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Geochemical evidence of denitrification in the Benguela upwelling system

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Abstract

This paper presents analysis of nitrate, phosphate and silicate data from the Benguela upwelling system. Evidence is presented that suggests denitrification occurring close to shore, and also nutrient trapping. Denitrification leaves an imprint on the water properties in terms of a nitrate deficit, that is to say nitrate concentrations that are significantly less than predicted by multiplying the phosphate concentrations by the Redfield ratio. It is probable that denitrification also causes a decoupling of nitrate and carbon compared to Redfield processes, and large-scale losses of nitrate in the Benguela which are not accompanied by losses of carbon. Nitrate-driven CO_2 drawdown following upwelling will be less than it might otherwise be, because of denitrification.

Nutrient trapping (secondary remineralisation) is apparent as enhanced phosphate concentrations, some of which are several μmol higher than in the offshore source waters for upwelling. Waters also become enriched in silicate and to a lesser extent nitrate as they advect across the shelf. By implication the same process should also "supercharge" waters in dissolved inorganic carbon, leading to stronger outgassing of CO_2 immediately after upwelling. The effect is again to increase the size of the estimated Benguela upwelling system CO_2 source.

Keywords: Benguela; Denitrification; Nutrient trapping; Nitrate deficit; Nitrate; Phosphate

1. Introduction

1.1. Ecological competition to extract energy from organic material

Particulate organic matter (POM), i.e. the collection of living and dead organisms and faecal pellets, is the primary energy and nutrient supply for remineralising bacteria in the sea. This crucial resource is competed for by the different species of bacteria, many of which use different remineralisation reactions. The outcome of the ecological competition depends primarily on which reactions are possible in the local conditions, and then which out of those reactions yields most energy from the decomposition of POM (Canfield, 1993) (Table 1).

When a sufficient concentration of oxygen is present, aerobic bacteria are the most efficient recyclers of organic material (they extract the

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Table 1
Organic matter oxidation pathways, energy yields (taken from Canfield, 1993) and electron acceptor abundances

Reaction	Energy yield (kJ mol^{-1} of CH_2O)	Abundance of TEA[a] (μmol kg^{-1})
Oxic respiration	−475	O_2: 200
Denitrification	−448	NO_3: 30
Mn-oxide reduction	−349	Mn: $\ll 1$
Fe-oxide reduction	−114	Fe: $\ll 1$
Sulphate reduction	−77	SO_4: 28,000
Methane production	−58	

[a] TEA stands for terminal electron acceptor. Concentrations in the table are approximate averages for deep water.

highest energy yield), and they outcompete those species which use other chemical reactions. If oxygen becomes depleted (hypoxic or anoxic conditions), but nitrate is present, then the next most efficient energy-extractors are the denitrifying bacteria, and they become dominant under these conditions (Knowles, 1982). If the rate of supply of organic matter is sufficient to strip both oxygen and nitrate from the water, then (once rather small quantities of dissolved manganese and iron are also removed) microbes that use the sulphate reduction reaction become dominant. Each remineralising reaction (process) in the sequence requires the use of a particular molecule as a terminal electron acceptor in order for the energy yield to be gained. In the process the concentration of that terminal electron acceptor is depleted. Although a sequence of one reaction after the other is the rule, some overlap can take place. Denitrification and aerobic oxidation, for instance, sometimes take place simultaneously at low oxygen.

This ecological competition takes place in all marine water columns and sediments. In today's ocean it is unusual for oxygen levels to approach zero in the water column, but more common in sediments. Where photosynthetic rates are very high though (e.g. in upwelling systems), the great biological oxygen demand further down in the water column can lead to complete oxygen utilisation. In these conditions a typical sequence is seen: aerobic oxidation → denitrification → sulphate reduction.

1.2. The Benguela upwelling system

Denitrification has been demonstrated in the eastern tropical South Pacific (Codispoti and Christensen, 1985), in a number of upwelling systems (Codispoti, 1983) and is significant in the Peruvian (Codispoti et al., 1986) and Brazilian upwelling system at 23°S (Braga and Müller, 1998). It was proposed to be important in the Benguela upwelling system nearly 30 years ago (Calvert and Price, 1971). More recently, Dittmar and Birkicht (2001) have examined N:P ratios within a limited region of the northern Benguela system close to the Angola–Benguela Front and have shown low ratios consistent with denitrification.

Low oxygen events within the Benguela system have been well known for some time (Chapman and Shannon, 1985), although hypoxic ($[O_2] < 0.5$ ml l^{-1}) events within the northern and southern Benguela regions have somewhat differing origins.

1.2.1. Northern Benguela low oxygen

The northern boundary of the Benguela system (the Walvis Ridge) is regarded as the "merging zone of the Angola Current and north littoral branch of the Benguela Current" (Moroshkin et al., 1970). Shannon and Nelson (1996) note a poleward undercurrent everywhere south of the Cunene River although Stramma and Peterson (1989) recorded very little mean flow across the Walvis Ridge between the coast and 7°E.

Nevertheless, off-shelf (200–300 m) poleward flowing water from the Angolan Basin region introduces warm, fresh, low oxygen water into the northern Benguela region, particularly during so-called Benguela Niños (Shannon et al., 1986; Gammelsrød et al., 1998). The most recent event occurred in 1994/95 when severe anoxic conditions ($[O_2] < 0.5$ ml l^{-1}) prevailed over the shelf in bottom and near-bottom waters from 21–24°S. These events have a decadal time scale but there are also seasonal intrusions (Boyd et al., 1987). When low oxygen water originating from the Angola Basin is upwelled onto the shelf, it adds to in situ hypoxia originating from the decomposition of organic carbon buried over the shelf.

