

MARINE NITROGEN CYCLING—SOME RECENT OBSERVATIONS IN THE NORTHWESTERN INDIAN OCEAN

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ABSTRACT

Published estimates of the rate of denitrification in the Arabian Sea have been evaluated and some new data on the nitrogen cycle have been presented in this paper. Secondary nitrite maxima and nitrate reduction appear to be associated with oxygen concentrations of $<3 \mu\text{mol. dm}^{-3}$. A vertical section of the nitrate deficit along the latitude 17°N highlights an unusual feature of denitrification in the Arabian Sea. That is, contrary to the pattern expected from the data on primary productivity, the process appears to be most intense not along the continental margin off the Indian Coast but some distance away. This is probably due to the presence of a hitherto undetected subsurface counter-current. It is shown that, provided that denitrification in the Arabian Sea conforms to the global trend, the high rate derived in a recent study from the exports of nitrate deficits out of the denitrification zone ($\sim 30 \text{ Tg y}^{-1}$) is probably the closest estimate of the true value.

INTRODUCTION

Recent accounts on the budgets of marine combined nitrogen (e.g., Table I, after Codispoti & Christensen, 1985) present something of a puzzle in that the total losses from the sea appear to far exceed the net inputs. The imbalance could imply a non steady state system, where the sea may alternately act as a net source or a sink of fixed nitrogen on time scales involving a few thousand years (McElroy, 1983; Codispoti & Christensen, 1985). It has been suggested that such a variability of the oceanic nitrogen cycling could regulate the atmospheric CO_2 content, thereby contributing to climatic changes (McElroy, 1983; Codispoti *et al.*, 1986). However, the size of the anomaly in the oceanic nitrogen budget rests heavily on the accuracies of the estimates of its various components. Some of these might suffer from large uncertainties. For example, it is quite likely that the quantum of nitrogen fixation in the ocean has not been fully appreciated so far (Martinez *et al.*, 1983; Naqvi *et al.*, 1986). Similarly, the estimates of sedimentary and water column denitrification could also be considerably off the mark. This is particularly true for the northwestern Indian Ocean — an area where one of the three major oceanic denitrification sites is found, but the quantitative contribution of which to global denitrification remains uncertain (Table II). This introduces considerable uncertainty in the estimates of global water column denitrification (probably, a value of 5 Tg N y^{-1} has been selected for the budget reproduced in Table I). Evaluating the previous results in the light of the trends observed elsewhere, and presenting some new data, the present communication aims at reducing the magnitude of such an uncertainty.

TABLE I Marine combined nitrogen budget (from Codispoti and Christensen, 1985)

	$TgN y^{-1}$
INPUTS	
Marine nitrogen fixation	25
Rain and atmospheric fallout (NH_4 and N-oxides)	40
Runoff	25
<i>Total</i>	90
SINKS	
Water column denitrification	60
Sedimentary denitrification	60
N_2O loss to the atmosphere	1
Burial	21
Export of organic nitrogen	16
<i>Total</i>	158

TABLE II Estimates of the rate of denitrification in the Arabian Sea.

Rate ($TgN y^{-1}$)	Method	Reference
0.1—1	“Standing crop” (4 Tg)/renewal time (3–30 y); nitrate deficit estimated from nitrates-salinity regression.	Deuser <i>et al.</i> (1978).
3.2	“Standing crop” (95 Tg)/renewal time (30 y); nitrate deficit estimated from stoichiometric model.	Naqvi <i>et al.</i> (1982).
29.5	Exports of nitrate deficits (estimated with the procedure involving “No”) out of denitrification zone.	Naqvi (1986, 1987).

