The nitrogen isotope biogeochemistry of sinking particles from the margin of the Eastern North Pacific

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Abstract

The nitrogen isotopic composition of time-series sediment trap samples, dissolved NO_3^-, and surficial sediments was determined in three regions along the margin of the eastern North Pacific: Monterey Bay, San Pedro Basin, and the Gulf of California (Carmen and Guaymas Basins). Complex physical regimes are present in all three areas, and each is influenced seasonally by coastal upwelling. Nevertheless, sediment trap material evidently records the isotopic composition of new nitrogen sources, since average $\delta^{15}N$ is generally indistinguishable from $\delta^{15}N$ values for subsurface NO_3^-. Surficial sediments are also very similar to the average $\delta^{15}N$ value of the sediment traps, being within 1‰. This difference in $\delta^{15}N$ between trap material and sediment is much less than the previously observed 4‰ difference for the deep sea. Better organic matter preservation at our margin sites is a likely explanation, which may be due to either low bottom O_2 concentrations or higher organic matter input to the sediments. All sites have $\delta^{15}N$ for sub-euphotic zone NO_3^- (8–10‰) substantially elevated from the oceanic average (4.5–5‰). This isotopic enrichment is a result of denitrification in suboxic subsurface waters (Gulf of California) or northward transport of denitrification influenced water (Monterey Bay and San Pedro Basin). Our results therefore suggest that downcore $\delta^{15}N$ data, depending on site location, would record the intensity of denitrification and the transport of its isotopic signature along the California margin. Temporal variations in $\delta^{15}N$ for the sediment traps do appear to respond to upwelling or convective injections of NO_3^- to surface waters as

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a result of isotopic fractionation during phytoplankton uptake. Overall, though, the coupling between NO_3^- injection, $\delta^{15}N$, and flux is looser than previously observed for the open-ocean, most likely the result of the smaller time/space scales of the events. In the Gulf of California, wintertime convective mixing/upwelling does produce distinct $\delta^{15}N$ minima co-occurring with particle flux maxima. Interannual variations are apparent in this region when these wintertime $\delta^{15}N$ minima fail to occur during El Niño conditions. There appears to be a positive relationship between the Southern Oscillation Index (SOI) anomaly and annual average $\delta^{15}N$. One explanation calls for hydrographic changes altering the $\delta^{15}N$ of subeuphotic zone NO_3^-.

1. Introduction

Nitrogen isotopic ratio ($\delta^{15}N$ measured as ‰ variation in $^{15}N/^{14}N$ relative to atm. N_2) has been used as a unique natural recorder of marine nitrogen cycling and marine biogeochemistry. An important finding has been that since phytoplankton produce nitrogen isotopic fractionation during the uptake of NO_3^- (e.g. Miyake and Wada, 1971; Wada and Hattori, 1978; Montoya and McCarthy, 1995; Altabet, 1996; Sigman et al., 1997; Waser et al., 1998), the $\delta^{15}N$ of particulate nitrogen (PN) varies with the degree of surface nutrient utilization (Altabet and Francois, 1994a, b). In open-ocean settings, this phenomenon is generally manifest as both spatial and temporal decreases in $\delta^{15}N$ of both near-surface suspended and sinking PN with increases in NO_3^- concentrations (e.g. Altabet and McCarthy, 1985; Altabet and Deuser; 1985; Goering et al., 1990; Altabet et al., 1991; Nakatsuka et al., 1992; Voss et al., 1996). When there is complete utilization, however, average $\delta^{15}N$ values are determined by the $\delta^{15}N$ of subsurface NO_3^-, which varies in the ocean chiefly in response to water-column denitrification (Altabet et al., 1995; Cline and Kaplan, 1975; Liu and Kaplan, 1989).

Studies of the contemporary ocean have been used to examine the linkages in the cycle of new nitrogen input to the euphotic zone, its utilization by phytoplankton, and transport to the deep sea as rapidly sinking particles. This work has also been the basis for development of sedimentary $\delta^{15}N$ as a paleo-recorder for marine biogeochemistry, with work to date showing glacial changes in both water column denitrification regions and the Southern Ocean that would lead to reduced atmospheric pCO_2 (Altabet et al., 1995; Ganeshram et al., 1995; Francois et al., 1997).

There has been little recent work, though, regarding the nitrogen isotope biogeochemistry of ocean margin systems. While making up only about 10% of the ocean's, area, they are generally much more productive than the open-ocean perhaps equaling its total production (Walsh, 1991). In the case of the California Current system, enhanced productivity is the result of seasonal upwelling, which is dependent on coastal topography and local wind fields. Upwelling and its biogeochemical response therefore take place in physically complex systems with time/space scales of variability smaller than found in much of the open ocean (Hayward and Mantyla, 1990). Time-series $\delta^{15}N$ signals may therefore be substantially modified in this system as compared to the open ocean. How the sediments record surface ocean ^{15}N signatures may also vary between open ocean and margin systems due to contrasts in depositional
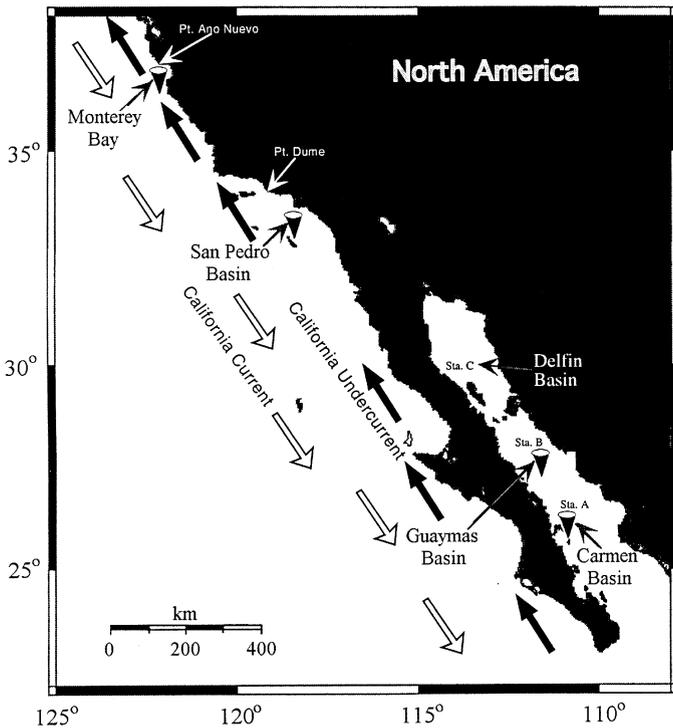
Fig. 1. Map of the sediment trap sites and Gulf of California hydrostations. Key geographic features and the approximate location and direction of the California Current and California Undercurrent are also shown.

environment. Sedimentary organic matter preservation will be enhanced by higher productivity, reduced water depth, high sediment accumulation rate, and suboxic water overlying margin sediments (Emerson and Hedges, 1988). While these factors would tend to enhance the fidelity of the isotopic record, downslope transport, scouring by bottom currents, and inputs from terrestrial sources may obscure them.