Nitrite (NO_2) is an intermediate in both the denitrification and nitrification processes and has been found in high concentration (up to 10 μmol kg^{-1}) in the suboxic waters off the coast of Peru where denitrification is intense (Codispoti and Christensen, 1985; Codispoti et al., 1986). Likewise NO_2 concentrations of up to 4 μmol kg^{-1} were found over the western Indian shelf in hypoxic water where denitrification also occurred (Naqvi et al., 2000). Dittmar and Birkicht (2001) measured NO_2 concentrations up to 0.6 μmol kg^{-1} in the northern Benguela close to the coast.

1.2.2. Southern Benguela low oxygen

Within the southern Benguela system, however, oxygen depletion is more of a local event, mainly due to the decay of diatom-dominated blooms but also due to decay of expansive red-tides dominated by the dinoflagellates *Ceratium furca* and *Prorocentrum micans* (Pitcher, 1998), all of which contribute to the substantial vertical flux of particulate carbon onto the shelf (Waldron et al., 1992). This large flux of POM onto the shelf, and its remineralisation there, enriches the NO_3 concentration of the upwelling water (Bailey, 1987). However, we find (see below) that the amount of enrichment of NO_3 is reduced by destruction of NO_3 by denitrification in suboxic sediments.

1.2.3. Benguela sulphate reduction

In continental margin sediments off central Chile, bacterial dissimilatory sulphate reduction is a commonly observed process (Thamdrup and Canfield, 1996), as it is also in the organically rich shelf sediments ($\sim$40–75 mg C org g^{-1} dry weight surface sediment) off the coast of Angola and Namibia (Ferdelman et al., 1999; Fossing et al., 2000). Although nitrate reduction is energetically favoured over sulphate reduction, the latter is by far the most common form of anaerobic decomposition of organic matter, because of the greater availability of sulphate as an electron acceptor in the Benguela surface sediments (Table 1).

Sulphate reduction in the top 0–20 cm of the sediment attains rates of 2–29 nmol cm^{-3} d^{-1} and is maximal at 2–5 cm depth, mediated by dense populations of barotolerant giant sulphide oxidising bacteria (Schulz et al., 1999). Highest rates of sulphate reduction were recorded between Walvis Bay (28°S) and Luderitz ($\sim$26.5°S) along the 1300 m isobath. This area is characterised by year-round upwelling, high rates of primary production (175–240 mmol C m^{-2} d^{-1}) (Summerhayes et al., 1995), sediments dominated by marine diatomaceous ooze and very little terrigenous input as there is no significant riverine input (Ferdelman et al., 1999). Highest rates of sulphate reduction also tracked the major upwelling centres and were strongly correlated with sediment surface organic carbon concentrations derived from high organic carbon sedimentation rates of $\sim$0.9–1.4 mmol m^{-2} d^{-1} (Wefer and Fischer, 1993). In the same region, Bailey (1991) has measured similar fluxes of organic carbon and has demonstrated the association of this with the development of continental shelf water column anoxia. Ferdelman et al. (1999) argue that sulphate reduction accounts for between 20–96% of total respiration in the sediments of the Cape Basin at 1300 m depth.

The high rates of sulphate reduction in this region can be expressed at the surface of the water column as so-called sulphur "events" (e.g. 1997) which it now appears can be detected by satellite remote sensing because of the way the colouring of the water is altered (Weeks et al., 2002). This approach has emphasised that sulphate reduction (and presumably denitrification) is much more widespread than usually detected by ship-board observations.

1.3. Ecological importance

The west coast upwelling systems of southern Africa support significant commercially important pelagic, demersal and rock lobster fisheries, which are underpinned by high rates of new production (for review see Hutchings and Field, 1997). Extreme environmental conditions associated with Benguela Niño's (Section 1.2.1) and persistent hypoxic events ($[O_2] < 0.5$ ml l^{-1}) over the shelf (e.g. in 1994/95) have caused major mortalities to the marine biota. In that year, as in others, there was distributional displacement of Cape hake on the Namibian shelf of the northern Benguela

(Hamukuaya et al., 1998) as well as catastrophic juvenile Cape hake mortality (Woodhead et al., 1997). In the southern Benguela, there can be equally catastrophic results of local hypoxia and H_2S accumulation (e.g. 1997), resulting in mass mortalities of shellfish, rock lobster and even kelps (Pitcher, 1998; Copenhagen, 1953).

2. Methods

2.1. Using nitrate deficits to detect denitrification occurrence

Nitrate and phosphate concentrations ($[NO_3]$ and $[PO_4]$) in seawater typically increase and decrease together proportionately, upon descent or ascent through the water column, in the ratio of 15 or 16:1. This is because (Redfield, 1934) the ratio of the two elements N and P in POM is likewise ~16:1 (Copin-Montegut and Copin-Montegut, 1983), and because inorganic N and P are released at apparently very similar rates from decaying organic material (Shaffer et al., 1999; Anderson and Sarmiento, 1994; Takahashi et al., 1985; but see also Loh and Bauer, 2000). The strong and linear correlation apparent in scatterplots of $[NO_3]$ versus $[PO_4]$ occurs because photosynthesis and remineralisation cause movements up and down a line with slope close to 16:1, but do not cause any significant deviations away from it (Fig. 1). Scatterplots of ($[NO_3] + [NH_4] + [NO_2]$) versus $[PO_4]$ would be expected to show even stronger correlation.

Denitrification and nitrogen fixation, on the other hand, do cause deviations away from the ~15:1 line. Nitrogen fixation is not a significant process in the Benguela system (Carpenter, 1983) and will therefore be ignored in the rest of this paper. Denitrification has the net effect of removing ~100 mol of NO_3 from the water per 1 mol addition of PO_4 (Codispoti and Christensen, 1985). The N:P ratio of denitrification is therefore about −100:1, in contrast to the +16:1 of aerobic remineralisation (Fig. 1).