DENITRIFICATION

A secondary nitrite maximum embedded within a large body of oxygen-deficient water ($O_2 < 0.1 \text{ cm}^3 \text{ dm}^{-3}$), generally found north of Lat. 12–14° N, has been taken to provide an evidence for denitrification, especially since it is also associated with a conspicuous deficiency in combined nitrogen (Sen Gupta *et al.*, 1976; Deuser *et al.*, 1978; Lukashev, 1980; Naqvi *et al.*, 1982; Qasim, 1982; Naqvi & Qasim, 1983; Sen Gupta & Naqvi, 1984; Naqvi & Sen Gupta, 1985; Naqvi, 1986, 1987). Microbiological studies have shown that denitrifiers are quite abundant within the main secondary nitrite maximum (MSNM) zone (Naqvi, 1986; N. Ramaih, unpublished data). Concentrations of dissolved oxygen within the oxygen deficient layer (*ca.* 100–1,000 m), determined colorimetrically, are invariably below $5 \mu\text{mol. dm}^{-3}$ – often much lower – very close to the detection limit (Naqvi, 1986, 1987). A plot of nitrite vs O_2 within the MSNM (Fig. 1) indicates that a secondary nitrite maximum occurs when the oxygen concentrations fall below approximately $3 \mu\text{mol. dm}^{-3}$. In fact, most of

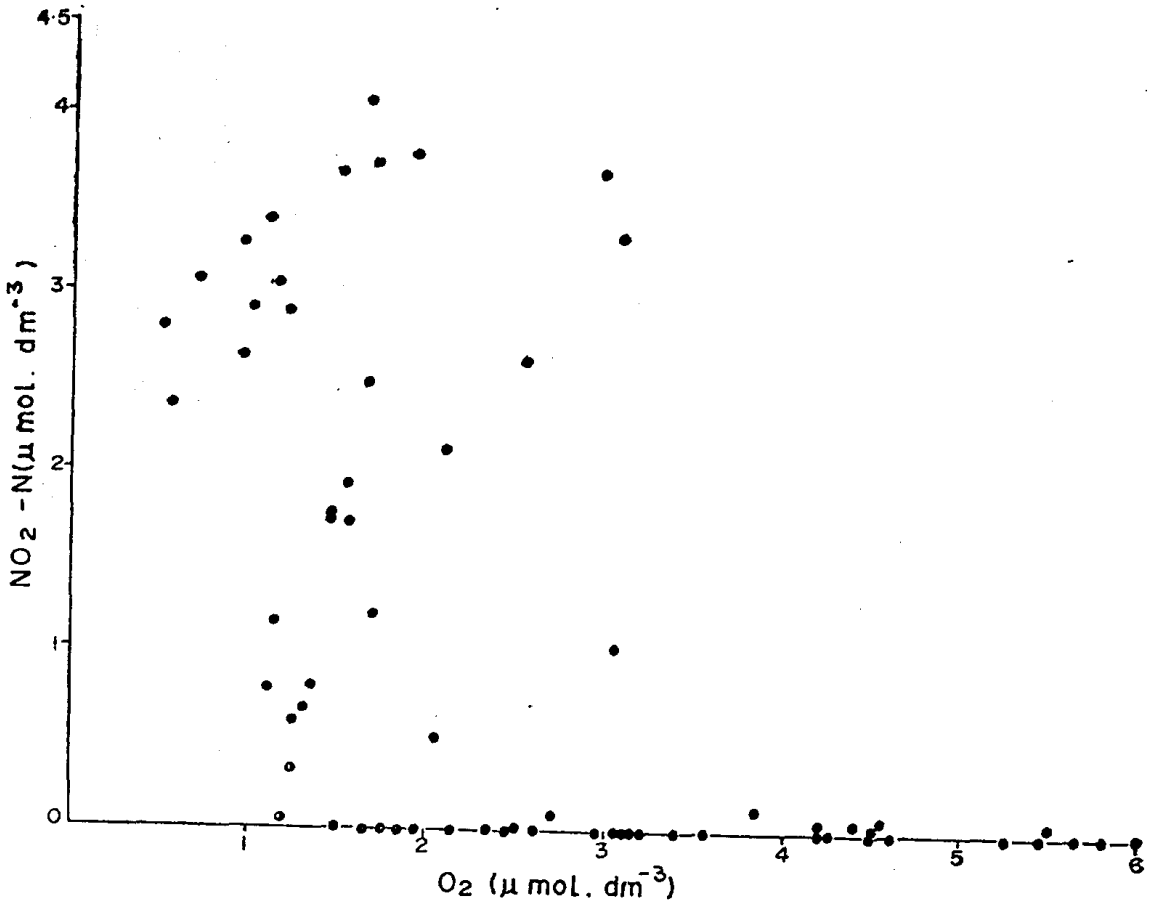


Fig. 1: Plot of nitrite vs dissolved oxygen (determined colorimetrically) within the secondary maximum zone.