We have examined three regions along the margin of the eastern North Pacific between 26° and 36°N (Fig. 1). Monterey Bay and San Pedro Basin are in the California Current system proper. The central Gulf of California is an extension of the Eastern Tropical N. Pacific (ETNP), which marks the southern boundary of the California Current. The ETNP has special significance for the California margin, since it appears to supply ^{15}N enriched NO_3^- to subsurface waters through the California Undercurrent (Liu and Kaplan, 1989). At all sites, we compare time-series data for δ^{15}N in sediment trap material with corresponding time-series for material fluxes. Additionally, average δ^{15}N values for the sediment traps are compared with δ^{15}N values for subsurface NO_3^- and surficial sediments. In general, we find a looser linkage between the δ^{15}N time-series and indicators of transients in surface ocean [NO_3^-] than observed in the open ocean. However, average trap values reflect with high

fidelity the $\delta^{15}N$ of sub-euphotic zone NO_3^-. Sediment $\delta^{15}N$, in turn, is very similar to trap values, indicating strong potential for application of this proxy to paleoceanographic study in this region.

2. Sampling and analytical methods

2.1. Site description

Sediment trap locations are given in Fig. 1 and Table 1. All sites studied are influenced by periodic injections of subsurface nutrients to the euphotic zone that produce seasonal increases in productivity and hence particle flux. As a result, all can be characterized as highly productive with respect to a variety of particle flux parameters (Table 2). In the California Current system, this is the result of wind-driven coastal upwelling that is both sporadic and physically complex. Typically, an upwelling episode results in a filament of cold, nutrient rich water being brought to the surface off one section of the coast with subsequent advection at the surface by the alongshore current. Direction is usually to the south or offshore (Hayward and Mantyla,

Table 1
Sediment trap site information

Site	Lat.	Long.	Time period	Trap depth (m)	Above bottom (m)	Temporal resolution	Methodological citation
Monterey Bay	36°45′N	122 03′W	8/89 to 12/92	450	ca. 500	Biweekly	Pilskaln et al. (1996)
San Pedro Basin	33°33′N	118°30′W	1/88 to 7/88	500	350	Biweekly	Thunell et al. (1994a)
Gulf of California Carmen Basin	26°02′N	110°55′W	7/90 to 8/92	665	180	Biweekly	Thunell (1997)
Gulf of California Guaymas Basin	27°53′N	111°40′W	2/91 to 3/96	485	180	Biweekly	Thunell (1997)

Table 2
Average fluxes for each sediment trap time series

Site	Avg. total mass flux (g m^{-2} d^{-1})	Avg. opal flux (g m^{-2} d^{-1})	Avg. CaCO$_3$ flux (g m^{-2} d^{-1})	Avg. org. C flux (mmol m^{-2} d^{-1})
Monterey Bay	0.89	0.16	0.05	4.46
San Pedro Basin	0.52	0.07	0.10	2.67
Gulf of California Carmen Basin	0.40	0.11	0.07	1.94
Gulf of California Guaymas Basin	0.38	0.15	0.05	1.55

1990; Mooers and Robinson, 1984). In Monterey Bay, for example, upwelled water comes to the surface to the north at Pt. Año Nuevo, with subsequent transport to the south into the central Bay (Rosenfeld et al., 1994). Periods of maximum upwelling are March through July, with variability dependent on wind strength and direction. The resulting surface enhancement of nutrients causes episodes of high productivity and particle flux (Chavez, 1996; Pilskaln et al., 1996). El Niño conditions occur on an interannual time scale and result in a sharp reduction in nutrient injection and productivity due to lack of persistent upwelling-favorable winds and the subsidence of nutrient rich water (Chavez, 1996). From the coast to up to 100 km offshore, the poleward flowing California Undercurrent is typically present. It resides from 10 to 20 m down to 600 m with its core at 150 m (Collins et al., 1998), and is the likely source of upwelled waters.

San Pedro Basin in the Southern California Bight experiences similar seasonality in upwelling. The likely upwelling center nearest our trap location is the vicinity of Pt. Dume, approximately 60 n.m. to the northwest. Considering that the trap site in Monterey Bay is about 1/3 that distance from Pt. Año Nuevo, the San Pedro Basin trap site by comparison is likely to receive upwelled waters that have been at the surface and experiencing biological activity for a longer period of time. The San Pedro Basin is silled at 700 m, such that bottom water O_2 content is low to suboxic. The California Undercurrent is also the likely source of water to the basin (Liu and Kaplan, 1989).

Monsoonal climatology dominates the Gulf of California (Bray and Robles, 1991). Summer winds are weak and from the south. Strong winter northwesterlies drive surface cooling, such that winter SST's are between 15 and 17°C compared with summertime values of 30 to 32°C (Thunell, 1998). The wintertime condition results in convective mixing down to about 130 m (Robinson, 1973; Pride et al., 1998). In summer, NO_3^- concentrations at this depth are about 25 μM (see below), suggesting a substantial input of nutrients to the surface zone in winter. Wind-driven upwelling further enhances wintertime injection of nutrients. Satellite remote sensing observations of surface chlorophyll concentrations indicate that phytoplankton blooms occur in association with the northerly winter winds (Thunell et al., 1994b; Pride et al., 1998). These blooms are dominated by diatoms, and the Gulf of California is an important site for sedimentary opal accumulation (Thunell et al., 1994b). A strong oxygen minimum zone (OMZ) is present between 300 and 900 m and largely corresponds to the intrusion of Pacific Intermediate Water into the Gulf from the ETNP (Bray, 1988). From the mouth of the Gulf to the sill at the northern edge of Guaymas Basin (500 m depth), waters in the upper layer are a mixture of California Current, subtropical, and tropical waters. North of Guaymas Basin, Northern Gulf Water formed in the upper Gulf is present throughout.

2.2. Sediment traps

In Monterey Bay, a cone-shaped sediment trap (0.05 m^2 collection area) was used employing a timed release of Teflon beads to collect time-series samples in a single collection tube (Pilskaln et al., 1996). Deployment was at 450 m and spanned the

period from August 1989 through November 1992. Samples had biweekly temporal resolution and were preserved with buffered formalin.

In the San Pedro Basin and Gulf of California, larger diameter Mark VI time-series sediment traps ($0.5 \, m^2$ collection area) were used (Honjo and Doherty, 1987). Time-series samples were collected by means of a rotating tray of sample cups with biweekly resolution. The San Pedro trap was located at 500 m depth, and the sampling period lasted from Jan. to July, 1988. Buffered formalin was used as a preservative (Thunell et al., 1994a).

