Nitrogen isotope patterns in the oxygen-deficient waters of the Eastern Tropical North Pacific Ocean

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Received 2 August 2000; accepted 1 November 2000

Abstract

We analyzed the stable nitrogen isotope composition of an extensive set of samples of particulate matter (PM) and seawater nitrate collected during October/November 1997 along the Mexican coastline from 24° to 11.5°N. At the northern and southern end of our study area, the $\delta^{15}$N of PM ranged between 5 and 7\%\textsubscript{o} in the upper 200 m of the water column with higher values at intermediate depths. These data are very similar to those reported from other parts of the open ocean. In the oxygen minimum zone (OMZ), we found significantly higher $\delta^{15}$N values for suspended particles. Furthermore, the $\delta^{15}$N of nitrate (NO$_3$) was elevated within the OMZ and we found a strong relationship between the oxygen concentration, nitrate deficit and the $^{15}$N content of the nitrate. The core of the OMZ between 22°N, 105°W and 15°N, 110°W coincided with higher nitrate deficits and $\delta^{15}$N values relative to the stations near the boundaries. The $\delta^{15}$N of nitrate was highest, with values up to 18.7\%\textsubscript{o}, where oxygen concentrations were below 1–2 μmol/l. This pattern is consistent with an overall nitrogen isotopic enrichment factor of 22.5\%\textsubscript{o} for denitrification in the core of the OMZ using the Rayleigh equation (closed-system approach). Results from a diffusion model (open-system approach), however, gave a fractionation factor of 30 $\pm$ 7.5\%\textsubscript{o}, implying that the Rayleigh formula only gives a lower estimate of the fractionation factor $\varepsilon$. The vertical flux of particles collected in short-term deployments (ca. 35 h) of a drifting sediment trap was not significantly correlated with the water column nitrate deficit. The isotopic signature of the nitrate within the gradient is very similar to the $\delta^{15}$N value of sedimenting particles, suggesting that there might be a strong link between the production and sedimentation of particles. Upward flux of nitrate across the thermocline can account for less than half of the particle flux leaving the mixed layer. Mixing and transport of nitrate across the lower boundary of the OMZ can lead to significant enrichment in the $^{15}$N content of deep waters, and our isotopic data imply that at least 14\% of the nitrate in the waters below the OMZ originates from this source. © 2001 Elsevier Science Ltd. All rights reserved.
1. Introduction

The Eastern Tropical North Pacific (ETNP) is one of the three major regions of the world ocean where organic matter is decomposed by bacterial respiration based on oxidized nitrogen rather than on oxygen (Deuser et al., 1978; Somasundar and Naqvi, 1988). Total denitrification has not yet been estimated precisely for this region, because the residence time of the water is unknown and the vertical input of particulate organic matter (POM) is poorly constrained in relation to the oxygen deficit (Cline and Richards, 1972; Codispoti and Richards, 1976). A number of studies therefore have attempted to model lateral advection and vertical diffusion to estimate the extent of denitrification in this region (Brandes et al., 1998; Codispoti and Christensen, 1985; Cline and Kaplan, 1975; Cline and Richards, 1972). They demonstrated that the inflow of Antarctic intermediate water entering the oxygen minimum zone (OMZ) from the south is a considerable source of nitrate and even carries an elevated nitrogen isotopic signature. Wyrtki (1962), however, emphasized the importance of vertical processes.

The fractionation of nitrogen isotopes associated with denitrification leads to significant increases in the $\delta^{15}N$ of the residual nitrate (Liu and Kaplan, 1989; Saino and Hattori, 1987; Wada and Hattori, 1976; Cline and Kaplan, 1975), generating a useful isotopic indicator of denitrification. In contrast, the nitrogen isotopic composition of POM provides only an indirect measure of the effects of denitrification in the OMZ, since the isotopic signature of denitrification can propagate to POM only by vertical transport of the isotopically heavy nitrate into the surface layer and subsequent assimilation by phytoplankton (Saino and Hattori, 1987). Very low nitrogen isotope ratios in surface POM are an indicator of the activity of N fixing cyanobacteria (Carpenter et al., 1997), a process that may also influence nitrogen isotope systematics in the ETNP. Brandes et al. (1998) suggested that up to 20% of the new nitrogen might originate from N$_2$ fixation in the area.