the points with $\text{NO}_2 > 0.2 \mu\text{mol. dm}^{-3}$ correspond to $\text{O}_2 < 2 \mu\text{mol. dm}^{-3}$. The corresponding oxygen concentrations observed in the eastern tropical Pacific are $1 \mu\text{mol. dm}^{-3}$ north of the equator (Cline & Richards, 1972) and $2.2 \mu\text{mol. dm}^{-3}$ off Peru (Codispoti & Christensen, 1985). These compare very well with the experimentally determined critical oxygen concentrations (below which denitrification should occur) for bacteria isolated from the oxygen-depleted environments of the eastern tropical North Pacific (ETNP) and Saanich Inlet ($1.2\text{--}3.85 \mu\text{mol. dm}^{-3}$ - Devol, 1978). Thus, the oxygen levels in the Arabian Sea are low enough to trigger denitrification, and the available evidence, both chemical and microbiological, strongly points to the dissimilatory nitrate reduction to be the dominant respiratory process at mid-depth.

Nitrate Deficits

Direct measurements of the extent of denitrification have not been attempted in the Arabian Sea, and all the studies undertaken so far have involved the estimation of the "expected" nitrate, from which the sum of the observed concentrations of nitrate and nitrite are subtracted to determine the degree of reduction beyond nitrite. There is a good reason

to assume that the "nitrate deficits" so estimated approximately correspond to the amounts of molecular nitrogen produced (Naqvi, 1986). The "expected" nitrate has been estimated either from the nitrate-salinity relationship (Deuser *et al.*, 1978), or from a stoichiometric model (Sen Gupta *et al.*, 1976; Naqvi *et al.*, 1982; Qasim, 1982; Naqvi & Qasim, 1983). Application of the nitrate-salinity regression involves the assumption that denitrification is restricted by and large to the Persian Gulf Water; this may not always be true (Naqvi *et al.*, 1982; Naqvi & Qasim, 1983; Naqvi, 1986). When a stoichiometric model is employed, the "expected" nitrate is estimated as the sum of "oxidative" and "reserved" (performed) fractions (cf. Cline & Richards, 1972). The "oxidative" fraction could be estimated from the apparent oxygen utilization (AOU) and the oxidative ratios (Redfield *et al.*, 1963). Oxygen - nutrients relationships have been established in several areas of the Indian Ocean to deduce the oxidative ratios (cf. Sen Gupta & Naqvi, 1984); these values may, however, be subject to some errors in view of the work of Takahashi *et al.* (1985). Uncertainties involved in the computation of the "reserved" nitrate are even larger as most procedures utilize the phosphate data, the chemistry of which is not very well resolved in the denitrifying environments (Anderson *et al.*, 1982).

A procedure that approximately accounts for the "reserved" nitrate without involving phosphate has been proposed by Naqvi & Sen Gupta (1985). It is based on a linear correlation between the property "No" (cf. Broecker, 1974), defined as $O_2 + 8.65 NO_3$, and potential temperature (\emptyset) outside the denitrification zone (South of Lat. $11^\circ N$), apparently in two different ranges, and the application of "No"- \emptyset relationships for estimating the "expected" nitrate within the denitrifying layer. An assumption involved here is that for a given potential temperature, the "reserved" nitrate will remain constant; this at best could be approximately valid. Further, the $\Delta AOU/\Delta NO_3$ ratio of 8.65 (by moles) selected by Naqvi & Sen Gupta (1985) is lower than the value (10.75) deduced by Takahashi *et al.* (1985). Incidentally, the latter value is very close to the $\Delta AOU/\Delta NO_3$ ratio reported from the Red Sea (10.85 - Naqvi *et al.*, 1986). However, as the same value has been utilized for establishing the "NO"- \emptyset relationships, and for computing the "expected" nitrate, the errors to a large extent will cancel out. The above shortcomings notwithstanding, the procedure is perhaps more reliable than any other method employed so far. Applying it to a large data base, Naqvi (1986, 1987) has determined the rate of denitrification in the Arabian Sea, and examined the variability of the process in space and time. His results indicate a large short-term variability in the process implying a quick renewal of the intermediate waters and a relatively unstable environment.