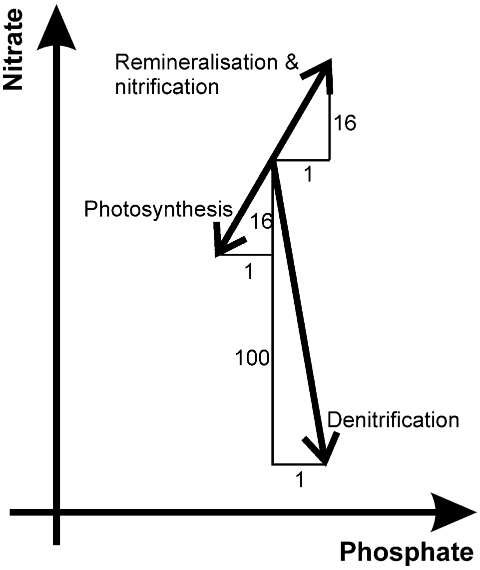

Fig. 1. The impacts of photosynthesis, remineralisation plus nitrification and denitrification on concentrations of nitrate and phosphate (not to scale). Adapted from (Gruber and Sarmiento, 1997).

It is, therefore, possible (Smith and Hollibaugh, 1998; Gruber and Sarmiento, 1997; Gordon et al., 1996; Smith et al., 1991; possibly first used by Cline and Richards, 1972) to calculate a tracer based on nitrate and phosphate—one that is insensitive to photosynthesis and remineralisation processes, but which is sensitive to denitrification and nitrogen fixation. An example of such a tracer is the nitrate deficit (ΔN) which can be calculated as

$$\Delta N = 16 * [PO_4] - [NO_3]. \quad (1)$$

If nitrogen fixation is assumed to be unimportant then any increase in ΔN above its initial value in deep water offshore is a measure solely of the denitrification history of the water parcel. Another assumption is that the production and remineralisation of dissolved organic N and P is either not significant or else also occurs at about a 16:1 ratio (nitrite and ammonium are also omitted because usually only present in small amounts). If these assumptions are reasonable then ΔN records how much denitrification has taken place in that volume of water. ΔN calculations are used to calculate rates of nitrogen fixation and denitrification in many coastal locations around the world as part of the LOICZ programme (see http://data.ecology.su.se/MNODE/), but have not yet to our knowledge been applied to anywhere in the Benguela upwelling system.

Nitrate deficit is a better indicator of denitrification than N:P ratio. Consider for instance deep water with $[NO_3] = 28\ \mu mol\ kg^{-1}$ and $[PO_4] = 2\ \mu mol\ kg^{-1}$ ($N:P = 14:1$) which upwells to the surface. If it then loses $24\ \mu mol\ kg^{-1}$ of NO_3 and $1.5\ \mu mol\ kg^{-1}$ of PO_4 (loss is in 16:1 or Redfield proportions) to photosynthesic uptake, then concentrations will decrease to $[NO_3] = 4\ \mu mol\ kg^{-1}$ and $[PO_4] = 0.5\ \mu mol\ kg^{-1}$. Despite phytoplankton growth being the only process affecting the water since upwelling, the N:P ratio decreased from 14:1 to an apparently more anomalous 8:1. Nitrate deficit, on the other hand, must by definition remain unaltered because of the constant 16:1 ratio of uptake or remineralisation.

2.2. *Detecting enrichment by comparison to deep offshore concentrations*

We compare nutrient concentrations in water over the Benguela shelf to concentrations in the source water from which flow onto the shelf is derived. This allows us to determine if water becomes depleted or enriched as it travels onto and across the shelf.

The concentration of nutrients in the source water depends on where the source water is assumed to come from. Calvert and Price (1971) give 150–250 m as the depth from which upwelled waters are derived, whereas other authors suggest 200–300 m (Section 1.2.1). We calculated nutrient concentrations of source waters by assuming that offshore (greater than 160 km from the shore) water between 150 and 300 m depth is the source of water advected onto the shelf. We then examined our dataset (see below) for samples taken from bottles fired between 150 and 300 m during offshore casts. Nutrient concentrations measured in those bottles were:

$[NO_3]$: average = $15\ \mu mol\ kg^{-1}$,
range = $5–30\ \mu mol\ kg^{-1}$.
$[PO_4]$: average = $1.5\ \mu mol\ kg^{-1}$,
range = $0.5–3.0\ \mu mol\ kg^{-1}$.
$[SiO_4]$: average = $11\ \mu mol\ kg^{-1}$,
range = $2–17\ \mu mol\ kg^{-1}$.

3. Data and results

Nutrient data collected by Geoff Bailey (SFRI) and others were obtained from the South African Data Centre for Oceanography (SADCO) archive and analysed. We did not perform any quality control or screening of this data, other than to exclude data collected before 1970. Data from more than 1000 casts from the period 1973–1993 and the area (12–17°E, 20–32°S) (Fig. 2) were used. Anticipating strong denitrification associated with the low oxygen waters of many parts of the Benguela system, we analysed the data for nitrate deficits.