Our goal in this study is to understand the relationship between POM export from the mixed layer, the extent and structure of the OMZ, the nitrate deficit in the water column, and the distribution of stable nitrogen isotopes in the dissolved and particulate fractions of combined nitrogen in the eastern tropical North Pacific. We have, therefore, investigated an extensive data set of chemical variables, suspended and sedimented particles, and dissolved nitrate for nitrogen stable isotope composition in an area 24° to 10° N and 105° to 110° W. We consider regional differences in these variables in relation to important N transformations such as the degradation of particulate matter, uptake of dissolved nitrogen, and denitrification.

2. Material and methods

In all, 24 stations on several transects along and perpendicular to the coast of Mexico were sampled for this study (Fig. 1). At eight stations (P-stations), an extended set of experimental rate
measurements was carried out in addition to the routine hydrographic and isotopic measurements performed elsewhere (Fig. 1, Montoya et al., in prep.). Samples from the water column were obtained with a Seabird CTD-rosette system equipped with temperature, pressure, conductivity and oxygen sensors and 24 10-l Niskin bottles. Additionally, high precision measurements of O\textsubscript{2} concentrations below 25 \(\mu\)mol O\textsubscript{2} l\textsuperscript{-1} were carried out by the colorimetric method of Broenkow and Cline (1969) on samples drawn from the water bottles with gas tight syringes immediately after retrieval of the rosette. The concentrations of nitrate, nitrite, and phosphate were measured with a Technicon Auto Analyzer. POM was collected by gentle vacuum filtration through precombusted (500°C for 2 h) Whatman GF/F filters and dried at 60°C for 24 h. The filtrate was collected from samples containing more than 10 \(\mu\)mol nitrate l\textsuperscript{-1} per liter and stored in acid cleaned, well rinsed, and dried plastic bottles. For preservation of samples, 0.7 ml concentrated HCl was added to each 500 ml sample volume, resulting in a pH no lower than 1–2.
A funnel-shaped sediment trap (Salzgitter Electronics) with a mouth area of 0.5 m² was deployed as a drifting trap at a depth of 130 m for 33–38 h at each of the 8 P-stations. The trap was equipped with a single sample bottle filled with a brine solution with a salinity roughly 5 psu above that of the surrounding water. Since no preservatives were added, the ammonia concentrations in the recovered trap samples were measured as a check on the extent of bacterial degradation of the trap contents; in all cases, the concentration of NH₄⁺ was below 300 nmol l⁻¹. Swimmers were picked immediately after recovery of the trap, and the sample was split into 4–8 subsamples. These were also filtered onto precombusted GF/F filters, two of which were dried at 60°C for 24 h, and the remainder were frozen.

In the laboratory filters were slightly moistened with distilled water before acidification by fuming HCl in a desiccator for 24 h. The filters were then dried, packed into tin cups, and formed into small pellets. The isotope determination was carried out by continuous-flow isotope ratio mass spectrometry (CF-IRMS) with a Fisons Elemental Analyzer 1108 connected to a mass spectrometer (Finnigan Delta S) via an open split interface (Finnigan Conflow II). As reference gases, pure nitrogens calibrated against air and IAEA N1, N2, N3 and carbon dioxide calibrated against NBS 22, USGS 24 were used. Data are reported in the usual delta notation as \[ \delta^{15}N = \left( \frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right) \times 1000, \ R = ^{15}N/^{14}N. \] As an internal standard, Peptone (Merck) was measured after every 5 samples. The Peptone isotope values have a standard error of < 0.2‰ for \( \delta^{15}N \).