In the Gulf of California, two locations were initially sampled. The Carmen Basin trap, located on the western side of the Gulf, sampled at 665 m depth (180 m above seafloor) between July 1990 and August 1992. The Guaymas Basin trap located on the eastern side of the Gulf began sampling February 1991 at 485 m depth (also 180 m above seafloor). The Guaymas Basin trap is still in operation, with data through March 1996 reported here. Both traps were located within the OMZ, and sodium azide was used as a preservative (Thunell, 1997). Prior comparisons by one of us (Thunell) show little difference in particle fluxes observed using formalin versus azide preservation. A direct comparison of isotopic composition of sinking particles with different preservation methods was also made during the JGOFS EqPac experiment using three different sediment traps vertically separated by 100 m at single site. On average, little difference was observed in the $\delta^{15}N$ of collections using formalin, sodium azide, or mercuric chloride. (M.A. Altabet et al., unpublished data). The EqPac study also showed examples of no significant alteration of the $\delta^{15}N$ of the materials with holding time in the sediment trap cups.

Sample handling was similar for all three sites, including hand-picking of visually obvious 'swimmers', wet splitting of the material, and drying.

2.3. Other sample collection

Water column samples were collected from Monterey Bay (NO_3^- isotopic analysis only) and the Gulf of California (POM and NO_3^- isotopic analysis) using Niskin Bottles. POM was vacuum filtered onto precombusted Whatman GF/F filters. Water samples for $\delta^{15}NO_3^-$ analysis were preserved for later extraction by acidification to pH 2.5 with HCl. We have found no change in the $\delta^{15}NO_3^-$ of samples preserved this way and stored at room temperature for at least a 4 year period. NO_3^- concentrations were determined as $NO_3^- + NO_2^-$ both colorimetrically (Gulf of California and Monterey Bay time-series) and by conversion to NO followed by chemiluminescent detection (Monterey Bay $\delta^{15}NO_3^-$ samples) following the method of Garside (1982). PO_4^{3-} concentrations were determined using standard colorimetric methods.

2.4. Isotopic analysis

NO_3^- was extracted from seawater for isotopic analysis using a Devarda's reduction to NH_3 followed by diffusion onto acidified glass-fiber filter through a Teflon membrane (Sigman et al., 1997). Recent improvements in this technique allow for 95–100% yields and low blanks ($< 0.1 \, \mu mol$), with reproducibility in $\delta^{15}N$ for seawater samples equal to instrument performance.

All nitrogen isotopic ratio measurements were made using automated systems (Owens and Rees, 1989) consisting of elemental analyzers coupled to mass spectrometers for isotopic analyses in a continuous flow mode. The Monterey Bay, San Pedro Basin, and part of the Gulf of California samples were analyzed on a Europa/Finigan MAT 251 system (Altabet). The balance of the Gulf of California samples were analyzed on a Carlo Erba/VG Optima system (Thunell). Splits of samples run on both instruments showed no significant difference in $\delta^{15}N$. All samples are prepared by encapsulation in tin foil cups. POM and sediment trap samples needed no further pre-treatment. Reproducibility is better than $\pm 0.2\%_{oo}$. Standardization is both by combustion of solid materials of known isotopic composition and by injections of standard gases into the carrier gas (He). All $\delta^{15}N$ data is relative to atmospheric N_2.

3. Results and discussion

3.1. Monterey Bay

Subsurface NO_3^- was found to have $\delta^{15}N$ values of 7–8‰ (Fig. 2A), significantly higher than the oceanic average of 4.5–5‰ (Sigman, 1977; Sigman et al., 1997). While upper thermocline waters in central N. Pacific have $\delta^{15}NO_3^-$ values approaching 6‰, a likely source for these higher values is the California Undercurrent (Liu and Kaplan,
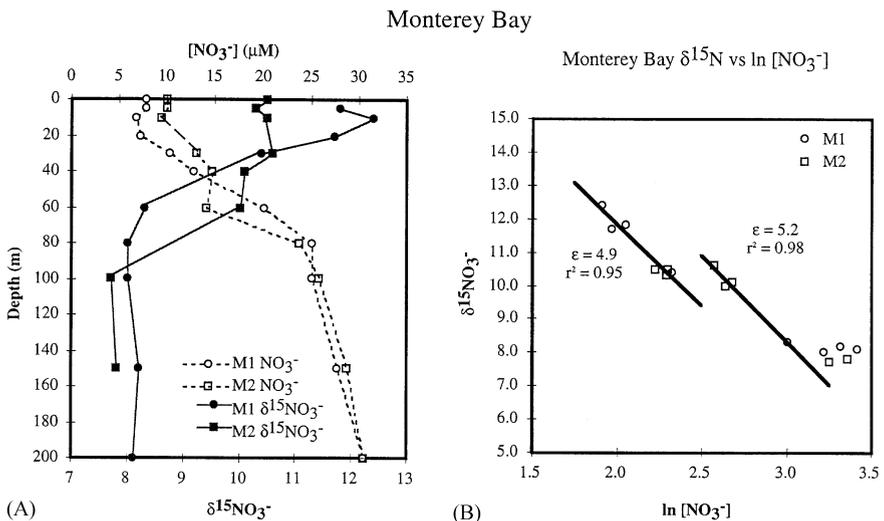

Fig. 2. (A) Vertical profiles of $[NO_3^-]$ and $\delta^{15}NO_3^-$ at two stations in Monterey Bay taken in March 1997 during the upwelling season. M1 is at the sediment trap site. M2 is 30 km further offshore; (B) $\delta^{15}NO_3^-$ vs ln $[NO_3^-]$. The fractionation factor for NO_3^- uptake is the inverse of the slope of the linear regression. A break in the linearity of the data prompted two regressions to be made, which have statistically different intercepts (see text). Regressions include data only within the euphotic zone (0–80 m), where biological uptake can influence $[NO_3^-]$.

1988). Its source waters appear to include the denitrification zone of the Eastern Tropical N. Pacific (ETNP), where maximal $\delta^{15}NO_3^-$ can reach 20‰ (Cline and Kaplan, 1975; Altabet and Sheehan, unpubl. data). The two water sampling stations shown were occupied during moderate upwelling, as seen in surface $[NO_3^-]$ between 7 and 10 μM. The increase in $\delta^{15}NO_3^-$ with decreasing $[NO_3^-]$ toward surface within the euphotic zone has been previously observed (Altabet, 1996; Wada, 1980) and is direct evidence for isotopic fractionation during NO_3^- uptake by phytoplankton. Rayleigh fractionation describes the increase in $\delta^{15}N$ with NO_3^- removal:

$$\delta^{15}NO_{3\,(f)}^- = \delta^{15}NO_{3\,(f=1)}^- - \varepsilon \times \ln(f) \qquad (1)$$

