

Models of oxic respiration, denitrification and sulfate reduction in zones of coastal upwelling

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Abstract

Coastal upwelling zones support some of the highest rates of primary production in the oceans. The settling and subsequent decomposition of this organic matter promotes oxygen depletion. In the Eastern tropical North and South Pacific and the Arabian Sea, large tracts of anoxic water develop, where intensive N_2 production through denitrification and anammox accounts for about 1/3 of the total loss of fixed nitrogen in the marine realm. It is curious that despite extensive denitrification in these waters, complete nitrate removal and the onset of sulfate reduction is extremely rare. A simple box model is constructed here to reproduce the dynamics of carbon, oxygen and nutrient cycling in coastal upwelling zones. The model is constructed with five boxes, where water is exchanged between the boxes by vertical and horizontal mixing and advection. These primary physical drivers control the dynamics of the system. The model demonstrates that in the absence of nitrogen fixation, the anoxic waters in a coastal upwelling system will not become nitrate free. This is because nitrate is the limiting nutrient controlling primary production, and if nitrate concentration becomes too low, primary production rate drops and this reduces rates of nitrate removal through N_2 production. With nitrogen fixation, however, complete nitrate depletion can occur and sulfate reduction will ensue. This situation is extremely rare in coastal upwelling zones, probably because nitrogen-fixing bacteria do not prosper in the high nutrient, turbid waters as typically in these areas. Finally, it is predicted here that the chemistry of the upwelling system will develop in a similar manner regardless whether N_2 production is dominated by anaerobic ammonium oxidation (anammox) or canonical heterotrophic denitrification.

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1. Introduction

Coastal upwelling occurs when winds or bottom topography push surface water away from the coast, and this surface water is replaced by water originating from deeper in the water column. A classic example is the upwelling system off the coast of Peru and northern Chile. Here, predominantly southeasterly winds, acting through the Coriolis force, move water to the West, away from the coast, and deeper water upwells to replace this water. Upwelled water typically originates from depths of 100 to 200 m (Smith, 1995), but off the coast of Central Chile, for example, the water source may be as deep as 300 m (Leth and Middleton, 2004). Upwelled water is usually nutrient rich,

typically promoting rapid rates of primary production. High rates of primary production lead to high sinking fluxes of particulate organic carbon, and the decomposition of this carbon substantially reduces oxygen concentrations in the water column.

In some instances, such as in the North and South tropical eastern Pacific, the Arabian Sea, and in parts of the Benguela upwelling system in northwestern coastal Africa, the particulate flux is so intense that oxygen is completely removed (e.g., Codispoti and Packard, 1980; Olson et al., 1993; Helly and Levin, 2004). When this happens, fixed nitrogen is removed as N_2 gas through the processes of heterotrophic denitrification and anaerobic ammonium oxidation (anammox) (e.g., Goering and Cline, 1970; Cline and Richards, 1972; Codispoti and Packard, 1980; Howell et al., 1997; Codispoti et al., 2001; Dalsgaard et al., 2003, 2005; Kuypers et al.,

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2005; Thamdrup et al., in press). The anammox process, where ammonium is combined with nitrite to form N_2 gas ($NO_2^- + NH_4^+ \rightarrow N_2 + 2H_2O$; Jetten et al., 1999), has only recently been described in the marine realm (Thamdrup and Dalsgaard, 2002; Dalsgaard et al., 2003), and it may be a very significant process of N_2 production in anoxic upwelling zones (Dalsgaard et al., 2003; Kuypers et al., 2005). Overall, water column N_2 production is estimated to account for about one-third of the total fixed nitrogen loss in the oceans (Codispoti et al., 2001). In many instances, the intensity of N_2 production varies in step with climatic forcing. For example, in the Arabian Sea and in the tropical North and South Pacific, nitrogen isotope evidence suggests that N_2 production is most intense during interglacial periods. By contrast, it is much reduced, if present at all, during glacial times (Ganeshram et al., 2000; Altabet et al., 2002; Pol-Holz et al., 2006). Rates of N_2 production also respond to less extreme climate variability, and at least in the Arabian Sea, its intensity is significantly correlated to the occurrence of Dansgaard-Oeschger events (Altabet et al., 2002). In many cases, increases in N_2 production rate are apparently coupled to increased rates of primary production, and probably increased upwelling intensity (Ganeshram et al., 2000). However, in the eastern South Pacific, increases in deglacial denitrification were probably caused by increased stratification resulting from the melting of the Patagonian ice sheet (Pol-Holz et al., 2006).

In general, increased primary production leads to increased N_2 production, but one might reasonably ask, does this ever naturally lead to complete nitrate depletion and the onset of sulfate reduction? A survey of coastal upwelling systems suggests that this situation is rare indeed. Where oxygen depletion occurs, nitrate (plus nitrite) concentrations are typically rather high, in the 15–40 μM range (e.g., Fiadeiro and Strickland, 1968; Goering, 1968; Codispoti and Richards, 1976; Codispoti and Packard, 1980; Codispoti, 1983; Morrison et al., 1998), sufficiently high to inhibit sulfate reduction (e.g., Froelich et al., 1979; Berner, 1980). Occasional nitrate (plus nitrite) depletion, and even sulfide accumulation, has been observed in the Peruvian upwelling system (Dugdale et al., 1977; Copin-Montégut and Raimbault, 1994). However, these are typically isolated pockets of water, and they are not particularly common. They do not seem to represent the upwelling system in general (Codispoti, 1983) but may be related to short-lived stochastic events such as bursts of unusually high upwelling rates (Codispoti, 1983). Sulfide also accumulates in the very bottom waters of the Namibian shelf in water depths up to about 100 m (Brüchert et al., 2003). In this case, however, sulfide accumulation is probably related to an oxygen sink and sulfide source from the sediments (Brüchert et al., 2003). This is also true, at least occasionally, in the inner shelf regions of other upwelling areas (Ahumada et al., 1996; Naqvi et al., 2000). Such sulfide accumulation is not normal, however, in coastal upwelling situations where

oxygen-depleted water is underlain by oxygenated water, and where the sediment plays a minor role in controlling water column chemistry (Bange et al., 2000).

We are then left wondering if feedbacks might operate within the upwelling system to maintain nitrate-rich conditions within the anoxic zone. More generally, we are left wondering how the mix of physical and biological parameters including upwelling, water exchange, primary production and carbon decomposition act in concert to control the chemistry of coastal upwelling zones. In this contribution, an upwelling model is constructed which explores the controls on water chemistry. Specific attention is paid to nitrogen and to which factors control N_2 production rate and nitrate concentration, and how these factors feed back into controlling rates of primary production. The model is first developed and explored assuming fixed nitrogen is removed by canonical heterotrophic denitrification. The influence of N_2 fixation on water column chemistry is also explored, and the influence of the anammox on water chemistry is discussed.