3.1. *Scatterplots*

As a first step, we grouped all of the data, irrespective of season, year, depth or location into a scatterplot of $[NO_3]$ versus $[PO_4]$ (Fig. 3a). A least absolute deviation best-fit line (Press et al., 1992) to all of the data produces $[NO_3] = 9.0*[PO_4] - 1.0$. This is substantially different from the $[NO_3] = 14.1*[PO_4] - 1.53$ of the main trend in the World Ocean Atlas '94 global data set (NODC, 1994) used by Tyrrell and Law (1997), but the global best-fit line was obtained by excluding LNP points (where LNP = low nitrate:-phosphate, such that $(NO_3/PO_4) < 3.0$ and $PO_4 > 1.5\ \mu mol\ kg^{-1}$; shaded area in Fig. 3a). When only the main trends of both datasets are considered, the Benguela dataset is similar to the global dataset.

There are many LNP points (7% of the total) in this data, and these are separate from the cluster of LNP points reported by Tyrrell and Law (1997) from the Agulhas Retroflection area, which were later found to be incorrect (Tyrrell and Law, 1998).

Does the Fig. 3a scatterplot as a whole provide evidence of denitrification? The low slope of the best-line fit to all the data is general evidence of denitrification. In addition, there is a clear asymmetry in the scatter of points, with a much greater number of points below and to the right of the main trend than above and to the left of it. This indicates that a non-random process is either removing N without simultaneously removing P,

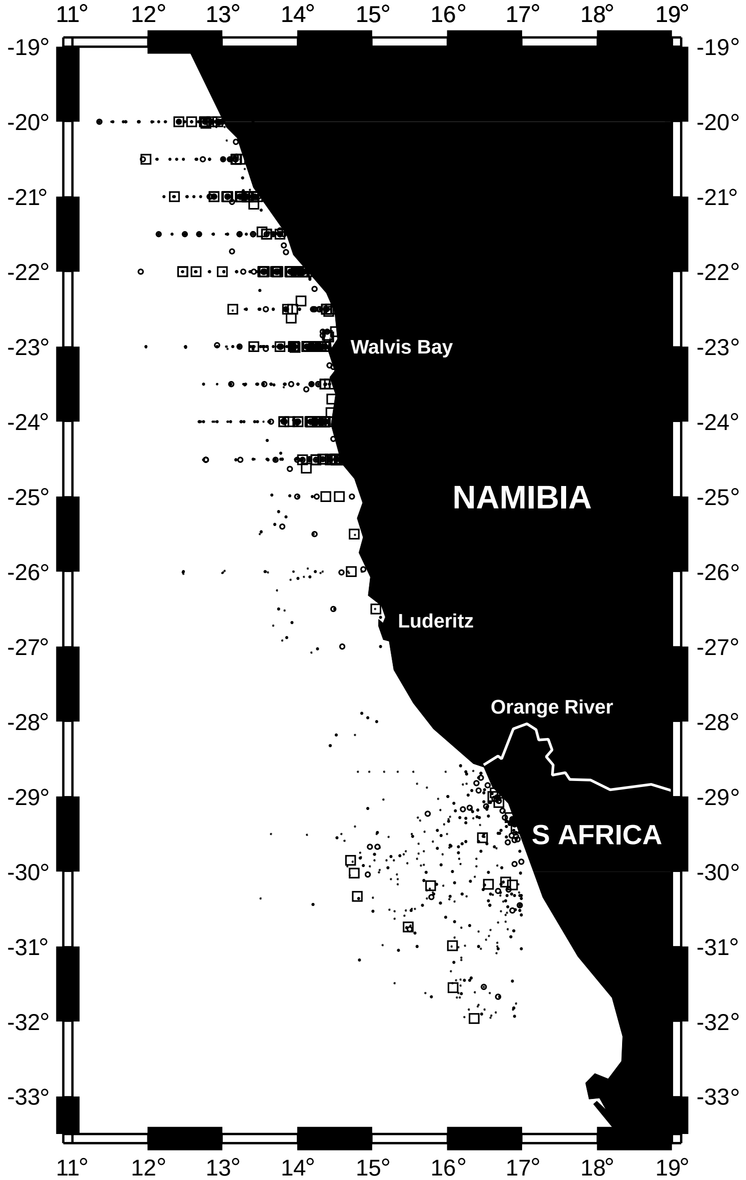

Fig. 2. Data locations: each symbol shows the position of one cast during which nutrient concentrations were measured from one or more bottles. The type of symbol used indicates the maximum nitrate deficit (ΔN; μmol NO_3 kg^{-1}) measured during that cast, as follows: (·), $\Delta N < 10$; (●), $10 < \Delta N < 20$; (◦), $20 < \Delta N < 30$; (□), $\Delta N > 30$.

or else adding P without simultaneously adding N. We suggest this process is denitrification. LNP points are found in other high-productivity coastal areas in which denitrification is known to occur (Tyrrell and Law, 1998; Naqvi et al., 2000; Codispoti, 1989). However, the lack of a large number of points where both ($[NO_3] \simeq 0.0$) and ($[PO_4]$ significantly greater than 0.0), is evidence against denitrification proceeding to nitrate exhaustion throughout the area. The observations of