where f is the fraction of NO_3^- remaining and ε is the fractionation factor in ‰ units. Assuming that each point in the vertical had the same initial $[NO_3^-]$ and $\delta^{15}NO_3^-$ before biological NO_3^- removal, a linear relationship between $\delta^{15}NO_3^-$ and $\ln[NO_3^-]$ should be observed (Altabet, 1996). The data as a whole come close to this expectation, though there appears to be a break in the linear relationship at $\ln[NO_3^-] = 2.5$, which corresponds in the vertical profiles to a depth of about 30 m (Fig. 2B). Whereas the slope for the entire data set would suggest a value for ε of about 3‰, grouping data as shown gives a value near 5‰. The separate regressions have significantly different intercepts (two-tailed t-test at the $p < 0.002$ level), demonstrating the validity of grouping the data in this way. This estimate of ε is indistinguishable from recent field estimates of ε from the Southern Ocean (5 ± 1‰; Sigman, 1997) and the Eq. Pacific (5.2‰; Altabet, 1998) as well as laboratory estimates using diatom cultures (Montoya and McCarthy, 1995; 5.2‰, Waser et al., 1998). While ε can vary with phylogenetic group (Montoya and McCarthy, 1995), the suspected dominance of diatoms with respect to NO_3^- uptake (Dugdale et al., 1995; Landry et al., 1997) is a likely explanation for the similarity in ε between Monterey Bay, the Eq. Pacific, and the Southern Ocean. The break in the linearity of the data set suggests that the upper 30 m in Monterey Bay has a different source and history than the depth region below and perhaps constitutes a filament of remotely upwelled water. This depth is near the upper boundary of the California Undercurrent (Collins et al., 1998), dividing southward flow at the surface from northward flow below. If initially upwelled water had a $\delta^{15}NO_3^-$ of 8‰, the regression for points from the upper 30 m suggests an initial $[NO_3^-]$ of 16 μM as compared to 21 μM for the second regression line. An apparently lower initial $[NO_3^-]$ could also be achieved by mixing of the upwelled filament with low nutrient surface water either at the upwelling center or during subsequent advection.

Elevated $\delta^{15}NO_3^-$ in the source of upwelled waters should be directly reflected in the average isotopic signature of the export production. If all the upwelled NO_3^- is converted to PN on an annual basis, and if sinking PN is the only significant loss term, then the average $\delta^{15}N$ of sinking PN should average the $\delta^{15}N$ of subsurface NO_3^- transported to the euphotic zone (Altabet and McCarthy, 1985; Altabet, 1988). The average Monterey Bay trap $\delta^{15}N$ of 7.8‰ (Fig. 3, Table 3) is indistinguishable from the NO_3^-, value suggesting these assumptions apply. In addition, it appears that despite the physical complexity of the region, sampling at one geographic point can capture the average nitrogen isotopic signature of sinking particles. A further
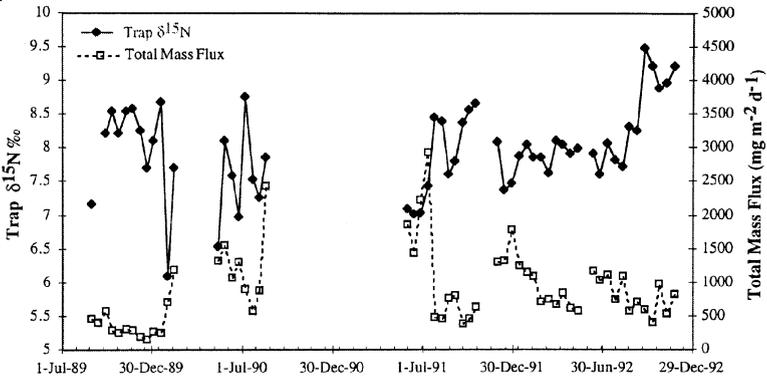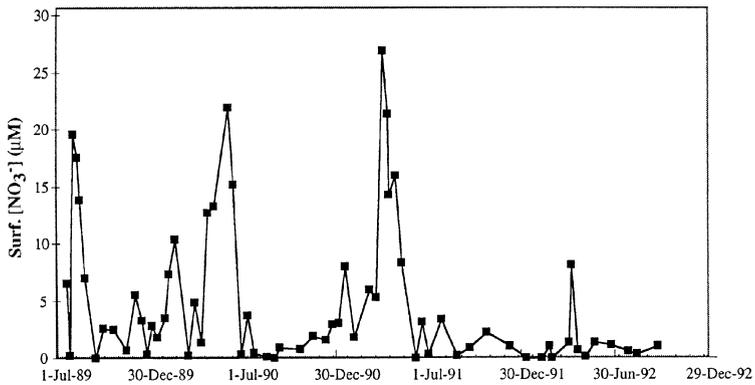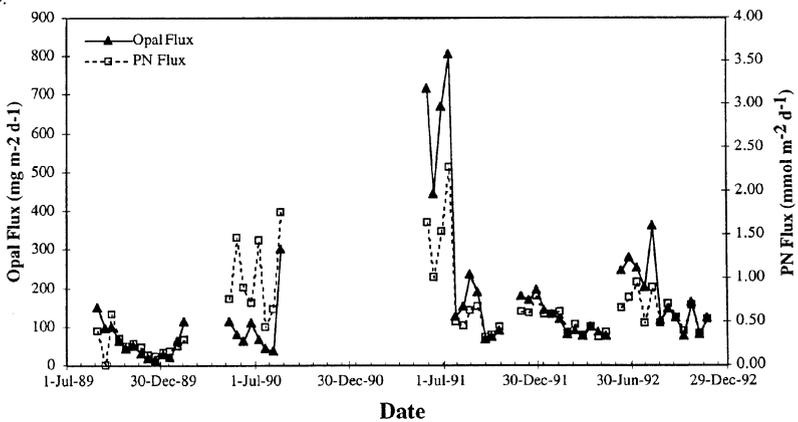
Fig. 3. Monterey Bay time-series data. (A) $\delta^{15}N$ for sediment trap samples and mass flux. (B) Sea-surface $[NO_3^-]$. (C) Sediment trap time-series data for opal and PN flux.

Table 3
N flux weighted average $\delta^{15}N$ values for the sediment trap time series and comparison to sub-euphotic zone NO_3^- and surficial sediment. Data from an upper water-column hydrocast in the Delfin Basin, Gulf of California, is included for comparison (Station C)

Site	N flux wt. avg. trap $\delta^{15}N$ (‰)	Min. trap $\delta^{15}N$ (‰)	Max. trap $\delta^{15}N$ (‰)	NO_3^- $\delta^{15}N$ (‰)	Euphotic zone POM $\delta^{15}N$ (‰)	Bottom sed. $\delta^{15}N$ (‰)	Sed. %N
Monterey Bay	7.8	6.1	9.1	8.0	nd	7.1	0.11%
San Pedro Basin	8	6.9	10.7	8.0	nd	8.5	0.33%
Gulf of California Carmen Basin	9	5.6	10.0	9.7	9.3	10.4	0.45%
Gulf of California Guaymas Basin	9.4	6.6	11.3	11.5[a]	10.0	11.1	0.50%
Gulf of California Delfin Basin	nd	nd	nd	11.8	12.0	nd	nd

[a] These samples appear to have come from the northern side of a surface water hydrographic front in this area.

implication is that bottom sediments receive and preserve this signal. The $\delta^{15}N$ of sea-floor sediments near the trap site (7.1‰) is very similar to average trap $\delta^{15}N$ (Table 3). This is in contrast to observations from the deep-sea, where sediments are enriched by about 4‰ relative to average sediment trap values (Altabet, 1996). The lack of diagenetic enrichment in sediment $\delta^{15}N$ is likely associated with higher %N and presumably better preservation. Similar results are found for the other trap sites in this study (see below).

