupled. Experiments may then 'demonstrate', for example, that algal growth is N-limited.

It is our contention that such experimental results, when extrapolated back to natural systems, may be artifacts of decoupling algal growth from the other biochemical processes which occur elsewhere in the system. System-level organic production is not demonstrated to be N-limited simply because local algal growth is. We further contend that it is difficult to reconstruct the couplings, short of a return to the natural environment. It is far less unnatural to use a total-system 'macrocosm' which has evolved to contain all the internal biological couplings but lacks significant hydrographic terms than it is to use any kind of artificially constructed microcosm.

CONCLUSIONS

This paradigm of carbon-controlled nitrogen cycling is by no means proven and should not be a basis for widespread environmental management decisions without further testing. However, we believe that attempting to control eutrophication by reducing DIN emissions alone would be an equally, or even more, premature management strategy. Indeed, the most environmentally conservative (although also the most expensive) management strategy would be the simultaneous control of DIN, DIP, and organic matter until more hard experimental evidence is available to be

used in long-term decisions. If environmental management questions are primarily concerned with control of system-level eutrophication, then it is inappropriate to address these questions with experiments performed at smaller space and time scales. Large-scale experiments are difficult, but not impossible, to conceive and conduct (Schindler 1977). In addition to valuable, but restrictive, microcosm and mesocosm experiments, very slowly exchanging natural systems like Tomales Bay can be treated as large 'macrocosms'. Time-series analysis of macrocosm responses to varying inputs can provide at least one class of feasible, large-scale 'experiments'.

Acknowledgements. We thank Steve Dollar and Sue Vink for assistance in field work, and Keith Chave, Chris D'Elia, Gordon Tribble, and Ken Webb for critical comments on drafts of the manuscript and for fruitful discussions. This research was supported by NSF Grant No. OCE-8613647, awarded to SVS. Contribution No. 773 of the Hawaii Institute of Marine Biology and 2093 of the Hawaii Institute of Geophysics.

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This article was presented by Professor S. W. Nixon, Narragansett, Rhode Island, USA

Manuscript received: June 10, 1988

Revised version accepted: December 22, 1988