2. The model

The model developed here is a simple five box model which seeks to capture the basic features controlling

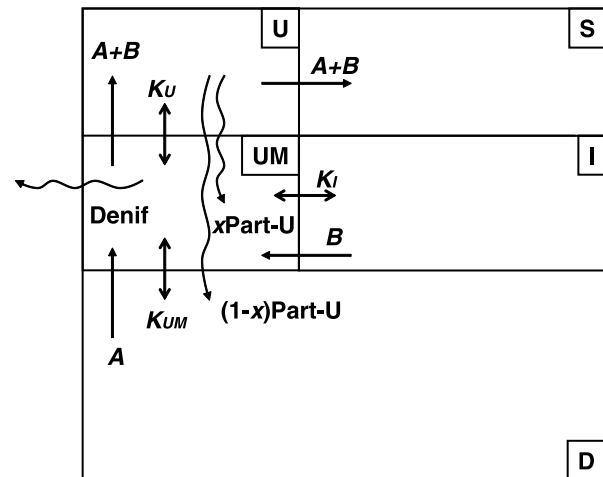


Fig. 1. A simplified box model representing a coastal upwelling zone. The U box represents the upper ocean region into which water is upwelled. The UM box underlies the U box, where some fraction, x , of the new production coming from the U box decomposes. It is in this box where anoxic waters may develop. When this happens, nitrogen can be lost by denitrification (Denif). The S box represents ocean surface water away from the upwelling zone, while the I box represents water of intermediate depth, also away from the upwelling zone, but which exchanges with the UM box. The deep box, D, represents the deep ocean. Water is exchanged by vertical mixing between the U box and the UM box, through the mixing coefficient K_U , while K_{UM} expresses vertical mixing between the UM box and the deep box, D. Horizontal mixing, K_I , occurs between the intermediate box, I, and the UM box. Water is also transported by advection from the deep box, D, to the UM box and the advective rate is represented by A . Likewise, water is also connected from the I box into the UM in this rate is represented by B . The advective flux of water into the U box is given by the sum $A + B$. See text for further details.

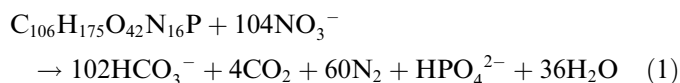
nutrient chemistry, oxygen, and carbon dynamics in a coastal upwelling zone (Fig. 1). The model has two surface boxes, U and S, where the first represents the surface waters in the coastal upwelling region, and the second represents the surface waters away from the influence of upwelling. There are also two intermediate boxes, UM and I, where the first represents the region below the surface mixed layer of the upwelling zone, and it is here where oxygen depletion occurs. The second box represents waters of intermediate depth, and away from the influence of the upwelling zone, but which exchanges water with the UM box. The last box, D, represents the deep water. Two of these boxes are active, UM and U, whereas the others provide prescribed chemical boundary conditions feeding into the active boxes. In principle, these boxes could also become active if fed by other models controlling global ocean chemistry. This would be a natural extension of the model, but outside the scope of the present contribution.

In the model here, vertical exchange occurs between the surface upwelling box (U) and the lower region of oxygen depletion (UM), and is represented by K_U (cm h^{-1}). Velocity units are used here to describe vertical exchange and these are obtained by combining the unit used for eddy diffusion ($\text{cm}^2 \text{h}^{-1}$) with the length scale (cm) over which diffusion applies (e.g., Sarmiento et al., 1988), which is in the range of 20–100 m for coastal upwelling zones. Vertical exchange, K_{UM} (cm h^{-1}), also occurs between the UM box and the deep box (D) while horizontal exchange, K_I (cm h^{-1}) operates between the UM box and intermediate box (I). Horizontal exchange normally occurs over great distances (hundreds of kilometers) due to rapid mixing along isopycnal surfaces. In this model, horizontal exchange influences the box where oxygen depletion occurs (UM box). This box normally has a vertical dimension of 100's of meters and a horizontal dimension of 100's of kilometers. Thus, any chemical constituent mixed into the box across the vertical dimension of the box will be spread out across its horizontal dimension. To obtain the values of K_I used in this model, we start with the horizontal diffusion coefficient K_{HO} presented in units of diffusion ($\text{cm}^2 \text{h}^{-1}$), and this is multiplied by a scalar representing the ratio of the height (H) to the length (L) of the box. This value is then divided by the length over which diffusion applies. Thus, $K_I = HK_{HO}/L^2$. Horizontal exchange will also occur between the two surface boxes U and S, but this has been ignored here. This is because in all modeling scenarios, nitrate will have a concentration of zero in the U box, and since nitrate will also be depleted in the S box, horizontal exchange between U and S will have no influence on nitrate systematics. There would be a small influence on the concentration of phosphorus in the U box, but only under circumstances, where P does not control primary production and can accumulate here. Ignoring this exchange significantly simplifies the equations and has absolutely no influence on the final results and conclusions.

Advective upwelling, A (cm h^{-1}), delivers water from the deep box, D, to the UM box, and since upwelled water

is usually sourced from rather shallow depths of 100–200 m (Codispoti, 1983; Smith, 1995), another advective flow, B (cm h^{-1}), has been introduced from the intermediate box (I) to the region of oxygen depletion (UM). The term B does not represent the actual velocity of water through the vertical dimension of the intermediate box, but rather the contribution of this water to vertical upwelling from the intermediate box into the surface box. The total flux of water from the UM box to the surface ocean of the upwelling zone (U box) is given by the sum of flows $A + B$.

Organic matter productivity is driven by the upwelling of nutrients from the zone of oxygen depletion (UM) into the upper box (U). This input of nutrients stimulates primary production, a portion of which falls back out of this box into the underlying water column. In the following analysis, nitrogen is followed, and the particulate flux of organic nitrogen out of the surface box (U) is defined as PartU. A fraction of the organic nitrogen, $x\text{PartU}$, is liberated into the zone of oxygen depletion just below, the rest of which, $(1 - x)\text{PartU}$ is liberated in the deep water. When the zone of oxygen depletion becomes oxygen free, fixed nitrogen is lost as N_2 through denitrification and anammox. In the following model, N_2 production is assumed to occur through denitrification, which can be given as follows with the organic matter stoichiometry of Anderson (1995) and Gruber and Sarmiento (1997). Note that this equation is written so that ammonium does not accumulate, which is consistent with observations (e.g., Richards, 1965):



Nitrogen limitation in upwelling waters is a natural consequence of nitrogen gas loss through N_2 production (e.g., Dugdale et al., 1977; Mantoura et al., 1993; Copin-Montégut and Raimbault, 1994; Davies and Morales, 1998). This is seen clearly when comparing phosphate and total inorganic nitrogen (in this case nitrate + nitrite) concentrations from oxygen-depleted upwelling zones. In all three cases, the tropical North Pacific, the tropical South Pacific and the Arabian Sea (Fig. 2), a substantial nitrogen deficit is observed at high concentrations of phosphate, a clear sign of nitrogen loss through denitrification and anammox (see also Codispoti and Richards, 1976; Codispoti, 1983; Brandes et al., 1998; Voss et al., 2001). The nitrate deficit is, in part, advected into surface waters, generating a significant nitrogen deficit relative to phosphate. This is easily seen when N and P concentrations in upwelling zones are compared to areas distal to the zone of upwelling and the influence of denitrification and anammox (see also Gruber and Sarmiento, 1997; Louanchi and Najjar, 2000). This is particularly true for the Eastern tropical South Pacific and the Arabian Sea, whereas the surface nitrate deficit in the Eastern tropical North Pacific is less pronounced.