During our period of observation seasonal upwelling in Monterey Bay produced elevated surface $[NO_3^-]$ as high as 30 μM (Fig. 3). A large range in the $\delta^{15}N$ of sinking PN would be expected, considering that the $\delta^{15}N$ of sinking PN produced at any time point should be given by

$$\delta^{15}N_{PN} = \delta^{15}NO_3^- - \varepsilon \tag{2}$$

$$\delta^{15}N_{PN} = \delta^{15}NO_3^-{}_{(f=1)} - \varepsilon \times \ln(f) - \varepsilon \tag{3}$$

Newly upwelled water with $\delta^{15}NO_3^-$ of 8‰ should produce PN with $\delta^{15}N$ of 3‰ ($\varepsilon = 5$‰). If initial $[NO_3^-]$ is 30 μM, when depleted to 1 μM, the $\delta^{15}N$ of sinking PN would be 20‰. However, the observed temporal variation in $\delta^{15}N$ in the Bay is considerably less, from 6 to 9.5‰. This range in $\delta^{15}N$ is even marginally smaller than observed for our two $\delta^{15}NO_3^-$ profiles (Fig. 2, ca. 4‰). In contrast, Rau et al. (1996) have reported a 2–8‰ range in $\delta^{15}N$ for near-surface suspended POM. The $\delta^{15}NO_3^-$ data suggest that dilution of upwelled filaments with low-nutrient water can account for part of the reduced range in $\delta^{15}N$ values. The suspended $\delta^{15}N$-PN data, though, suggest that residence time considerations may also account for part of our observations. If particle residence times in the euphotic zone are a substantial fraction of the drawdown time for NO_3^- in the upwelled filament, a reduced amplitude in the $\delta^{15}N$ of the sinking PN compared to suspended PN would result (Altabet, 1996).

Previous open-ocean studies suggest that upwelling events should at first cause $\delta^{15}N$ minima and then, as NO_3^- is exhausted, $\delta^{15}N$ maxima. Particle flux maxima should occur during the transition in $\delta^{15}N$ values (Altabet, 1996; Altabet et al., 1991). Our data is in substantial agreement with this perspective. The four periods of highest surface $[NO_3^-]$ (10–30 μM) are associated with the most ^{15}N depleted samples (6–7.2‰). However, the relationship is not as simple as in previous open-ocean studies. The highest $[NO_3^-]$ does not correspond to the lowest $\delta^{15}N$ values, and the phasing between them appears to vary. The gaps in the $\delta^{15}N$ data also hinder a more precise characterization. Total particle mass flux in Monterey Bay also qualitatively shows the expected relationship, with highest values associated with or just lagging $\delta^{15}N$ minima. An exception is at the beginning of the time-series. For opaline silica flux (opal), the relationship with $\delta^{15}N$ is less tight but still apparent as expected given that upwelling events tend to result in diatom blooms (Chavez, 1996; Pilskaln et al., 1996). Paradoxically, an even weaker overall correspondence is observed between PN flux and $\delta^{15}N$. Since the increase in $\delta^{15}N$ after an upwelling event is associated with the depletion of NO_3^- and production of PN, a closer linkage would be expected. POM flux and primary productivity over the trap site are, in contrast, well correlated for the non-El Niño portions of the time-series (Pilskaln et al., 1996).

The end of the Monterey Bay time-series hints at interannual variability. In 1992, there are no strong $\delta^{15}N$ minima and from July to Dec. $\delta^{15}N$ is distinctly higher as compared to the rest of the time-series. The years 1991 to 1994 were a period of extended El Niño conditions (Fig. 4), a likely cause of the observed variability. In fact, the El Niño index (SOI anomaly) is particularly extreme in the first third of 1992. Chavez
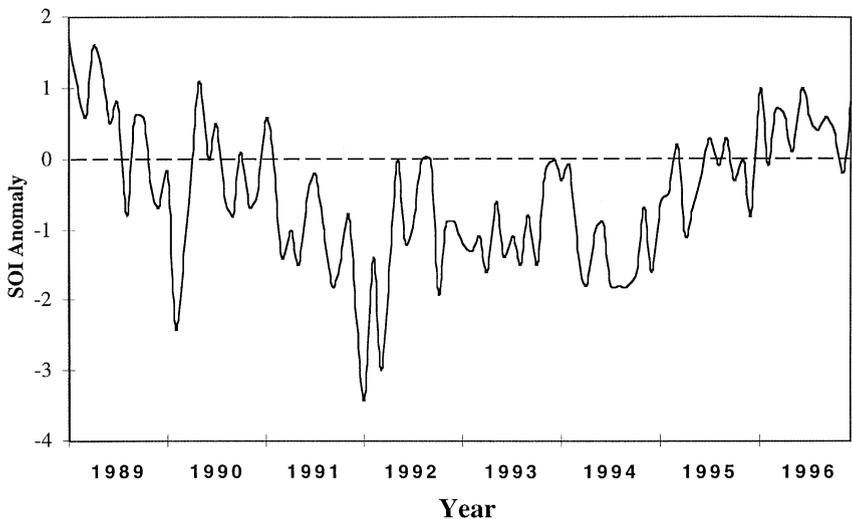

Fig. 4. Southern Oscillation Index (SOI) anomaly for the period 1989–1996. This index is based on sea level pressure difference between Tahiti and Darwin. ENSO (El Niño) conditions are indicated by negative values.

(1996) and Pilskaln et al. (1996) associated El Niño conditions with a suppression of upwelling in Monterey Bay, as can be seen by the fact that there is only one relatively small peak in surface $[NO_3^-]$ in 1992 and no large peaks in the particulate mass flux. As a result, the lack of distinct $\delta^{15}N$ minima is reasonable. The approximate 1‰ increase in $\delta^{15}N$ after July 1992 is more difficult to understand but may be associated with increases in the $\delta^{15}N$ of subsurface NO_3^-. This could occur if the California Undercurrent intensifies during El Niño and this is the source of NO_3^- enriched in ^{15}N (Liu and Kaplan, 1979). Unfortunately, our Monterey Bay $\delta^{15}NO_3^-$ data dates only from a period of normal upwelling conditions.