A vertical section of the nitrate deficit, based on *Sagar Kanya* observations along Lat. $17^\circ N$ made in February-March 1985, is presented (Fig. 2). This section has been selected to depict an unusual feature. That is, the zone of the most intense denitrification in the Arabian Sea does not lie along the continental margin unlike the two denitrifying environments found in the eastern tropical Pacific. Instead, it is located some distance away from the continental slope. This is against the pattern expected from primary productivity which increases shoreward (Qasim, 1982). Naqvi (1986) postulated that this could result from a more vigorous renewal through a mid-depth counter current just off the continental slope.

Rate of Denitrification

As indicated above, published estimates of the rate of denitrification in the Arabian Sea differ widely (Table II), presumably because of the different procedures followed by various workers. Also, the choices of the renewal time and diffusion constants have been subjective, if these were not arbitrary. Estimates of Deuser *et al.* (1978) and Naqvi *et al.* (1982) have been based on a relatively small data base. Both groups of workers have combined the estimated "standing crop" of denitrified nitrogen with the residence time of the denitrifying layer. Low (4 Tg) "standing crop" estimated by Deuser *et al.* (1978) was ostensibly due to the fact that their method yielded lower deficits, although it appears that considerably milder reducing conditions could have prevailed in January 1977 when the observations were made (Naqvi, 1986, 1987). The broad range (0.1–1 Tg y⁻¹) of their estimate reflects the wide choice of the renewal time (3–30 y). Selecting the upper extreme of this range of residence time, together with an estimated "standing crop" of 95 Tg, Naqvi *et al.* (1982) arrived at a rate of 3.2 Tg y⁻¹. In any case, both the estimates appear to be too low, as could be seen in Fig. 3, adopted and modified from Liu & Kaplan (1984). Utilizing the data from the various oceanic denitrification sites, these authors found a direct correspondence between the fluxes of the organic carbon consumed during denitrification, normalized to surface productivity, and the fraction of organic carbon available within the denitrifying layer as macroparticles, calculated from Suess' (1980) model. The data point from the Arabian Sea, based on the observations of Deuser *et al.* (1978), however, deviated from the global trend in that the flux of organic carbon consumed during denitrification was anomalously low (0.4% of the surface productivity as compared to 6% in the ETNP).

An order-of-magnitude check on the estimate of Naqvi (1986), based on the advective and diffusive transports of the nitrate deficits from the denitrification zone (29.5 Tg y⁻¹), could be made using the Liu-Kaplan model. It may be pointed out that this estimate is based on a fairly large amount of data. Also, as noted above, the procedure followed for estimating the nitrate losses is probably more reliable than the other methods. Combining the estimate of the rate of denitrification with that of the "standing crop" of denitrified nitrogen, Naqvi (1986, 1987) calculated the renewal time of the oxygen deficient layer as 3.9y. Utilizing the data from 7 stations located within the denitrification zone, Somasundar & Naqvi (1987) computed the total amount of carbon consumed during nitrate reduction as 3.86 ± 0.32 g-at m⁻². These estimates together with Qasim's (1982) value for primary productivity north of Lat. 15°N (835 mgC m⁻² d⁻¹) indicate that approximately 4% of the organic carbon produced within the surface layer in the Arabian Sea is used up for denitrification. Plotted in Fig. 3 against the fraction of organic matter available as macroparticles within the denitrifying layer ($17.6 \pm 4.3\%$ —Somasundar & Naqvi, 1987), the data point from the Arabian Sea falls very close to that representing the ETNP – an area which is far more similar to the Arabian Sea in several respects than any other reducing environment (Naqvi, 1986).

Accounting for the high rate of denitrification in the Arabian Sea, which conforms to the global trends, the present estimates of oceanic water column denitrification need to be scaled up by about 25 Tg. This would mean that the magnitude of the anomaly in the budget (Table I) will go up further. However, until the uncertainties in at least two other estimates (nitrogen fixation and sedimentary denitrification) are eliminated, the size of the anomaly remains speculative.