Therefore, when zones of intense upwelling generate complete oxygen consumption and N_2 production in the underlying waters, primary production in surface waters

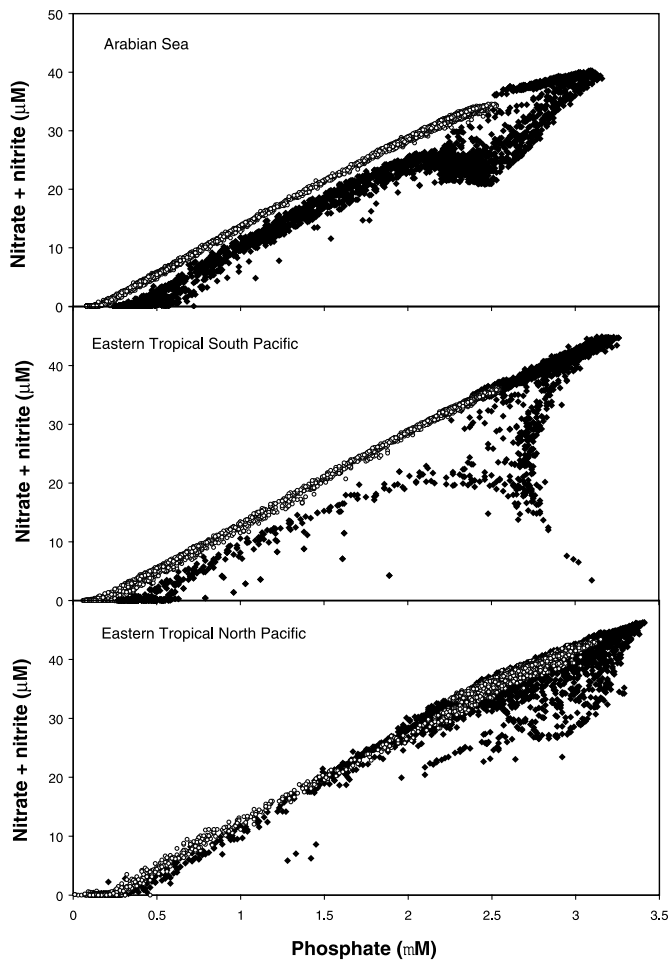


Fig. 2. Nutrient chemistry of coastal upwelling regions supporting anoxic water columns and influenced by N_2 production (black diamonds), compared to the nutrient chemistry of adjacent water bodies unaffected by water column anoxic conditions (open circles). For the Arabian Sea, data for the upwelling region come from JGOFS cruises TN053 (early NE monsoon) and TN050 (late SW monsoon) (see Morrison et al., 1998), compared to WOCE cruise I07C for the Southern Indian Ocean uninfluenced by N_2 production. For the Eastern Tropical South Pacific, upwelling zone data come from WOCE cruise P21, stations 5 to 300, which are compared to stations 176–294 from the same cruise in the Western tropical South Pacific. For the Eastern tropical North Pacific, data for the coastal upwelling region come from WOCE cruises P04E (stations 120–220) and P19C (stations 360 to 422), compared with WOFS cruise P04W from the Northern tropical Western Pacific. For data sources see, <http://whpo.ucsd.edu/index.htm> and, <http://usjgofs.whoi.edu>.

is often severely nitrogen limited. This situation will be modeled below. Also considered is the situation where nitrogen fixation in the surface waters makes up any nitrogen deficit. Nitrogen fixation, along with blooms of nitrogen-fixing cyanobacteria (*Trichodesmium* spp.), has been identified in the Arabian upwelling system (Capone et al., 1998). A nitrogen deficit in coastal upwelling regions could also be supplemented with terrestrial runoff if the N/P ratio of the runoff water exceeded the demands of the primary producers. This could be a natural extension of the present model, but this situation will not be formally explored.

Nitrogen fixation is incorporated into the model in the case where denitrification produces a nitrogen deficit in

upwelled waters. In the modeling, the fates of nitrogen, oxygen, and phosphorus are followed. Somewhat different equations must be written for when oxygen persists in the UM box and for when it is depleted. Beginning with the condition where oxygen persists, the following mass balance equations are written for nitrogen inputs and outputs in both the U box and the UM box. Starting with the U box:

$$N_{UM}(A + B) + K_U(N_{UM} - N_U) = N_U(A + B) + \text{PartU} \quad (2)$$

After assuming that nitrate in the U box, N_U , is zero, and simplifying, we have:

$$N_{UM}(A + B + K_U) = \text{PartU} \quad (3)$$

The mass balance for nitrate and the UM box is:

$$\begin{aligned} AN_D + BN_I + x\text{PartU} = N_{UM}(A + B) + K_U(N_{UM} - N_U) \\ + K_{UM}(N_{UM} - N_D) \\ + K_I(N_{UM} - N_I) \end{aligned} \quad (4)$$

After substituting Eq. (3), and solving for N_{UM} :

$$N_{UM} = \frac{(A + K_{UM})N_D + N_I(B + K_I)}{(A + B + K_U + K_{UM} + K_I) - x(A + B + K_U)} \quad (5)$$

The equation for O_2 in the UM box is:

$$\begin{aligned} AO_{2D} + BO_{2I} + K_I(O_{2I} - O_{2UM}) + K_{UM}(O_{2D} - O_{2UM}) \\ + K_U(O_{2U} - O_{2UM}) = (A + B)O_{2UM} + r_a x \text{PartU} \end{aligned} \quad (6)$$

After substituting Eq. (3) and solving for O_{2UM} , we have:

$$O_{2UM} = \frac{O_{2D}(A + K_{UM}) + O_{2I}(B + K_I) + K_U O_{2U} - r_a x N_{UM}(A + B + K_U)}{(A + B + K_U + K_{UM} + K_I)} \quad (7)$$

Here, r_a is the stoichiometric relationship between oxygen utilization and nitrate production during organic matter decomposition (see Table 1). From a phosphate mass balance in the U box, and after substituting Eq. (3), the following expression is obtained for the concentration of phosphate in the upper U box:

$$P_U = P_{UM} - \frac{N_{UM}}{r_p} \quad (8)$$

Here, r_p is the stoichiometric relationship between nitrate and phosphate liberation during oxic respiration (Table 1). A mass balance equation can also be written for phosphate in the UM box, which takes a very similar form to the mass balance equations for oxygen and nitrate (Eqs. 4 and 6). After substituting Eq. (8), the expression for phosphate concentration in the UM box is:

$$P_{UM} = \frac{P_D(A + K_{UM}) + P_I(B + K_I) - \frac{K_U N_{UM}}{r_p} + \frac{x N_{UM}}{r_p}(A + B + K_U)}{(A + B + K_{UM} + K_I)} \quad (9)$$

We now switch to the condition, where the concentration of O_2 in the UM box is 0, and denitrification can occur.

Table 1
Constraints on model parameters

Parameter	Description	Range	Units	Most likely	Refs.
K_U, K_{UM}	Vertical exchange	0.1–1.0	$\text{cm}^2 \text{s}^{-1}$	0.1–0.3	1–6
$A + B$	Upwelling rate	0.27–7.2	cm h^{-1}	1–3	7–10
K_I	Horizontal exchange	100–1800	$\text{m}^2 \text{s}^{-1}$	500–1800	11–13
newprod	New production	2.5–24	$\text{nmol N cm}^{-2} \text{h}^{-1}$	10–20	3, 14–17
Denif	Denitrification rate	10–28	$\text{nmol N cm}^{-2} \text{h}^{-1}$	10–20	4, 5, 7, 17, 18
x	Remineralization ratio in UM box	0.3–0.85	Dimensionless	0.6–0.7	14, 15, 17, 18
N_{deficit}	Nitrate deficit	5–20	μM	10–15	3, 7, 8, 19
O_{2^D}	Deep water O_2 in coastal upwelling zone	100–200	μM	140	20
O_{2^I}	Intermediate depth O_2 adjacent to UM box	50–150	μM	100	20
r_a	O_2 -used/ NO_3 -produced during OC oxidation	8.6–10.6	Dimensionless	10.6	21, 22, 25
r_p	N/P liberated during OC oxidation	15–16	Dimensionless	16	21, 22, 23, 25
r_c	C/N ratio of OC oxidation	6.63–7.31	Dimensionless	6.63–7.31	21, 22, 23, 25
r_{den}	OC oxidized/ NO_3 used in denitrification, w/o NH_4 accumulation	1.02	Dimensionless	1.02	23
r_{SR}	OC-used/sulfate reduced	2	Dimensionless	2	24