Nitrate was isolated for isotopic measurement by the diffusion method of Sigman et al. (1997). Two hundred milliliters of sample containing roughly 3–8 μmol NO₃ were used. Samples were preincubated at 65°C for 5 days in the presence of MgO to raise the pH above 9.7 to remove traces of ammonia. The volume was then reduced to 40–50 ml by boiling and the sample sealed after addition of Devarda’s alloy and a “diffusion packet” consisting of an acidified filter (precombusted GF/D 10 mm diameter) sandwiched between 2 Teflon membranes with 10 μm pore size. Samples were then incubated for 5 days at 65°C and 5 additional days on a shaker table at 60°C. After a total incubation time of 15–18 days, the diffusion packets were removed and dried in a desiccator for 2 days, after which each GF/D was packed into a tin capsule and pelletized for CF-IRMS as described above. Two blanks (distilled water and reagents) and 2 standards (200 ml of 50 μmolar NO₃ solution) were prepared and run through the entire extraction and analytical process with each set of 8 samples. The overall recovery was between 85 and 120% for standards and samples, and the \( \delta^{15}N \) values for the standards have an error of 0.47‰ (n = 16). The blanks always contained less than 0.5 μmol N.

Hydrographic sections (Fig. 2) were splined by a kriging method (with Surfer v.6.0). Values were interpolated onto a grid with a vertical resolution of 100 m and a horizontal resolution equal to the mean station spacing on a given transect.

3. Results

The stations sampled are shown in Fig. 1. Figs. 2A–C show sections of oxygen concentration (μmol l⁻¹) along 3 legs of the cruise track: stations 2 to 9/17 (transect 1), stations 11P/15 to 24 (transect 2), and stations 11P/15 to 20P (transect 3). Our major along-shore transect (stations 2–9) extended roughly parallel to the Mexican coast from 25°N to 17°N and showed a clear decrease in
the concentration of O$_2$ from north to south, though midwater concentrations were below 10 μmol l$^{-1}$ between 200 and 1000 m depth along the whole transect (Fig. 2A). Transect 2 extended further south from 18.4°N to 10°N along 105°W, starting within the center of the OMZ and showing slightly increased O$_2$ concentrations at stations 25 and 24 (Fig. 2B). The third transect, which runs directly offshore, has a pronounced O$_2$ minimum at mid-depth (200–900 m) and elevated concentrations at the westernmost station (Fig. 2C). The center of the OMZ during this cruise can be located between 13°N and 18°N and between 105°W and 108°W. The profiles from stations 9, 17, and 20 consist of up to 3 combined casts and include measurements of the concentrations of nitrate, oxygen, and PON as well as the stable nitrogen isotope composition of PON and nitrate.

The apparent oxygen utilization (AOU) was calculated for all stations between the base of the mixed layer and the bottom of the OMZ as defined by 10 μmol l$^{-1}$. This was performed by calculating the difference between measured oxygen concentration and the oxygen concentration at 100% saturation using temperature and salinity data from the CTD. The AOU varied between 192 and 340 μmol O$_2$ l$^{-1}$.

We calculated a nitrate deficit (in μmol l$^{-1}$) for all stations, using the approach of Cline and Richards (1972). Expected nitrate concentrations were calculated using a Redfield ratio of 14.8 for the “preformed nitrate”, which holds for our data between 900 and 2000 m depth:

$$\text{NO}_3(\text{deficit}) = 14.8 \times \text{PO}_4(\text{measured}) - \text{NO}_3(\text{measured})$$

The total nitrate deficit for each station was then calculated by integration between sampling depths and given in mol m$^{-2}$. Our results clearly show higher nitrate consumption along the
Fig. 3. (A) Regional pattern of the water column nitrate deficit. Calculations are described in the text. The radius of each circle shown is proportional to the integrated nitrate deficit (mol m$^{-2}$) at that station; (B) regional pattern of the apparent oxygen utilization (AOU), again, the radius of each circle is proportional to the value.

Mexican coast and on the westward transect (Figs. 3 and 4). Station 26, the P-station furthest south, shows no clear deficit at depths of 100–300 m, but a higher deficit below 300 m, although the oxygen concentrations at this station do not differ from those at the other P- stations (Figs. 4 A and C).

The oxygen profiles show rapidly decreasing concentrations below the mixed layer (upper 100 m) with rather small differences among stations. At the center of the OMZ, O$_2$ concentrations reached the limit of detection below 100 m depth (see also Fig. 4A). Particulate organic nitrogen (PON) concentrations were also near the limit of detection, ranging between 0.05 and 0.15 μmol N1$^{-1}$ in the deep water and 0.1–0.7 μmol N1$^{-1}$ in surface waters. POC concentrations were uniformly below 1 μmol l$^{-1}$ except for a number of surface samples with values above 2 μmol l$^{-1}$.