3.2. San Pedro Basin

Like Monterey Bay, $\delta^{15}N$ values for San Pedro Basin sediment traps should also be influenced by: (1) episodic upwelling events temporarily enriching surface $[NO_3^-]$ and (2) the average $\delta^{15}NO_3^-$ in subsurface waters. The second condition is clearly evident. Liu and Kaplan (1989) report $\delta^{15}NO_3^-$ values of about 8‰ at the base of the euphotic zone (Fig. 5) equal to average $\delta^{15}N$ values for sediment trap material (Table 3). This $\delta^{15}N$ value is indistinguishable from our Monterey Bay observations. In this location, though, $\delta^{15}NO_3^-$ increases to a maximum of nearly 12‰ at 350 m. Since this part of the water column is not suboxic, high $\delta^{15}NO_3^-$ must have been advected from a region of water column denitrification with subsequent mixing with oxic waters. Liu and Kaplan (1989) concluded that the ETNP is the source region. The amount of NO_3^- removed by denitrification can be assessed by calculating a NO_3^- anomaly relative to PO_4^{-3} (N*, Gruber and Sarmiento, 1997). There is an inverse relationship between N*
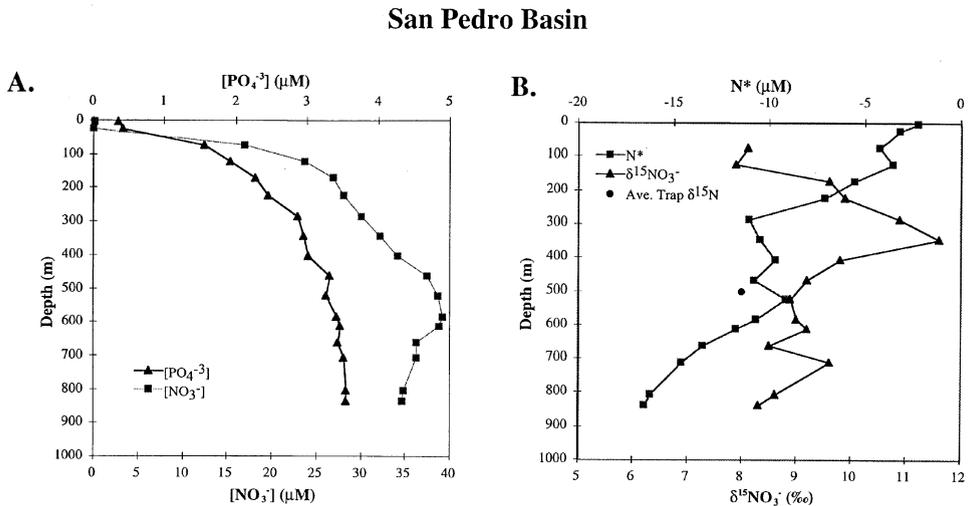
San Pedro Basin

Fig. 5. Data for San Pedro Basin replotted from Liu and Kaplan (1989) and Liu (1979). Note the sill depth is just below 700 m: (A) NO_3^- and PO_4^{-3} concentration with depth; (B) vertical profiles for $\delta^{15}NO_3^-$ and N* (see text) with average trap $\delta^{15}N$ shown.

and $\delta^{15}NO_3^-$ down to about 500 m (Fig. 5). Below this depth the magnitude of the negative N* anomaly increases though $\delta^{15}NO_3^-$ decreases. The sill depth for San Pedro Basin is about 720 m, and these deeper observations may be the result of sedimentary denitrification. There appears to be little isotopic fractionation associated with this process as compared to water column denitrification due to rate limitation by transport through the sediments (Brandes and Devol, 1997).

Sediments from this basin have $\delta^{15}N$ values as reported by Nelson et al. (1987) indistinguishable from the trap values (Table 3). Supporting our contention that the 0.5 years worth of data from San Pedro Basin is representative of a longer term average, Nelson et al. (1987) also reported the same $\delta^{15}N$ for material from floating sediment traps (8‰) as we find for the moored traps. It should be noted that the strong subsurface maximum in $\delta^{15}NO_3^-$ observed in the vicinity of 350 m suggests the possibility of $\delta^{15}N$ values for sediment trap material varying with the depth of origin of upwelled waters.

The San Pedro Basin sediment trap time-series is too short and fragmentary to characterize well the seasonal and episodic variations in $\delta^{15}N$. A much longer sediment trap time-series from the Santa Barbara Basin should provide this level of detail (Thunell et al., 1995). However from the present data, it would appear that instead of being characterized by distinct minima, the series is characterized by brief periods of high $\delta^{15}N$ (Fig. 6). Four out of five of these maxima correlate with minima in total particulate mass and opal flux. As in Monterey Bay, the strongest $\delta^{15}N$ signals do not correspond to the largest fluxes, and the relationship with PN flux is somewhat weaker than for opal and total mass flux. Temperature records (Thunell et al., 1994a) show late April to early June to be a period of upwelling in San Pedro Basin. The expected $\delta^{15}N$ minima are absent, though in this case NO_3^- data were not obtained. Aging filaments of upwelled water substantially depleted of nutrients would be enriched in ^{15}N and would not export ^{15}N-depleted sinking POM in the vicinity of the trap site. The peaks in $\delta^{15}N$ may reflect periods in which such filaments are in the vicinity of the trap site. By way of comparison with Monterey Bay, this explanation is sensible given that the San Pedro Basin trap is at greater distance from the presumed upwelling center.

3.3. Gulf of California

Average $\delta^{15}N$ values for the Carmen Basin and Guaymas Basin traps are very similar to each other (9 and 9.4‰) but $> 1‰$ higher than at the other trap locations (Table 3). The seasonal amplitude in variation in $\delta^{15}N$ is about 4.5‰. Summertime euphotic zone POM have values ranging from 9 to 12‰ depending on location, further demonstrating this system to be generally enriched in ^{15}N as compared to other regions (Fig. 7; Altabet, 1996). As expected, this isotopic enrichment in suspended and sinking PN reflects the $\delta^{15}N$ of subsurface NO_3^-. The Gulf of California is suboxic between about 300 and 900 m with denitrification influencing this layer. Accordingly, $\delta^{15}NO_3^-$ reaches a maximum of 14‰ at 500 m within the OMZ (Fig. 7). Aside from the shallowest sample, there is a clear inverse relationship between N* and $\delta^{15}NO_3^-$ in our deep hydrostation in the Carmen Basin (Station A). The near-surface