1, Shaffer (1989); 2, Wunsch and Ferrari (2004); 3, Voss et al. (2001); 4, Codispoti et al. (1988); 5, Yakushev and Neretin (1997); 6, Pacanowski and Philander (1981); 7, Codispoti and Christensen (1985); 8, Codispoti (1983); 9, Ianson and Allen (2002); 10, Sarma (2002); 11, Saunders et al. (1999); 12, Richards and Pollard (1991); 13, Huck et al., 1999; 14, Schlitzer (2002); 15, Escribano et al. (2004); 16, Olson et al. (1993); 17, Bange et al. (2000); 18, Bange et al. (2005); 19, Brandes et al. (1998); 20, World Ocean Circulation Experiment (<http://whpo.ucsd.edu/index.htm>); 21, Anderson and Sarmiento (1994); 22, Shaffer et al. (1999); 23, Gruber and Sarmiento (1997); 24, Berner (1980); 25, Körtzinger et al. (2001).

In this case, the mass balance for nitrogen needs to include nitrogen loss by denitrification, which is given by:

$$AN_D + BN_I + x\text{PartU} = N_{UM}(A + B) + K_U(N_{UM} - N_U) + K_{UM}(N_{UM} - N_D) + K_I(N_{UM} - N_I) + \text{Denif} \quad (10)$$

To solve for N_{UM} , an independent expression is needed for the rate of denitrification. This is obtained from a carbon balance, where the input of organic matter from the photic zone is balanced with its oxidation by oxic respiration and denitrification.

$$xr_c\text{PartU} = \frac{r_c}{r_a}[AO_{2^D} + BO_{2^I} + K_{UM}O_{2^D} + K_I O_{2^I} + K_U O_{2^U}] + r_{\text{den}}\text{Denif} \quad (11)$$

Here, r_c is the ratio between carbon and nitrogen in decomposing organic matter (Table 1) and r_{den} is the ratio between carbon oxidation and nitrate utilization during denitrification. Substituting Eq. (3) and rearranging Eq. (11) yields an expression for denitrification (Eq. (12)), which can be inserted into Eq. (10), allowing a solution for N_{UM} (Eq. (13)):

$$\text{Denif} = \frac{xr_c N_{UM}[A + B + K_U] - \frac{r_c}{r_a}[AO_{2^D} + BO_{2^I} + K_{UM}O_{2^D} + K_I O_{2^I} + K_U O_{2^U}]}{r_{\text{den}}} \quad (12)$$

$$N_{UM} = \frac{r_{\text{den}}[N_I(K_I + B) + N_D(K_{UM} + A)] + \frac{r_c}{r_a}[(A + K_{UM})O_{2^D} + (B + K_I)O_{2^I} + K_U O_{2^U}]}{r_{\text{den}}[(A + B + K_U + K_{UM} + K_I) - x(A + B + K_U)] + x\frac{r_c}{r_{\text{den}}}(A + B + K_U)} \quad (13)$$

The expressions for the concentration of phosphate in the surface upwelling box, U, and in the UM box remain the same as those given above (Eqs. (8) and (9)). When denitrification occurs, the nitrate deficit is calculated as the differ-

ence between the measured nitrate concentration and the concentration of nitrate expected in the absence of denitrification. The nitrate deficit, N_{deficit} , is calculated as:

$$N_{\text{deficit}} = r_p P_{UM} - N_{UM} \quad (14)$$

Here, r_p is same as for oxic organic matter decomposition (Table 1), consistent with current stoichiometric models for anaerobic organic carbon decomposition (Gruber and Sarmiento, 1997). The new production in the system is also calculated, and it is represented relative to nitrogen. Thus, the new production is the settling flux of particulate nitrogen from the U box into the UM box and is given as PartU (Fig. 1). The settling flux of particulate nitrogen is balanced by the inputs of nitrate into the U box and therefore new production, newprod, is given as (the expression is identical to Eq. (3)):

$$\text{newprod} = N_{UM}(A + B + K_U) \quad (15)$$

Nitrogen fixation can, in principle, make up the nitrogen deficit caused by denitrification, and this case is also considered. It is assumed that N-fixation adds nitrogen to the point where nitrogen and phosphorus are available in the U box in amounts just balancing the needs of the primary producers. When oxygen is greater than 0 in the UM box, denitrification does not occur, and nitrogen fixation is not necessary. In this case, the equations regulating water column chemistry are the same as those presented above for when oxygen persists. The equations, however, are different when oxygen is depleted in the UM box, and these are developed by first considering the mass balance for phosphate in the U box:

$$P_{UM}(A + B) + K_U(P_{UM} - P_U) = P_U(A + B) + \frac{\text{PartU}}{r_p} \quad (16)$$

which, after assuming that P_U is zero, gives:

$$P_{UM}(A + B + K_U) = \frac{\text{PartU}}{r_p} \quad (17)$$

A phosphorus mass balance for the UM box yields:

$$\begin{aligned} AP_D + BP_1 + \frac{x}{r_p} \text{PartU} &= P_{UM}(A + B) + K_U(P_{UM} - P_U) \\ &+ K_{UM}(P_{UM} - P_D) \\ &+ K_I(P_{UM} - P_I) \end{aligned} \quad (18)$$

Eq. (17) is substituted into Eq. (18) giving an expression for the concentration of phosphate in the UM box, P_{UM} :

$$P_{UM} = \frac{P_D(A + K_{UM}) + P_I(B + K_I)}{(A + B + K_{UM} + K_U + K_I) - x(A + B + K_U)} \quad (19)$$

The concentration of nitrate in the U box is also taken as 0, and the concentration of nitrate in the UM box can be obtained from the same mass balance as given in Eq. (10), yielding, upon simplification:

$$N_{UM} = \frac{(A + K_{UM})N_D + N_I(B + K_I) + xr_p(A + B + K_U) - \text{Denif}}{(A + B + K_U + K_{UM} + K_I)} \quad (20)$$

Thus, to know N_{UM} , one needs to know the denitrification rate, which can be obtained from a carbon balance as before (Eq. (11)). Combining Eq. (11) with Eq. (17) yields:

$$\text{Denif} = \frac{xr_p P_{UM}(A + B + K_U) - \frac{r_c}{r_a} [O_{2D}(A + K_{UM}) + O_{2I}(B + K_I) + K_U O_{2U}]}{r_{\text{den}}} \quad (21)$$

This equation is similar to Eq. (12), except that denitrification rate is now expressed in terms of phosphorus concentration in UM box rather than nitrate concentration.