Interestingly, the δ$^{15}$N of PON in the mixed layer is low relative to that of PON deeper in the water column, and many stations show considerable increases of 5 to 6%$_{oo}$ with depth (Fig. 5). At the northernmost process station (3P, 23.67°N), the δ$^{15}$N of PON showed little variation with depth, ranging between 5 and 7%$_{oo}$ through the upper 2000 m of the water column (Fig. 5). In contrast, we found consistently higher isotope values at depth further south and within the OMZ. The mean δ$^{15}$N of PON in the mixed layer varied between 4.4 and 8.2%$_{oo}$, while mean values in the OMZ
Fig. 4. (A) Vertical profiles (surface to 1000 m) of oxygen concentration at all P-stations except the northernmost, station 03; (B) vertical profiles of $\delta^{15}$N–NO$_3$ of all P-stations; (C) vertical profiles of nitrate deficit for all P-stations. Station 26 has a markedly lower deficit than the other stations sampled.

Fig. 5. Vertical profiles of $^{15}$N–PON at all P-stations sampled. Note that the scale for station 09 is different.
Fig. 6. Correlation of $\delta^{15}$N–NO$_3$ with the nitrate deficit (µmol l$^{-1}$) in the OMZ. $Y = 0.74X + 5.33$, $r^2 = 0.83$, $n = 50$. For calculation of the deficit see the text.

ranged between 4.0 and 11.6‰. For all stations investigated, the $\delta^{15}$N of PON increased by an average of 2–4‰ between the mixed layer and the underlying water mass.

All our nitrate concentration profiles through the OMZ clearly show the effects of nitrate respiration at oxygen concentrations below 2 µmol l$^{-1}$, a concentration typically reached at depths between 130 and 180 m (Fig. 4). However, our sampling resolution was not fine enough to define the relationship between the concentrations of nitrate and oxygen. Where nitrate $\delta^{15}$N values are available, we found an inverse relationship between nitrate concentration and $\delta^{15}$N. The highest $\delta^{15}$N–NO$_3$ values are found within the nitrate concentration minimum except at station 26. Our estimates of nitrate deficit ranged as high as 10–16 µmol l$^{-1}$ between 200 and 400 m depth. The $\delta^{15}$N–NO$_3$ showed a significant correlation with the NO$_3$ concentration deficit in the OMZ ($r^2 = 0.83$, $n = 50$, Fig. 6).

Sedimentation rates and $\delta^{15}$N–PON were measured at all 8 P-stations (Fig. 7). We found considerable variation between stations, with high fluxes and $\delta^{15}$N values along the northern transect (57–132 µmol N m$^{-2}$ d$^{-1}$ with $\delta^{15}$N values of 10–11‰) and lower rates and $\delta^{15}$N values further offshore (11 µmol N m$^{-2}$ d$^{-1}$ and 8.5‰ at station 20). Stations 26 and 27 on our third transect showed intermediate sedimentation rates and $\delta^{15}$N values (48 and 36 µmol N m$^{-2}$ d$^{-1}$ and $\delta^{15}$N values of 9.4–9.6‰).
Fig. 7. Regional pattern of the $\delta^{15}$N of sinking particles and the sedimentation rates collected at 130 m depth in a drifting sediment trap at the P-stations. The radius of each circle is proportional to the measured value. The respective values are given below each circle.