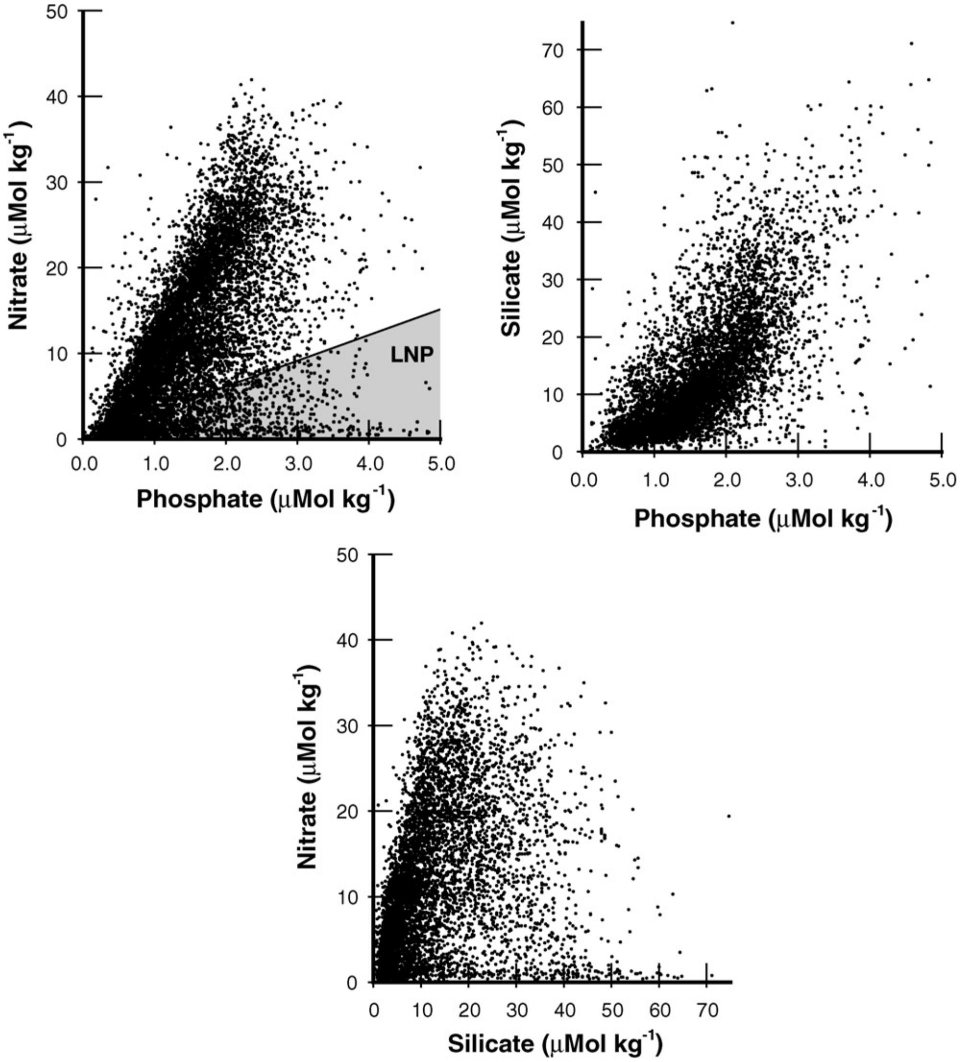

Fig. 3. Scatterplots of: (a) [NO_3] versus [PO_4], (b) [SiO_4] versus [PO_4], and (c) [NO_3] versus [SiO_4] (all μmol kg^{-1}). The shaded area in (a) shows the subset of the data designated as low N:P (LNP, see text).

sulphide production events (Pitcher, 1998) show that such strong denitrification must occur in some locations at some times though.

It is possible to get some idea of whether it is perturbations to nitrate or perturbations to phosphate that are causing the anomalous points away from the main trend. This is done by comparing scatterplots of silicate versus phosphate (Fig. 3b; same as Fig. 3a except nitrate is replaced by silicate), and nitrate versus silicate (Fig. 3c; same as Fig. 3a except phosphate is replaced by silicate). The result of this comparison is not wholly conclusive, in that anomalous points away from the main trend (to the right and beneath it) are found in both plots. However, many more occur in Fig. 3c, suggesting that it is mainly perturbations to nitrate that are responsible. Of course if both phosphate and silicate are preferentially released from particles (compared to nitrate) by dissolution under severely hypoxic conditions, then this too could account for the observed patterns, but the more parsimonious explanation (denitrification) is assumed here.

3.2. *Plot of nitrate deficit versus temperature*

As a second step, we plotted ΔN versus temperature in our data set (Fig. 4). This plot reveals that maximum nitrate deficits are large, 40 μmol NO_3 kg^{-1} or more. Large nitrate deficits seems to be correlated with water temperatures of 12–13°C, for reasons we do not understand. There are many more points above the main cluster than below it; that is to say there are more positive than negative nitrate deficits, as one would expect if the positive nitrate deficits are due to denitrification rather than to random measurement error.

3.3. *Plot of nitrate versus temperature*

Next we plotted [NO_3] versus temperature in our data set, with the symbol used depending on the nitrate deficit for that bottle (Fig. 5a). In an upwelling system nitrate and temperature should be correlated due to biological removal of nitrate occurring concurrently with heating of the initially cold upwelled water (Dugdale et al., 1989; Voituriez and Herbland, 1984), and this is generally apparent in Fig. 5a. The initial expectation was that points with high nitrate deficit (which have experienced significant denitrification) should have lower than normal nitrate and hence should be below the average trend in the NO_3 versus temperature plot. While this is most usually the case, there are also a number of points with high nitrate deficit on the "wrong" side of the average trend.

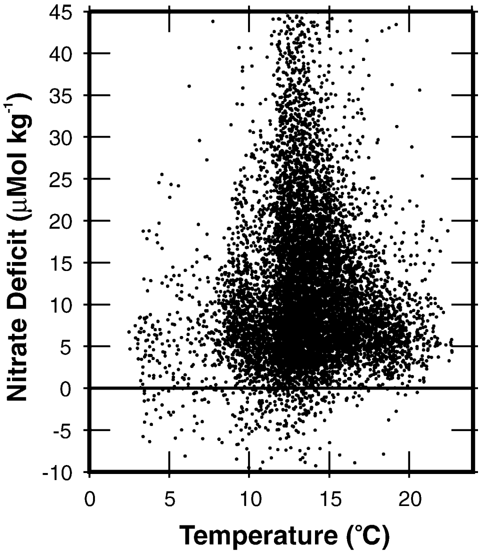

Fig. 4. Nitrate deficit (ΔN, μmol NO_3 kg^{-1}) versus temperature (°C).