The mass balance equation for nitrogen in the upper U box is given as:

$$\begin{aligned} N_{UM}(A + B) + K_U(N_{UM} - N_U) + N_{\text{fix}} \\ = N_U(A + B) + \text{PartU} \end{aligned} \quad (22)$$

from which an expression can be derived for the rate of nitrogen fixation, N_{fix} :

$$N_{\text{fix}} = \text{PartU} - N_{UM}(A + B + K_U) \quad (23)$$

As will be demonstrated see below, when nitrogen fixation is allowed, nitrate can become depleted in the UM box, and when this happens, sulfate reduction ensues. In order to compute the significance of sulfate reduction, a carbon balance must be constructed. This carbon balance accounts for all of the carbon oxidized by oxic respiration and denitrification, and any remaining carbon oxidation is attributed to sulfate reduction. Therefore:

$$\begin{aligned} r_c x \text{PartU} &= \frac{r_c}{r_a} [(A + K_{UM})O_{2D} + (B + K_I)O_{2I} + K_U O_{2U}] \\ &+ r_{\text{den}} [(A + K_{UM})N_D + (B + K_I)N_I + x \text{PartU}] \\ &+ \text{SR} r_{\text{SR}} \end{aligned} \quad (24)$$

where, in addition to the terms already defined, r_{SR} is the ratio between moles of organic carbon oxidized per mole sulfate reduced which is taken as 2 (Table 1). The term on the left gives the total flux of carbon decomposed in the UM box. The first term on the right gives the rate of carbon oxidation by oxic respiration when O_{2UM} is reduced to zero, whereas the next term gives the rate of carbon oxidation by denitrification, leaving the remaining for sulfate reduction. This equation is rearranged to yield rates of sulfate reduction:

$$\begin{aligned} \text{SR} &= \{r_c x \text{PartU} - \frac{r_c}{r_a} [(A + K_{UM})O_{2D} + (B + K_I)O_{2I} \\ &+ K_U O_{2U}] - r_{\text{den}} [(A + K_{UM})N_D \\ &+ (B + K_I)N_I + x \text{PartU}]\} / r_{\text{SR}} \end{aligned} \quad (25)$$

The sulfide concentration in the UM box, S_{UM} can be calculated from the sulfate reduction rate, and it is given by:

$$S_{UM} = \frac{\text{SR}}{(A + B + K_I + K_{UM} + K_U)} \quad (26)$$

When sulfate reduction occurs, all of the nitrogen fueling primary production comes from nitrogen fixation, and thus the nitrogen fixation rate is equivalent to the new production rate as expressed in Eq. (15).

In all of these models, the chemistry of the deep and intermediate boxes develops as would be expected with water derived from high latitudes with an oxygen concentration of 325 μM , and with a preformed phosphate concentration of 1.2 μM . The concentration of nitrate is assumed to be 16 times that of phosphate (r_p , Table 2), and

Table 2
Model input parameters

Parameter	Value	Units
K_{UM}	0.1	cm h^{-1}
K_U	0.1	cm h^{-1}
K_I	0.4	cm h^{-1}
A	0	cm h^{-1}
B	0.4	cm h^{-1}
x	0.7	
O_{2U}	250	μM
O_{2D}	140	μM
O_{2I}	100	μM
N_I	40.43	μM
N_D	36.65	μM
P_I	2.53	μM
P_D	2.29	μM
r_a	10.6	
r_p	16	
r_c	6.63	
r_{den}	1.02	
r_{SR}	2	
r_{an}	8.6	

Table 3
Equations used in model calculations

Parameter	O ₂ in UM box	Eq. used
N_{UM} (w/o N-fix)	>0	5
N_{UM} (w/o N-fix)	=0	13
O_{2UM} (w/o N-fix)	>0	7
P_{UM} (w/o N-fix)	≥ 0	9
P_U (w/o N-fix)	≥ 0	8
Denif (w/o N-fix)	=0	12
N_{UM} (w/N-fix)	>0	5
N_{UM} (w/N-fix)	=0	20
P_{UM} (w/N-fix)	>0	9
P_{UM} (w/N-fix)	=0	19
Denif (w/N-fix)	=0	21
N_{fix}	=0	23
SR (w/ N_{fix})	=0	24
S_{UM} (w/ N_{fix})	=0	25
newprod	≥ 0	15

phosphate is liberated as oxygen becomes depleted with a ratio of $\Delta O_2/P$ of 170/1 (Shaffer et al., 1999). Thus, the concentrations of nitrate and phosphorus in the deep and intermediate boxes adjust with the choice of oxygen concentrations within the boxes. A summary of the equations used to calculate water chemistry under the different model conditions is summarized in Table 3.

3. Results and discussion

3.1. Standard model

The model variables include choices for A , B , x , K_U , K_{UM} , K_I , O_{2D} , O_{2U} and O_{2I} , the magnitudes of which can be constrained from observations from anoxic upwelling zones such as found in the Arabian Sea or the Eastern Tropical North and South Pacific (Table 1). Within these ranges, choices were made to reproduce, as best as possible, the observed chemistry within the zone of complete oxygen depletion (UM box) as well as rates of denitrification and new production. The resulting model inputs are presented in Table 2, and the outputs are shown in Table 4. This model run will be referred to as the “standard model”. Most of the model inputs for the standard model are within the observed range, except for the upwelling rate ($A + B$), which is smaller than values usually assigned to coastal upwelling zones. The lower rates used here were necessary, however, to reproduce the observed and estimated rates of

Table 4
Standard model output

Parameter	Value	Units
O_{2UM}	0	μM
N_{UM}	37.26	μM
$N_{deficit}$	13.10	μM
Denif	11.79	$nmol N cm^{-2} h^{-1}$
newprod	18.63	$nmol N cm^{-2} h^{-1}$
P_U	0.82	μM
P_{UM}	3.15	μM

denitrification and new production (Table 1). Part of the discrepancy between the upwelling rate used here, and values presented in the literature, is that in some cases, particularly in Eastern tropical South Pacific, relatively high concentrations of both nitrate and phosphate are found in the surface waters (although phosphate is still in excess) (Codispoti and Christensen, 1985; Copin-Montégut and Raimbault, 1994). This means that not all of the upwelled nutrients are used in primary production, reducing rates of export production compared to the situation where all of limiting nutrient is used as is assumed in the model.

The variable model parameters are adjusted from the standard model conditions, and changes in water chemistry are monitored. Modeling begins with the situation where nitrogen fixation does not occur, and upwelling rate ($A + B$) is varied holding all other parameters constant. Actually, in the present calculations, upwelled water is sourced only from intermediate depths, meaning that B is the only upwelling parameter used. This is because, as discussed earlier, upwelled water is mainly sourced from intermediate depths (Codispoti, 1983; Smith, 1995; Leth and Middleton, 2004). However, A (the deep water source), could also be adjusted in concert with, or in addition to, B , providing very similar results to those presented here. Of all of the variable parameters, upwelling velocity is the one most frequently called upon to influence water column chemistry (Codispoti, 1983; Ganeshram et al., 2000; Altabet et al., 2002).