4. Discussion

4.1. Isotopic fractionation during denitrification

Microbial denitrification discriminates strongly against $^{15}$N, creating a residual pool of nitrate with elevated $^{15}$N content and a product pool of dissolved N$_2$ with low $\delta^{15}$N values (Brandes et al., 1998; Mariotti et al., 1982, 1981; Cline and Kaplan, 1975). Brandes et al. (1998) have demonstrated the importance of this process in regulating the isotopic composition of NO$_3^-$ in the mid-water oxygen minimum layers of the ETNP and the Arabian Sea, and have shown that advective and diffusive processes have different effects on the expression of isotopic fractionation within each such oxygen minimum zone (OMZ). In calculating isotopic fractionation factors, we tested the effects of both processes. We defined the OMZ as the mid-depth water mass with oxygen concentrations below 10 μmol l$^{-1}$. Denitrification is thought to be inhibited by oxygen concentrations above 2 μmol l$^{-1}$ (Lipschultz et al., 1990; Cline and Richards, 1972), and Barford et al. (1999) reported a constant fractionation of nitrate at oxygen concentrations between 0 and 1.2 μmol l$^{-1}$. Samples with oxygen concentrations between 2 and 10 μmol l$^{-1}$ were also included in our isotopic
Fig. 8. Linear regression of $\delta^{15}$N–NO$_3$ on ln $f$, where $f$ is the fraction of the original pool of nitrate still present (i.e. the nitrate concentration measured divided by the nitrate concentration expected). The regression is $y = -22.5x + 6.11$, with $r = -0.897$. The slope of the regression is equal to the isotopic enrichment factor $\varepsilon$ (here $-22.5\%_{oo}$) for denitrification in the OMZ. The symbols represent different potential density ($\sigma_o$) intervals (surface $p = 0$ is reference level). $\sigma_o < 26.3$ represents the depth interval 130 and 173 m, $\sigma_o$ 26.3–26.8 the 197–401 m depth interval, $\sigma_o$ 27.0–27.3 the 595–797 m depth interval, and $\sigma_o > 27.3$ the 894–992 m depth interval.

calculations. In our first approach, we considered the thermodynamically closed Rayleigh System in which water masses are advected into the OMZ with no mixing along or across isopycnals. We calculated an overall isotopic enrichment factor ($\varepsilon$) for denitrification in the OMZ of this region of $\varepsilon = 22.5\%_{oo}$ (Fig. 8) using a Rayleigh fractionation equation (Brandes et al., 1998; Mariotti et al., 1981) based on 50 discrete samples from 7 stations.

$$\delta^{15}N\text{--NO}_3 = -22.5 \ln (\text{NO}_3\text{measured}/\text{NO}_3\text{preformed}) + 6.2.$$  

Our estimate of $\varepsilon$ is slightly lower than the value found for this region by Brandes et al. (1998) and in between values from studies of lab cultures (Barford et al., 1999; Delwiche and Steyn, 1970; Mariotti et al., 1981). If all values above 200 m depth (potential density $\sigma_o < 26.3$), where remineralization and ventilation are most pronounced, are excluded, then the fractionation factor is slightly raised to $-23.3\%_{oo}$.

The second approach tests the effect of diffusive transport on the generation of the isotope signal. We applied a modified version of the diffusion model of Brandes et al. (1998) to simulate the isotopic composition of expected nitrate versus the ratio of measured to initial nitrate concentrations. The modification of the model is the treatment of the denitrification term. In Brandes (1998) the product of denitrification rate times the concentration is constant, which can result in negative $\delta^{15}$N values with a certain parameter set. To avoid negative values during computation, in this model the spatial reduction of nitrogen is considered in the denitrification term. This is permissible, because the system is considered to be a steady-state system. The model consists of two coupled non-linear diffusion reaction equations for $^{14}$NO$_3$...
and $^{15}\text{NO}_3$.

$$\frac{\partial [^{14}\text{NO}_3]}{\partial t} = -J[^{14}\text{NO}_3] + A\frac{\partial^2 [^{14}\text{NO}_3]}{\partial x^2},$$

$$\frac{\partial [^{15}\text{NO}_3]}{\partial t} = -\varepsilon QJ[^{14}\text{NO}_3] + A\frac{\partial^2 [^{15}\text{NO}_3]}{\partial x^2},$$