San Pedro Basin

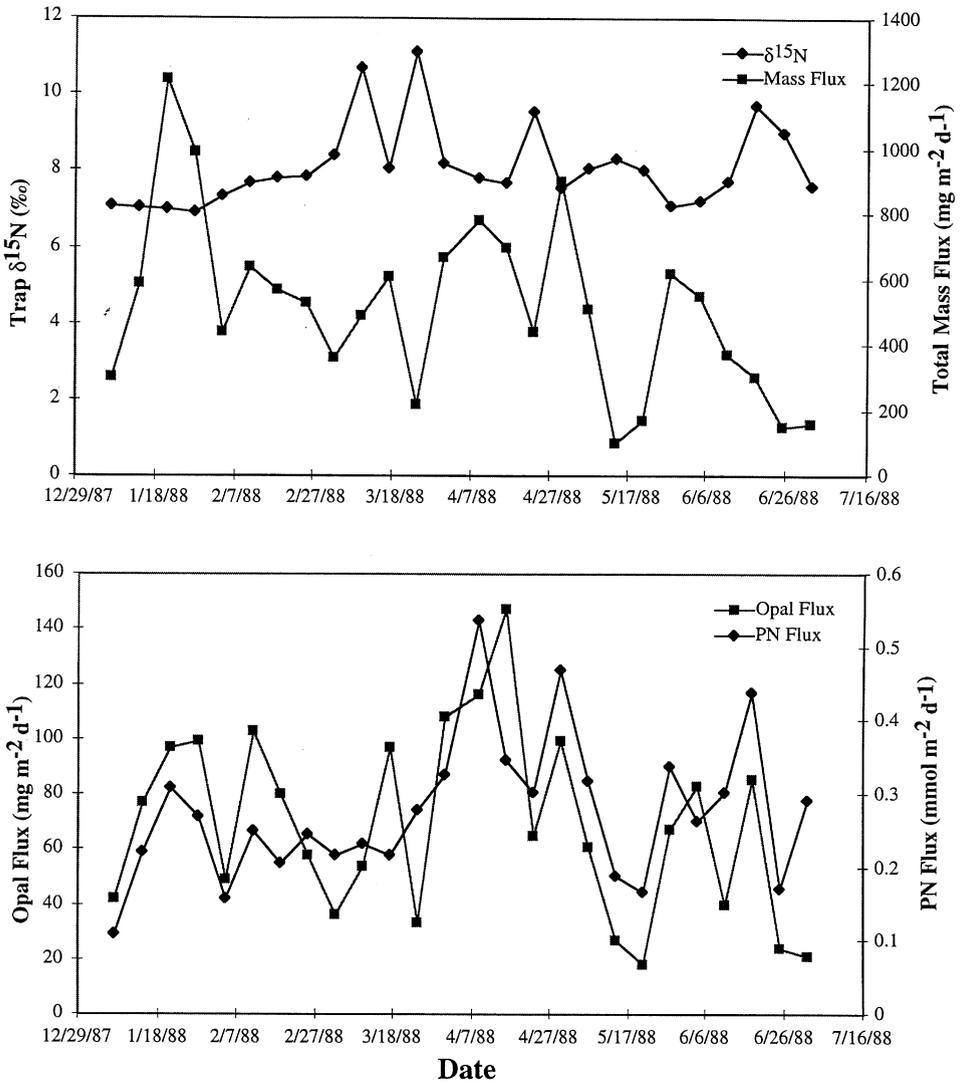

Fig. 6. San Pedro Basin time-series sediment trap data. (A) $\delta^{15}N$ and mass flux; (B) opal and PN flux.

enrichment in $\delta^{15}NO_3^-$ (< 60 m) is likely due to NO_3^- assimilation by phytoplankton, which would not influence N* because of concurrent removal of both NO_3^- and PO_4^{-3} in Redfield proportions. We also have $\delta^{15}NO_3^-$ and N* data from shallower hydrocasts taken at the northern boundary of the Guaymas Basin (Station B) and in Delfin Basin (Station C; Fig. 1). Though nutrient profiles are similar, $\delta^{15}NO_3^-$ at these two
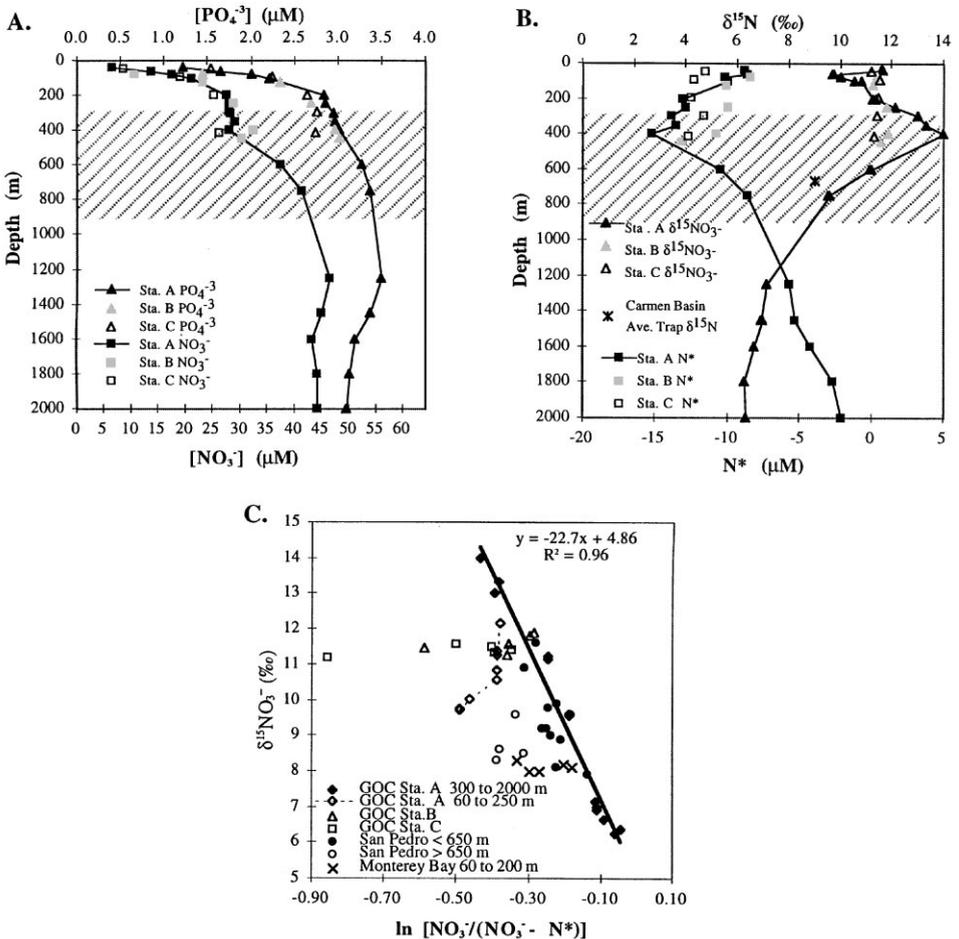
Gulf of California

Fig. 7. Vertical profiles taken in June 1990 from the Gulf of California. Station A is in Carmen Basin at 26°13′N, 110°36′W, Station B is at 27°54′N, 111°39′W at the northern edge of Guaymas Basin, and Station C is at 29°51′N, 113°53′W in Delfin Basin (see Fig. 1). The shaded area indicates the OMZ. (A) NO_3^- and PO_4^{3-} concentration data. (B) Vertical profiles for $\delta^{15}NO_3^-$ and N* (see text). $\delta^{15}N$ values for near-surface POM and the sediment trap average are shown. (C) $\delta^{15}NO_3^-$ vs ln $[\,NO_3^-/(NO_3^- - N^*)]$. The latter term is an estimate of the fraction of NO_3^- remaining after denitrification. The linear portion of the relationship indicates operation of Rayleigh fractionation in the >300 m portion of Station A (see text). Not plotted are Station A euphotic zone data, which are clearly influenced by phytoplankton removal of NO_3^-. Data for San Pedro Basin and Monterey Bay are plotted for reference.

sites is much more homogeneous that in the corresponding <500 m region of Station A, and its relationship with N* is considerably altered (see below). Our speculation is that (1) this is a characteristic feature of Northern Gulf water in the upper Gulf, and

(2) Station B is effectively just north of the front marking the southern boundary of this water mass.