Modelling reveals that the UM box is oxic at low upwelling rates (Fig. 3), where the settling flux of decomposing primary production is insufficient to completely consume all of the oxygen advected and diffused into the

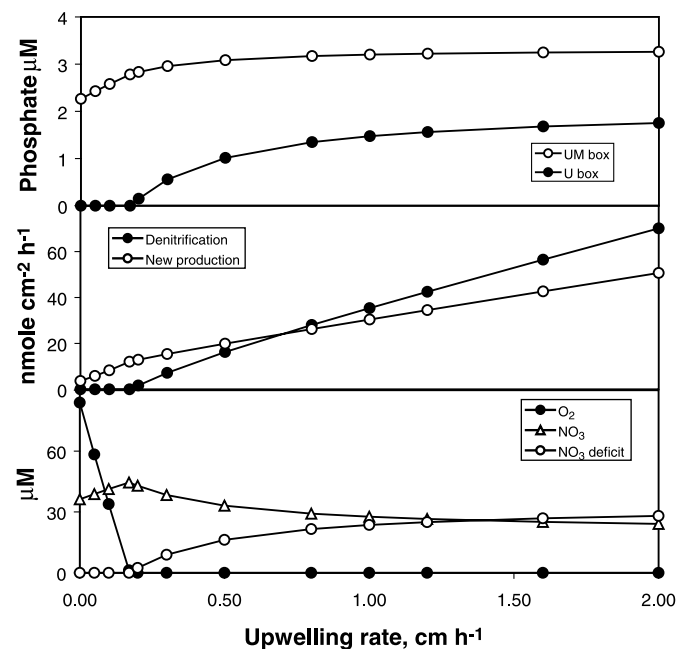


Fig. 3. Results of the standard model with variable rates of upwelling. In this case the upwelled water is sourced from the intermediate box, I. See text for details.

box. However, as upwelling rate increases, primary production rate increases, and the oxygen concentration in the UM box decreases. For the parameters used in the model, the box becomes anoxic with upwelling rates of $>0.17 \text{ cm h}^{-1}$. After this, nitrate concentrations decrease as a result of denitrification, and a nitrate deficit accumulates. With increasing upwelling rate, the new production increases as would also be expected, but the trend breaks in slope between oxic and anoxic conditions due to the nitrate deficit under anoxic conditions. Greater new production provides more organic matter for decomposition within the UM box, which drives progressively higher rates of denitrification. With increasing upwelling, the concentration of phosphate in the UM box stabilizes at about $3 \mu\text{M}$. The phosphate concentration in the upper, U, box is zero when the UM box is oxic, but it begins to increase as denitrification produces a continually larger nitrate deficit. As demonstrated in Fig. 2, excess phosphorus relative to nitrate is a common feature of coastal upwelling zones.

Perhaps the most important model observation is that, rather counter to intuition, nitrate does not become completely removed from the UM box with increasing rates of upwelling and primary production despite increasing rates of denitrification. Indeed, the concentration of nitrate plateaus at around $20 \mu\text{M}$, and this value persists to the highest rates of upwelling. The persistence of high nitrate concentrations, despite increasing rates of new production and denitrification, points to the operation of internal feedbacks to stabilize nitrate concentration. On close inspection, such feedbacks are in fact necessary for anoxia to persist. We can think about it like this: if nitrate becomes depleted in the UM box, then the source of nitrate to the upper box will be reduced. As a result, the primary production rate will drop, dropping the flux of organic matter into the UM box, which will reduce the rate of denitrification and the nitrate sink. This will allow nitrate concentration to increase. Complete nitrate depletion is untenable as primary production would cease, allowing nitrate to accumulate again in the UM box. Thus, there exists a dynamic balance between primary production rate, denitrification rate and nitrate concentration which combines to ensure that nitrate persists in the UM zone. This dynamic balance is proposed as the main reason for the persistence of nitrate within the oxygen-depleted waters of coastal upwelling zones.

Codispoti (1989) proposed a rather similar mechanism for stabilizing global nitrate concentrations, where increasing nitrate concentrations and new production would increase the extent and activity levels of oxygen minimum zones supporting denitrification. This would draw nitrate concentrations back down. Codispoti (1989) also surmised, as is explored further below, that the efficiency of this feedback mechanism would depend on the extent to which the nitrate deficit is augmented by nitrogen fixation. The discussion of Codispoti (1989), however, is not quantitative. Also, it does not focus on the controls of water column chemistry in oxygen-depleted oxygen minimum zones and

it does not consider what mix of processes might lead to the initiation of sulfidic water column conditions.

Variable parameters other than upwelling, of course, have a bearing on water chemistry. Starting with the “standard model”, a number of these parameters were varied in turn and their influence on water chemistry and nitrogen dynamics is shown in Figs. 4–6. In each case, the results are roughly comparable to those obtained by varying upwelling rate. In other words, values for a number of the variable parameters (O_{2D} , K_{UM} and K_U are explored here) can be found where the UM box is oxic, and with further variation, the UM box can be driven to anoxic conditions. For example, when the oxygen concentration of the deep (D) and intermediate (I) boxes increase above around $170 \mu\text{M}$, the UM box becomes oxic. At lower deep water oxygen concentrations, the UM box is anoxic and denitrification ensues. As oxygen concentration decreases, there is an increase in the nitrate deficit, and rates of denitrification also increase. This increase in denitrification rate is in the face of decreasing rates of new production, which are driven by decreasing nitrate concentrations in the UM box. Increasing denitrification rate, therefore, is driven mostly by decreasing rates of oxic respiration (not shown) as a result of lower inputs of oxygen to the UM box. With less oxic respiration, there is more organic matter available to fuel denitrification. As with changes in upwelling rate, nitrate persists even at low oxygen concentrations.

The present model does not consider the development of anoxia outside of the coastal upwelling zone. This could become important when the oxygen concentration in the deep and intermediate boxes becomes low and denitrifica-

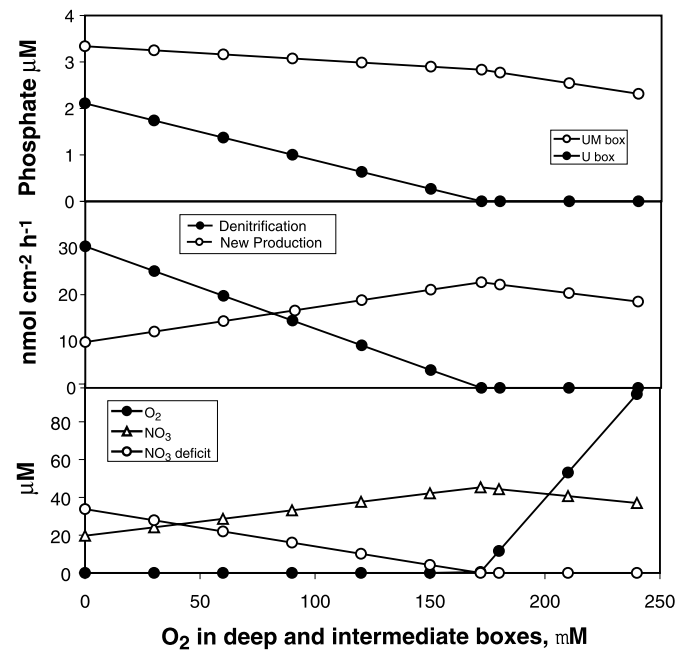


Fig. 4. Results of the standard model with variable concentrations of oxygen in the deep box, D, and the intermediate box, I. For these calculations, the oxygen concentrations in the deep box and the intermediate box were equivalent. See text for details.

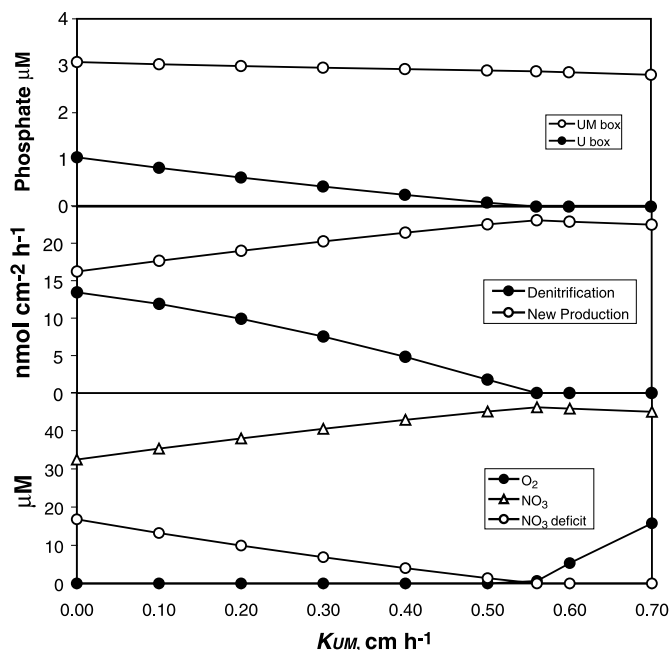


Fig. 5. Results of the standard model with variable rates of vertical exchange, K_{UM} , between the deep box, D, and the UM box. See text for details.