where $J$ is the denitrification rate, $A$ the coefficient of eddy diffusivity, $\varepsilon$ the fractionation factor (the enrichment factor $\varepsilon = (1 - \frac{x}{x_c}) \times 1000$), and $Q$ the $^{15}\text{NO}_3/^{14}\text{NO}_3$ ratio which makes the system non-linear. $\partial / \partial t$ and $\partial^2 / \partial x^2$ are partial derivatives in time and space. $X$ covers the OMZ horizontally which reaches from the edge $x = 0$ to the interior $x = x_c$. The boundary condition is the Dirichlet condition at $x = 0$ so that the $\text{NO}_3$ concentration is $28 \mu\text{M}$ with a $\delta^{15}\text{N}$ of 6$\%_{oo}$. At $x = x_c$, the von Neumann condition is applied: $\partial / \partial x^{14}\text{NO}_3 = \partial / \partial x^{15}\text{NO}_3 = 0$. The initial conditions in the model interior are a $\text{NO}_3$ concentration of $35 \mu\text{M}$ with a $\delta^{15}\text{N}$ of 4.5$\%_{oo}$. The steady-state system (J.A. Brandes, pers. comm.) is solved using a tridiagonal matrix solver (Roache, 1976). The model has four free parameters: the denitrification rate $J$, the eddy diffusivity $A$, the extension of the OMZ $x_c$, and the fractionation factor. A sensitivity test shows that the model is extremely sensitive to the variation of all parameters so that only a small band of meaningful parameters exists to receive a solution that fits the data. Here the following parameters are used: denitrification rate of $4 \times 10^{-9} \text{s}^{-1}$, eddy diffusivity of $1800 \text{m}^2 \text{s}^{-1}$, and the estimated spatial extension of the OMZ of 800 km. The parameters are taken from Brandes et al. (1998). The coefficient of eddy diffusivity parameterises in a steady-state model qualitatively the mixing in the intermediate depth water. The enrichment factor, $\varepsilon$, as the only free parameter was set to 22.5, 30, and 37.5, respectively. Fig. 9 shows the isotopic composition of nitrate versus $f$, the ratio of measured to expected nitrate.

Fig. 9. Results of the diffusion model in a plot of $\delta^{15}\text{N}$--$\text{NO}_3$ on $f$, where $f$ is the fraction of the original pool of nitrate still present. Three curves, for 3 different isotope enrichment factors are calculated. The dots indicate measured data in different density levels.
concentration for three computations with varying $\varepsilon$ and the measured values in different density levels. A fractionation factor of 30 seems to give the best fit for all data and corresponds to the values of Brandes et al. (1998). The range of $\varepsilon$ of 15% (instead of 10%) set by the model includes all measured values with $f < 0.9$ although the presented data set has more data than the one by Brandes et al. from the ETNP. Presumably an enrichment factor of 30 ± 7.5% comprises the total natural variability. The fractionation factor of 22.5% given by the Rayleigh equation seems to be the lowest meaningful $\varepsilon$-value. It is assumed that the Rayleigh equation underestimates the natural fractionation of a system. Many data points for $f > 0.9$ show a scatter around the curves (Fig. 9) which might show the influence of additional processes aside from denitrification. Upward diffusion and uptake by phytoplankton in the upper water column are processes that might account for some of the fractionation there. These processes are not included in the model.

Another process possibly contributing to the high $\delta^{15}N$-NO$_3$ values in the OMZ could be the degradation and oxidation of sedimenting and suspended particles with high $\delta^{15}N$ values. However, this process would not generate the vertical differences in $\delta^{15}N$ we found, but, would rather tend to produce isotopic homogeneity throughout the water column. In considering differences between stations, many authors discuss the role of lateral inputs of water masses already low in oxygen and containing isotopically enriched nitrate (Liu and Kaplan, 1989; Codispoti and Richards, 1976; Cline and Kaplan, 1975). Such lateral inputs to the ETNP should produce a meridional gradient in $\delta^{15}N$-NO$_3$ values and fractionation factors, which is partly the case. Our data show the highest $\delta^{15}N$-NO$_3$ values in the center of the OMZ, and fractionation factors for individual stations vary haphazardly between 19 and 29% through our study area (Table 1). In our interpretation, lateral transport and — as will be discussed in the next paragraph — to some extent also vertically oriented processes such as sedimentation are both important in nitrogen cycle dynamics within the OMZ of the ETNP.