3.4. *Plot of phosphate versus temperature*

The plot of [PO_4] versus temperature, however, shows a more defined pattern (Fig. 5b). There is a similar trend between temperature and phosphate because phosphate is also taken up by phytoplankton as upwelled water heats up at the surface. The higher the nitrate deficit, the higher above the main phosphate-temperature trend the points tend to lie. When compared to the nitrate-temperature plot (Fig. 5a), the points with large nitrate deficit are less randomly positioned compared to the main trend.

3.5. *Plot of silicate (silicic acid) versus temperature*

The plot of [SiO_4] versus temperature (Fig. 5c) also shows a more defined pattern than Fig. 5a. Silicate is taken up into diatoms, usually the dominant phytoplankton in upwelling systems, into their tests (shells), which then sink out along with the diatom organic matter. For this reason there is a similar trend between temperature and silicate. The highest silicate values are all from bottles with high nitrate deficits. This is perhaps to be expected (both being associated with intense remineralisation), and is evidence that the main patterns in the data are not solely due to random noise in measurements. Silicate is an independent measurement, because nitrate deficit is calculated from nitrate and phosphate.

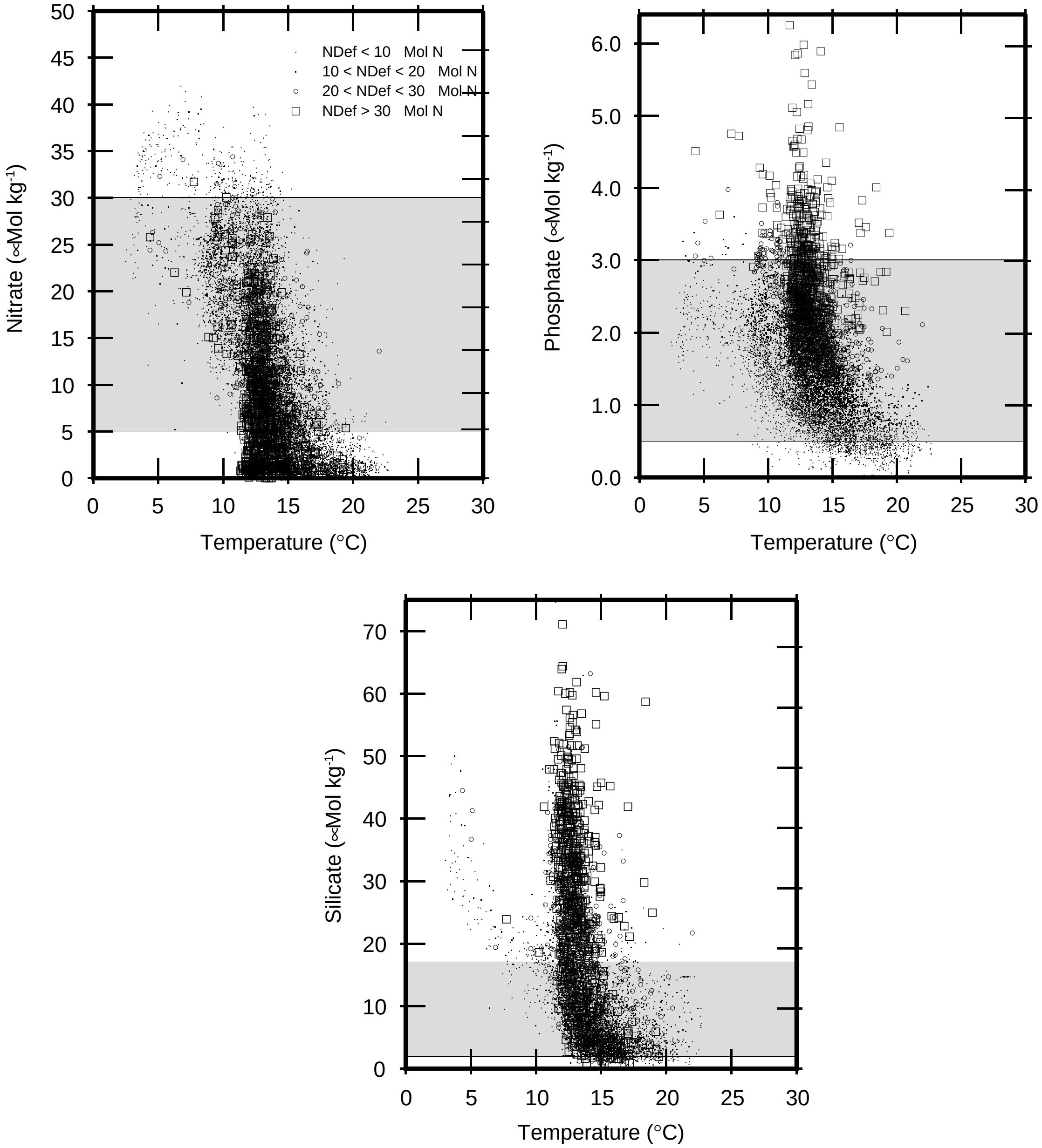

Fig. 5. (a) Nitrate, (b) phosphate and (c) silicate (all μmol kg^{-1}) versus temperature (°C); with symbols indicating nitrate deficit as shown in the legend in (a). The shaded area in each plot indicates the range of concentrations of that nutrient found in source waters offshore (150–300 m depth, see Section 2.2).