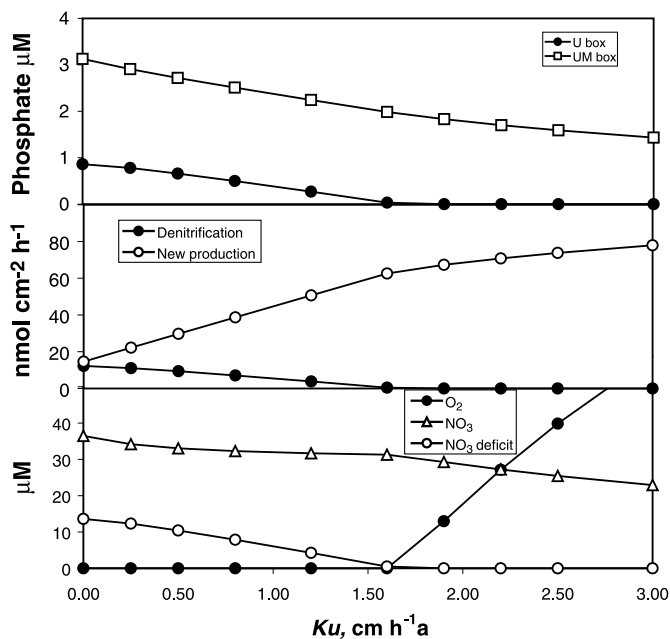


Fig. 6. Results of the standard model with variable rates of vertical exchange, K_U , between the upper box, U, and the UM box. See text for details.

tion occurs in these boxes as well. Therefore, the present results do not adequately reflect the influence of very low oxygen concentrations on the global ocean nutrient inventory and how this would influence the chemistry of the upwelling zone. This is worthy of study, but outside of the focus of the current manuscript.

Changes in the vertical mixing rate, both K_U and K_{UM} , also influence water chemistry, and in both cases, high rates of vertical mixing result in oxic conditions. A similar picture is also observed by increasing K_I , the horizontal mixing rate between the intermediate box, I, and the UM box (not shown). The mixing rates required to produce oxic conditions are extremely high, especially for K_U , and thus, vertical mixing rates may have less of an influence on water chemistry than upwelling rate on oxygen concentrations in the deep water and intermediate boxes.

3.2. Standard model with N_2 fixation

In a modification of the “standard model”, nitrogen fixation in the upper U box adds nitrogen to the point where the demand of primary production is satisfied. Thus, both nitrogen and phosphorus are available in the proportions required and, therefore, each limits primary production. Starting with the initial conditions of the “standard model” (Table 2), nutrient chemistry and carbon dynamics are allowed to develop with increasing upwelling rate (Fig. 7). At low rates of upwelling, oxygen persists in the UM box, and the system behaves exactly as explored earlier (Fig. 3). As upwelling rate increases beyond about 0.2 cm h^{-1} , the UM box becomes anoxic, and denitrification begins. However, unlike the situation explored above, complete nitrate depletion occurs at modest upwelling rates (around 0.4 cm h^{-1}), and sulfate reduction begins just after, with the accumulation of dissolved sulfide. Therefore, sulfidic conditions in coastal upwelling zones can occur if upwelling rates are high enough and if nitrogen fixation makes up the nitrate deficit. In an earlier model, Shaffer (1989) found that the oxygen minimum layer of the global ocean could become sulfidic under certain circumstances if

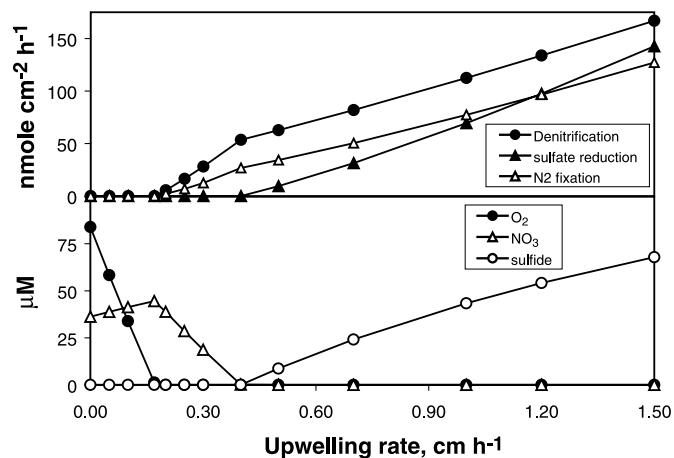


Fig. 7. Results of model where nitrogen fixation is allowed to completely supplement any nitrate deficits in the surface box. In this case, both nitrogen and phosphorus are available to phytoplankton in the amounts they require, and therefore, both limit primary production. The model is generated starting with the same input conditions as in the standard model, and upwelling rate is allowed to change. As in Fig. 3, upwelled water is sourced from the intermediate box, I. See text for details.

N₂ fixation fully amended the nitrogen deficit of the upper ocean.

Nitrogen fixation indeed has been identified in coastal upwelling areas. For example, a massive bloom of *Trichodesmium erythraeum* was observed in the Arabian Sea (Capone et al., 1998) during the spring intermonsoon. In this case, the bloom extended over about 20% of the Arabian Sea surface. Such booms, however, are relatively short-lived. Direct measurements suggest an annual fixation of about 1 Tg of N, which is only 3% of the estimated loss of nitrate by denitrification (Bange et al., 2000). Capone et al. (1998) noted, however, that the annual patterns of the *Trichodesmium* bloom formation are poorly known, and that their estimate of nitrogen fixation rate may be low. In another approach, Brandes et al. (1998) estimated N-fixation rates of 1–6 Tg y⁻¹ from a surface-water nitrate isotope balance. Taking all data together, Bange et al. (2000, 2005) choose 3.3 Tg y⁻¹ as the most likely value for N-fixation in the Arabian Sea. This is still 10 times less than estimated rates of denitrification and consistent with nutrient concentration data which show a pronounced phosphate excess over nitrogen in Arabian Sea surface water (Fig. 2).

The author is unaware of any direct determinations of N fixation rate in the upwelling areas of the Eastern tropical North and South Pacific. The results of Voss et al. (2001), however, are pertinent. They measured the isotopic compositions of water-column nitrate and organic particulate nitrogen intercepted in sediment traps running parallel to the Mexican coast between 10° N and 24° N. The δ¹⁵N of organic nitrogen settling from the photic zone ranged from 8.5‰ to 11.5‰ with an average of 9.8‰; values more closely reflecting the isotopic composition of the nitrate sourced from anoxic deeper waters than the isotopic composition of around -0.6‰ expected for nitrogen fixation (Brandes and Devol, 2002). Thus, only a relatively minor role is indicated for nitrogen fixation as a nitrogen source for primary producers.