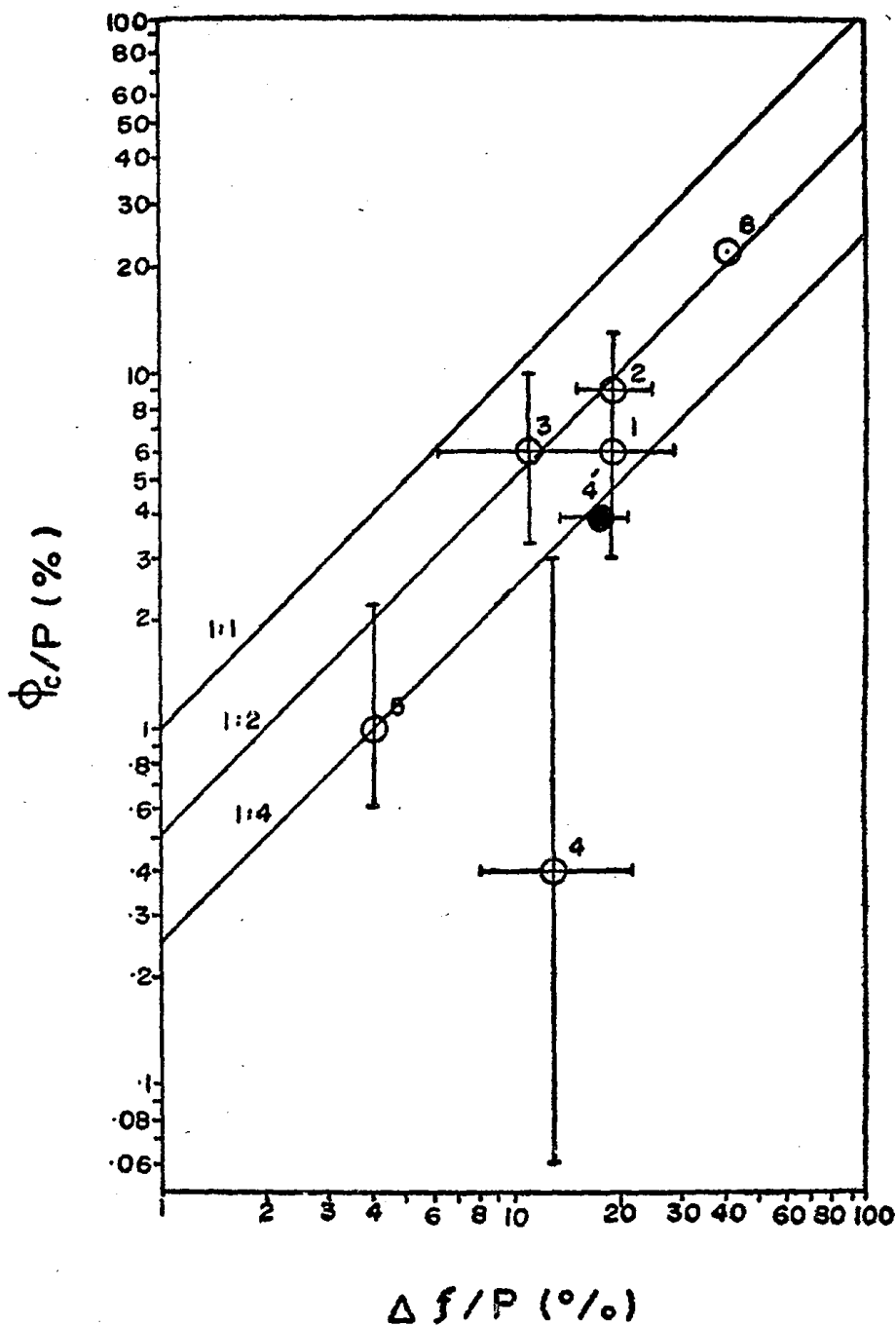


Fig.3. Normalized fluxes of organic carbon consumed during denitrification (ϕ_c/P) vs percentage of surface organic production available within the denitrifying layer as macroparticles ($\phi_o \Delta f/P$) (1 - ETNP; 2, 3 ETSP; 4-Arabian Sea, based on earlier estimates; 5 - Cariaco Trench; 6 - Darwin Bay; all adopted from Liu & Kaplan, 1984). The solid circle (4') represents the revised estimate from the Arabian Sea.

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