3.6. Plots of nitrate deficit, nitrate and phosphate versus distance from the coast

Finally, we also plotted [NO_3], [PO_4] and [ΔN] versus approximate distance from the coast (Fig. 6). The points come from all depths on each cast. An increase in ΔN with proximity to shore is apparent in this data. Average ΔN increases near to the shore, as does the fraction of high ΔN values. Phosphate

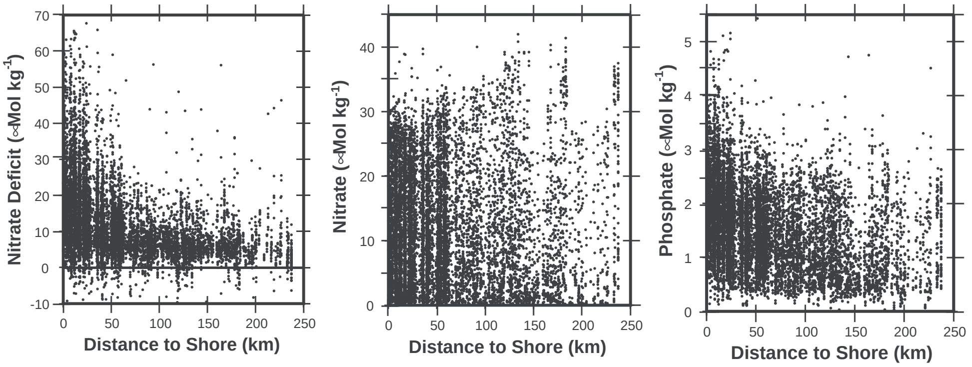

Fig. 6. (a) Nitrate deficit, (b) nitrate, and (c) phosphate (all μmol kg^{-1}) versus distance to the coast (km).

concentrations are also on average higher near to shore.

4. Discussion

4.1. What do the data tell us?

River inputs are unlikely to be responsible for the patterns seen here. River water on average (but by no means always) has a high molar N:P ratio (average ~30:1) (Berner and Berner, 1996), but in any case there are few rivers of any size draining into the ocean along this part of the African coast, with the Orange River being one exception. The mouth of the Orange River enters the ocean at 28.6°S.

We suggest that a more likely explanation for the patterns in the NO_3 and PO_4 data is a combination of nutrient trapping and denitrification. The possibility of nutrient trapping is shown in a schematic diagram in Fig. 7. Dittmar and Birkicht (2001) refer to this phenomenon by an alternative name, ‘‘secondary remineralisation’’. Cold, dense, nutrient-rich deep water from offshore can become yet further enriched in nutrients as it travels over the continental shelf sediments before upwelling to the surface. This can occur if organic particles sink into it from above, fuelled by nutrients extracted from previously upwelled surface water advecting back offshore (Fig. 7). Upwards diffusion of nutrients out of sediment pore waters will also enrich currents travelling over the sediments.

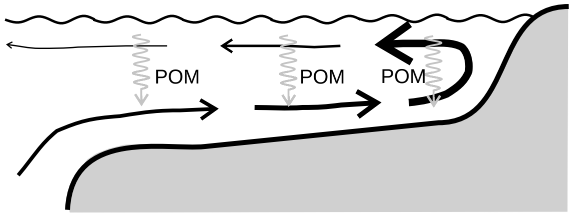

Fig. 7. Schematic of proposed nutrient-trapping mechanism: deep nutrient-rich water from off-shore acquires yet more nutrients as it passes over the shelf sediments, before it finally upwells closer to shore. The remineralisation in the sediments and/or the water column is of POM sinking from the surface, the POM creation there fuelled by nutrients stripped from the surface water advecting back off-shore. The thickness of the arrow represents nutrient concentration.

Nutrient trapping explains the very high phosphate concentrations shown in Fig. 5b, and denitrification explains the lack of equivalently high nitrate concentrations in Fig. 5a. Fig. 8 depicts how nutrient trapping and denitrification are envisaged to affect the two plots in Fig. 5. Bailey and Chapman (1985, 1991) found increased nutrients in water upwelling inshore (in St Helena Bay) relative to that in offshore source waters and attributed the increase to nutrients released by the organic-rich sediments. Calvert and Price (1971) came to similar conclusions to ourselves (denitrification and nutrient trapping), but based on only 20 stations carried out during October 1968. We support their findings using new analysis techniques (e.g. nitrate deficits) and with a dataset more than 50 times larger. Our only modification

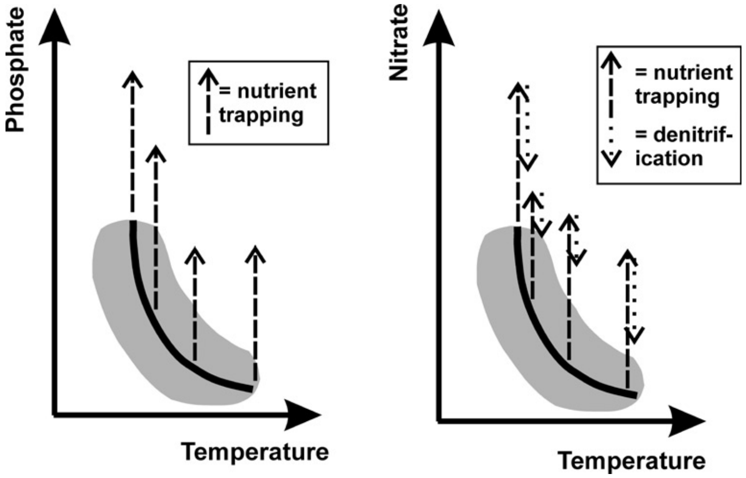

Fig. 8. Schematic showing how otherwise simple trends between nutrient concentration and temperature may be altered by nutrient trapping and, in the case of nitrate, by denitrification.

to their conclusions is that we find abundant evidence of phosphate enrichment due to nutrient trapping whereas they found none.