Still, as mentioned above, there have been scattered reports of sulfidic conditions in the upwelling zone off the coast of Peru during periods of intense upwelling (Dugdale et al., 1977). These conditions, however, are regionally and temporally restricted, and they do not represent the chemistry of the upwelling zone in general. There is no evidence that they are supported by high rates of nitrogen fixation, and as such, they would not appear to be sustainable except locally, as they seem to occur.

Overall, we can conclude that persistent sulfidic conditions are possible in coastal upwelling zones, even with relatively modest rates of upwelling, but this situation is rare due to limited nitrogen fixation. As nitrogen fixation has been poorly studied in these regions, we can only speculate as to why rates are so far reduced. However, we may take some clues from the growth physiology of *Trichodesmium*, the most important N-fixer in the marine realm (Capone et al., 1998, 2005). In a survey of the available information on *Trichodesmium* growth, Hood et al. (2004) argue that the optimal growth environment for *Trichodesmium* is clear

water with high light intensity, low concentrations of dissolved inorganic nitrogen (DIN) and relatively weak vertical mixing. Low concentrations of DIN encourage low phytoplankton growth and clear water, whereas shallow mixing allows *Trichodesmium* to prosper in the high-light regions of the upper photic zone. Furthermore, elevated nitrate levels of even 10 μM have a direct physiological effect on *Trichodesmium* by significantly reducing nitrogenase activity, where nitrogenase is a key enzyme in N₂ fixation (Holl and Montoya, in press).

When viewed in this way, it becomes obvious that coastal upwelling zones are not ideal environments for *Trichodesmium*. For example, the high nutrient flux due to upwelling produces high phytoplankton biomass (Olson et al., 1993; Ryabchenko and Gorchakov, 1998; Kawamiya, 2001; Montecino et al., 2004), yielding turbid water with significant light attenuation with depth (Copin-Montégut and Raimbault, 1994; Montecino et al., 2004). Also, when upwelling is most intense close to shore, high phytoplankton biomass is also accompanied by high surface water DIN concentrations (still depleted relative to phosphate) as seen in the Eastern tropical South Pacific (Codispoti and Richards, 1976; Codispoti, 1983; Copin-Montégut and Raimbault, 1994) and the Arabian Sea (Morrison et al., 1998). In this case, some factor such as light or trace nutrient (such as Fe) availability may be limiting the complete utilization of nitrate. It is also possible that in these cases, the supply rate of nutrients outpaces the utilization rate by phytoplankton. In any event, despite large nitrate deficits in coastal upwelling zones, high productivity and excess nutrients produce turbid water, and taken together, these conditions are not conducive for *Trichodesmium* growth. This may be why N₂ fixation in these regions is limited. Other N-fixing cyanobacteria are also found in marine waters (Mahaffey et al., 2005), but their role in coastal upwelling zones is unknown.

3.3. Anammox

The nitrogen liberated during anaerobic organic matter mineralization usually accumulates as ammonium (Berner, 1980), and for this reason, one might expect ammonium to accumulate in the oxygen-free marine water column. It does not, however, at least to significant amounts (Richards, 1965; Codispoti, 1983). The present model, consistent with older discussions of coastal upwelling zone chemistry (e.g., Richards, 1965), has dealt with this observation by assuming that ammonium is somehow oxidized through denitrification (see Eq. 1), without worrying too much about how this actually occurs. Recent work, however, shows that the anammox process is active and responsible for significant ammonium oxidation in anoxic non-sulfidic environments including coastal upwelling zones (Dalsgaard et al., 2003; Kuypers et al., 2003, 2005; Thamdrup et al., in press). Indeed, in the Benguela upwelling zone (Kuypers et al., 2005) and in the upwelling waters off the northern coast of Chile (Thamdrup et al., in press), most of the N₂

production apparently goes through anammox, with a very limited role for canonical denitrification.

This challenges our classical view of nitrogen and carbon cycling in the oxygen-free marine water column. For example, if denitrification is unimportant, how is carbon oxidized in these oxygen-free waters as anammox is usually viewed as an autotrophic process? Denitrifying bacteria might possibly couple carbon oxidation with the reduction of nitrate to nitrite, and then anammox bacteria oxidize the ammonium liberated with nitrate to N_2 gas. If this was the case, approximately 2 moles of nitrite would accumulate for every mole of organic carbon oxidized, liberating about 0.15 moles of ammonium for oxidation by anammox, assuming Redfield stoichiometry for the decomposing organic matter. Thus, accounting for the nitrite used in anammox, 93% of the nitrate reduced in carbon oxidation would persist as nitrite. Nitrite does not accumulate to this amount in the anoxic water column of upwelling areas, but only to around 20–40% of the nitrate reduced (e.g., Codispoti and Packard, 1980). This means that the coupled carbon and nitrogen cycle described above provides insufficient N_2 production.

There may be other possibilities as to how the carbon and nitrogen cycles are coupled. Anammox cultures enriched from waste-water treatment reactors are able to heterotrophically oxidize propionate with nitrate (and nitrite) and to couple this to N_2 production by anammox (Güven et al., 2005). Thus, they apparently oxidize propionate to CO_2 while reducing nitrate (and nitrite) to ammonia. They then combine ammonium with nitrite producing N_2 as in the anammox process. If this also occurs in nature with a broad spectrum of organic substrates, then anammox bacteria can both oxidize organic carbon to CO_2 , and couple this to N_2 production by anammox. This would be completely consistent with the chemistry of nitrogen cycling in oxygen minimum zones as envisioned by Richards (1965), and as modeled here using Eq. (1). Future study will hopefully reveal the true relationship between denitrifiers and anammox bacteria in the anoxic water column of upwelling regions.

4. Conclusions

A simple 5-box model was developed to explore the mix of processes controlling the cycling of carbon, oxygen and nutrients in oxygen-depleted upwelling zones like those found in the Arabian Sea and the Eastern tropical North and South Pacific. The model incorporates the major processes operating in these upwelling zones including vertical and horizontal exchange, advection, upwelling, new production, oxic respiration, denitrification, nitrogen fixation and sulfate reduction. The following major conclusions are offered:

- Anoxic waters in coastal upwelling zones can be generated through a variety of physical processes including low upwelling rate, reduced vertical and horizontal exchange, and low oxygen concentrations in adjacent water bodies exchanging with the upwelling zone.

- In the absence of nitrogen fixation, the anoxic zones in coastal upwelling areas should always contain relatively high concentrations of nitrate and support N_2 production through denitrification and anammox. This is because nitrogen is a limiting nutrient. As nitrate concentrations fall in upwelling waters, rates of primary production are reduced which in turn reduces rates of carbon export to the oxygen minimum zone. This decreases rates of nitrate loss through N_2 production by denitrification and anammox. Thus, a natural feedback mechanism keeps nitrate from disappearing completely from the anoxic waters.
- With nitrogen fixation meeting the nitrogen demands of the primary producers, sulfidic conditions in the anoxic region of the upwelling zone can develop. The situation, however, is rare. It seems that the activities of N_2 -fixing organisms are restricted by the high nutrient concentrations that sometimes persist in the surface waters of upwelling zones and by the turbidity resulting from high rates of primary production.
- The anammox process is distinctly different from denitrification as N_2 production is directly coupled to the oxidation of ammonium with nitrite. Recent work suggests that denitrification is of limited significance and that anammox may be the most important pathway of N_2 production in anoxic upwelling areas. The details of how the anammox process works in nature are still obscure, but the model presented here may still apply even if anammox contributes to the bulk of N_2 production in anoxic upwelling areas.

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