4.2. The role of sedimentation

The deficit in nitrate concentration integrated over the water column and the $\delta^{15}N$ of nitrate both varied significantly between stations. Our data show that the nitrate deficit varied somewhat independently of the low O$_2$ concentrations that characterized the OMZ. A plot of AOU as a function of the nitrate deficit shows considerable scatter with no trend (graph not shown). The oxygen minimum is most intense between 22°N and 15°N, with higher O$_2$ values along the offshore transect from Mexico southwest to 110°W. Thus, it appears that oxygen-based respiration of organic matter is effectively saturated in the whole investigation area; that is, enough organic material is exported from the mixed layer to consume the available oxygen through respiration. However, the “next step”, nitrate respiration, is limited by some factors and does not go to completion in our study area. This limitation might be the availability of electron donors, e.g. organic carbon, which has been found to limit denitrification in at least some pelagic systems (Brettar and Rheinheimer, 1992). The potential role of organic matter availability acting to limit denitrification is supported by the low sedimentation rates we measured during this cruise. They are low compared to rates estimated for the OMZ in the tropical South Pacific (Lipschultz et al., 1990), where fluxes of 4–23 mmol C m$^{-2}$ d$^{-1}$ were calculated from primary production using the relationship of Martin et al. (1987). Using a C/N ratio of 6.5 these ETSP carbon fluxes correspond to
nitrogen fluxes of 600–1700 μmol N m⁻² d⁻¹, a range much higher than our fluxes of 13–138 μmol N m⁻² d⁻¹. This may be one reason why our sedimentation rates show no significant correlation with the integrated water column nitrate deficit.

Sedimentation rates measured twice at one station, 9/17 (Fig. 7), were different by a factor of two, although the nitrate deficit and the AOU at this station did not show the same large variation between the two sampling dates. This might come from the general difficulty of relating short-term measurements of vertical flux to the large-scale distribution of NO₃ in the OMZ. A mismatch in time scales in the measurements is the obvious problem here, because the generation/sustainability of the OMZ on the one hand and the sedimentation rates of 1–2 days on the other hand are not really connected. The long-term export production together with a residence time of the water mass of decades is responsible for the generation of the OMZ, which was described for the Arabian Sea (Olson et al., 1993). Higher water column stability during the ongoing El Niño event (see below) might also cause lower than normal sedimentation rates.

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<th>Station</th>
<th>NO₃ deficit integrated (mol m⁻²)</th>
<th>AOU integrated (mmol m⁻²)</th>
<th>Mean δ¹⁵N-NO₃ factor, ε in OMZ</th>
<th>Fractionation factor, (ε)</th>
<th>Sedimentation N (μmol N m⁻² d⁻¹)</th>
<th>Sedimentation C (μmol C m⁻² d⁻¹)</th>
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4.4. Isotope budget considerations

During the time of investigation, an El Niño event took place with significant effects on the currents and water column stability in the area (Oberhuber et al., 1998). Surface water temperatures were elevated above normal by roughly 1°C in the area of investigation. This enhancement in upper water column stability must be considered in establishing an isotope budget for the area. Considering that lateral inputs and nitrogen fixation were negligible in our study area, then an eddy diffusion coefficient of $10^{-5}$ m$^2$ s$^{-1}$ (Ledwell et al., 1993) would result in a vertical nitrate transport of $10^{-5}$ mmol m$^{-2}$ s$^{-1}$, a flux which is much higher than the rate of sedimentation of nitrogen out of the surface layer; PON sedimentation accounts for only 1.5–41.5% of the daily injection of nitrate into the surface layer. This range is in general agreement with observations from other areas like the Indian Ocean (around 0.5 μmol C m$^{-2}$ d$^{-1}$, Pollehne et al., 1993). However, this should be weakened by the El Niño event when higher water column stability causes lower nitrate diffusion rates upwards. Nitrate $\delta^{15}$N values from 90 to 100 m depth are slightly higher than surface (0–60 m) $\delta^{15}$N–PON values (Fig. 10), a pattern that could arise through fractionation during the uptake of inorganic nutrients. On the other hand, the total consumption of nitrate is suggested by the extremely low residual concentration in the surface layer, which should lead to similar isotope values in the source pool (nitrate) and the product formed (PON).