Dittmar and Birkicht (2001) observed highest phosphate and silicate surface concentrations in the same place as a local minimum in nitrate. They attributed this to a bloom of non-siliceous phytoplankton, but we think a more likely explanation is high organic matter flux to sediments causing both strong local enrichment in [PO_4] and [SiO_4] and also intense local denitrification due to oxygen depletion.

4.2. *Biogeochemical implications*

Comparing Figs. 5a and b it is apparent that phosphate concentrations on the shelf become enriched more than nitrate concentrations, compared to original (source water) concentrations. We agree with Dittmar and Birkicht (2001) and Bailey and Chapman (1991) that phosphate does not as a rule fall to near-zero values either in aged or recently upwelled waters, and for that reason does not limit primary production in the Benguela. There are, by contrast, many near-zero nitrate values (Fig. 5a).

While above-shelf waters also become enriched in nitrate, the enrichment is not so great because of denitrification. We agree with Dittmar and Birkicht (2001) that there is evidence for "considerable nitrogen losses off Namibia", but not that "nitrate was not regenerated".

From a biogeochemical perspective, denitrification will clearly reduce the NO_3 flux into surface waters. This NO_3 flux has been used by Waldron and Probyn (1992) to calculate potential new production in the Benguela system and, from that, to calculate a carbon budget (Waldron et al., 1992, 1998). Their lack of consideration of denitrification (denitrification is not included in their schematic of probable NO_3–N pathways in the Benguela (Fig. 3, Waldron et al., 1992)) will not, however, have led them to underestimate new production or the carbon source strength, as has been argued by Dittmar and Birkicht (2001). This is because Waldron and Probyn's calculations are based on observed nitrate concentrations in the surface layer, and hence automatically take into account the effect denitrification has already had on these concentrations before the water reached the surface.

Nevertheless, there are important implications for the net ocean–atmosphere exchange of CO_2 based on the stoichiometric (un)coupling of [TCO_2] and [NO_3] during upwelling. The [TCO_2]:[NO_3] ratio presumably increases as the water flows over the shelf, acquiring TCO_2 as it does PO_4, but not simultaneously acquiring NO_3

(or acquiring less of it). Remineralisation dynamics of carbon are fairly similar to those of phosphorus, although carbon is released slightly more slowly from organic matter (Anderson and Sarmiento, 1994; Shaffer et al., 1999). If the data were available to construct a plot similar to Figs. 5a–c, but for [TCO_2], a similar plot to Fig. 5b would be expected, at least as regards the degree of enrichment above offshore deep water at the time when the upwelled water first hits the surface. After that time degassing of carbon dioxide but not phosphorus will tend to make the plots less similar.

If our analysis is correct then when upwelling water reaches the surface in the Benguela it must be "supercharged" with CO_2. That is to say [TCO_2] is even higher than in the offshore source waters before they advect onshore and then upwell. Strong outgassing is therefore to be expected. A simple Redfield ratio-based calculation predicts that the amount of supercharging of [TCO_2] will on occasion be as high as 200 μmol kg^{-1}, obtained by multiplying [PO_4] supercharging of up to 2 μmol kg^{-1} (Fig. 5b) by the Redfield ratio of organic matter of $C:P = 106:1$ (Redfield, 1934). A dissolved inorganic carbon system model (Lewis and Wallace, 1997) predicts that this should result in upwelled waters in which pCO_2(aq) (the partial pressure of CO_2 in water) is supercharged by several hundred ppm over the normal (upwelling without enrichment) case.

This strong CO_2 outgassing during the initial active phase of upwelling will not be matched by subsequent NO_3-driven CO_2 draw-down as long as phytoplankton primary production is created in Redfield elemental proportions and is not itself uncoupled. When [NO_3] has been exhausted, [TCO_2] will still be higher than in adjacent offshore nutrient-poor surface waters, because of the simultaneous enrichment in TCO_2 and partial removal of NO_3 by denitrification from the waters before they were upwelled.

4.3. Recommendations for future work

A testable prediction of this study is that TCO_2 concentrations in newly upwelled water near to the coast should be up to 200 μmol kg^{-1} higher than in the offshore source waters for upwelling. This prediction should hold true over parts of the shelf which have suboxic sediments or a suboxic water column. The partial pressure of carbon dioxide (pCO_2) should likewise be elevated above that expected purely from bringing offshore deep water straight to the surface without alteration.

Further nutrient measurements in the system, in particular along transects perpendicular to the coast and through suboxic waters, can test the hypotheses presented here. Direct assays of denitrification (e.g. Devol, 1991) in Benguela sediments would confirm or contest our interpretation as to the quantitative significance of denitrification in this system.

A combined numerical model of the system (for instance see Monteiro, 1996 for a previous study), including physics (currents), phytoplankton growth and decay, nutrient cycling, carbon cycling, and sediment processes is required to gain a full understanding of how the Benguela system functions as a biogeochemical whole.

5. Conclusions

The denitrification process leaves a geochemical fingerprint in the form of a nitrate deficit in the waters of the Benguela. Our analysis of multi-annual nutrient data from the Benguela system shows nitrate deficits of up to 40 μmol NO_3 kg^{-1}, with greater nitrate deficits close to the coast. Large amounts of nitrate are continuously being removed from the system by denitrification, thus preventing some of the "fuel" for primary production from reaching the surface.

There is also evidence of nutrient trapping leading to higher nutrient concentrations than found offshore in deep water. This holds for phosphate and silicate but not to the same extent for nitrate, because of denitrification. By implication it should also hold for dissolved inorganic carbon, but data are needed in order to test this claim.

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