Sedimenting particles intercepted in the trap deployed at 130 m depth are enriched in $^{15}$N relative to particles in the surface waters as well as the nitrate pool at 130 m. The range covered by the values is similar to data of Pride et al. (1999) from the Guyamas Basin (485 m water depth). This pattern may reflect trophic processing of nitrogen by zooplankton, whose fecal pellets are typically enriched in $^{15}$N by ca. 1‰ relative to the animals’ food (Altabet and Small, 1990; Montoya et al., 1990). In this case, the roughly 3–4‰ increase in $\delta^{15}$N between average mixed layer suspended PON and sinking particles collected at 130 m depth suggests that higher trophic levels play a critical role in generating the vertical flux of organic matter. For example, an animal feeding on herbivorous suspension feeders enriched by 3–4‰ relative to PON will produce fecal pellets that are enriched by roughly 4–5‰ relative to the suspended particles. This mechanism may play an important role in preferentially exporting $^{15}$N from the upper water column of the open ocean (Checkley and Miller, 1989) as well as from relatively productive systems like the ETNP.

Ammonia is a possible nutrient to fuel production at the base of the mixed layer, but it was analyzed only at some stations at the southern and western study area. We found concentration between 100 and 150 nmol l$^{-1}$ in the upper 100 m. Presumably these nutrients were rapidly turned over with little or no fractionation. However, since excreted ammonium is roughly 3‰ lighter than the body tissue of the animal (Checkley and Miller, 1989) it generally contributes to decreasing isotope values in the mixed layer and cannot explain the isotopic enrichment found in the suspended and sedimenting particles.

An explanation for the high $\delta^{15}$N values of sedimenting PON might be the production of phytoplankton that use nitrate from the gradient right below the mixed layer (see Fig. 4) with a $\delta^{15}$N value around 10‰. The nutrients are completely consumed by the phytoplankton, which then reflect the isotopic signature of the nitrate (Waser et al., 1998). If this organic material sinks out of the mixed layer, it carries the $\delta^{15}$N signal of the nitrate and may then be disintegrated and add to the suspended particle pool. Interestingly, the material collected in our trap has an isotopic
composition similar to that of bulk suspended particles in the OMZ. The vertical flux from the upper water column clearly makes an important contribution to the particle field at depth, and our isotopic data suggest that relatively little processing of the particles occurs during transit through the OMZ.

Finally, nitrate from below the OMZ has a mean $\delta^{15}N$ of $6.5 \pm 1.2\%$ (mean $\pm$ SD), a value significantly higher than the $4.5\%$ typical of deep water (Cline and Kaplan, 1975; Sigman et al., 1997) and in the range of values found by Liu (1989). Although the $\delta^{15}N$ of nitrate within the OMZ varies widely, we can use the maximal $\delta^{15}N$ of NO$_3^{-}$ within the OMZ (18.7$\%$) to calculate a lower limit for the contribution of nitrate from the OMZ to the nitrate pool in the underlying waters. The 2$\%$ elevation we observed in the $\delta^{15}N$ of deepwater values over the oceanic average of 4.5$\%$ (Sigman et al., 1997) would require at least a 14% contribution of high $\delta^{15}N$ nitrate from within the OMZ; since the $\delta^{15}N$ of the nitrate most likely to be injected into the deep water is much lower than this, the actual contribution of OMZ nitrate will be correspondingly higher. Liu (1989) have
suggested that isopycnal transport of high $\delta^{15}$N nitrate originating in the ETNP has a measurable effect on the isotopic composition of waters in the Southern California Bight, and perhaps elsewhere in the Pacific Ocean. Our observations imply a rather high rate of vertical mixing across the lower boundary of the OMZ, hence cross isopycnal mixing may also play an important role in transporting NO$_3$ from the OMZ to other regions of the Pacific. Additionally continuing denitrification at oxygen levels of up to 7 $\mu$M, which was shown to occur by Deuser et al. (1978), might raise the isotopic signature of nitrate at the lower end of the OMZ.

Acknowledgements

The crew of R.V. New Horizon was very helpful during the cruise. We would also like to thank Bianka Kurts and Heike Siegmund for isotopic analyses carried out in the laboratory and J. Brandes for model support. The work was funded by an NSF grant (Montoya and Lipschultz) and by DFG grant No. VO487/3-1.

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