The same general approach taken for estimating the NO_3^- uptake fractionation factor in Monterey Bay can be used for estimating ε associated with denitrification. However, the assumption of a homogeneous initial $[NO_3^-]$ need not be made. A value for f can be calculated if initial $[NO_3^-]$ is taken to be $[NO_3^-] - N^*$ such that

$$f = [NO_3^-]/([NO_3^-] - N^*) \tag{4}$$

For the OMZ and below (>300 m depth), such a relationship is observed with an r^2 of 0.96 (Fig. 7C). The magnitude of the slope is an estimate of the fractionation factor (22.7‰), which is within the range of previous estimates (Delwiche and Steyn, 1970; Miyake and Wada, 1971; Wellman et al., 1968). Open-ocean field studies have found both higher and lower values (Cline and Kaplan, 1975; Liu, 1979). The y-intercept predicts a value of 4.9‰ for NO_3^- uninfluenced by denitrification. This value is within the 4.5–5‰ range of average deep water $\delta^{15}NO_3^-$ (Sigman, 1997).

Within the oxic near-surface layer (<300 m depth) at Stations A, B, and C, this relationship breaks down, with points falling below the relationship expected from the deeper data. This may result from mixing of waters that have experienced denitrification with those that have not. Isotopic fractionation is logarthmically related to NO_3^- depletion by denitrification, while N^* values mix linearly. Moreover, N^* in the <300 m depth region may overestimate the denitrification-caused NO_3^- deficit if either preformed or regenerated $NO_3^- : PO_4^{3-}$ deviate negatively from the 16:1 ratio used in calculating N^*. Another possibility is that water <300 m in depth has experienced denitrification through contact with the sediments along the sides of the basin, which may produce little nitrogen isotopic fractionation (Brandes and Devol, 1997). Contributions from nitrogen fixation would also cause deviations from the deep $\delta^{15}NO_3^- : N^*$ relationship with the magnitude of N^* decreasing. However, points would deviate to the region above the regression in Fig. 7C, since N fixation is adding nitrogen more enriched in ^{15}N (-1‰; Hoering and Ford, 1960; Minagawa and Wada, 1986; Miyake and Wada, 1971) than the N_2 that had been produced by denitrification (-8 to -16‰) depending on $\delta^{15}NO_3^-$ ($\delta^{15}N\ N_2 = \delta^{15}NO_3^- - \varepsilon$).

San Pedro Basin (<650 m) and Monterey Bay (60–200 m) $\delta^{15}NO_3^-$ values fall near the linear trend supporting a similar source region in the ETNP for these California margin waters and those from the Gulf of California, though not without some modification. Deeper points from the San Pedro Basin deviate from the linear trend, again supporting other influences on $\delta^{15}NO_3^-$, such as sedimentary denitrification. Unlike the Gulf of California, the upper portion of the San Pedro Basin water column does fall near the regression line, indicating little mixing with other waters, etc. The relative dispersion of the Monterey Bay data is also likely due to greater influence of mixing with other water masses with distance from the ETNP.

As at the other sites, $\delta^{15}NO_3^-$ just below the euphotic zone is rather close to the average trap $\delta^{15}N$ value in Carmen Basin (Table 3). Denitrification is the obvious cause of ^{15}N-enriched NO_3^- to the euphotic zone and thus producing the high $\delta^{15}N$ values of the trap material. At Guaymas Basin, $\delta^{15}NO_3^-$ appears to be 2‰ higher than the trap value. Since the Carmen and Guaymas Basin traps are very similar in average

δ^{15}N, this difference is likely due to Station B being within Northern Gulf Water, whereas the Guaymas Basin trap is chiefly influenced by Central Gulf Water, as characterized by the Station A data. This is not unreasonable given the location of Station B at the northern boundary of Guaymas Basin.

Also in agreement with the other two trap sites is the similarity in δ^{15}N between the Gulf of California trap material and seafloor sediments (Table 3). Whether within the OMZ or the oxic zone below (Pride et al., 1998), surficial sediments have δ^{15}N values only 1.5‰ higher than the trap values, again showing little diagenetic influence. Interestingly, the $\delta^{15}NO_3^-$ values are even closer to sediment δ^{15}N. The paleoceanographic implications of these observations will be discussed below.

Seasonal variations in trap δ^{15}N appear at first very coherent in the Gulf of California; every year there is a discernible minimum in δ^{15}N (Fig. 8). Where the Carmen Basin and Guaymas Basin time-series overlap, values are very similar for both δ^{15}N and material fluxes, indicating that the seasonal variability observed is prevalent throughout this middle section of the Gulf and that they are both influenced by the same source waters for nutrients as surmised above. Similar seasonal variations are expected, since NO_3^- injection to surfaces waters is brought about in part by large-scale wintertime convective mixing. It is also expected that δ^{15}N minima would occur during this season and be correlated with large peaks in biogenic mass flux (Altabet and Deuser, 1985; Altabet et al., 1991; Nakatsuka et al., 1992). This pattern is observed in the winters of 1993–1994 and 1994–1995. However, other years are anomalous with respect to the prior open-ocean results. The minima in δ^{15}N from 1990–1992 (1991–1992 is a strong El-Niño period) occur in late summer and are not well correlated with mass flux. In particular, opal flux is low. As seen at the other sites the general relationship between δ^{15}N and PN flux is poorer than for mass and opal flux. Even in the more 'normal' years '93 to '96, the peaks in opal flux in the Gulf of California lead the minima in δ^{15}N, opposite to expectations.

Without a hydrographic time series companion to the Gulf of California sediment trap series, we have only a limited ability to understand these apparent anomalies in the δ^{15}N record. The vertical profiles for POM and NO_3^- were collected in June 1990, a non-El Niño period. Nevertheless several lines of evidence point to possible answers. The summertime minima in δ^{15}N occur during strong El Niño years (Fig. 4), when annual upper layer transport from the south should be enhanced due to the weakening of strong wintertime northwesterly winds (Thunell, 1997). The lack of wintertime opal maxima and δ^{15}N minima would then result from the relative failure of strong convective mixing/upwelling to inject nutrients into the euphotic zone.

More difficult to understand is the cause of the Gulf of California summertime minima in δ^{15}N, which are clearly not connected with NO_3^- enrichment of surface waters. The most likely cause is the input at these times of new nitrogen that is relatively depleted in ^{15}N as compared to observed sub-euphotic zone NO_3^-. This source could be exterior to the Gulf and manifest as enhanced northward transport of near-surface tropical waters with low $\delta^{15}NO_3^-$. The $\delta^{15}NO_3^-$:ln $[NO_3^-]$/ $([NO_3^-] - N*)$ relationship in Fig. 7c is consistent with persistent additions of low δ^{15}N NO_3^- relative to N* to the upper 250 m. The strength of this low δ^{15}N source may have increased during periods of distinct summertime minima in trap δ^{15}N,
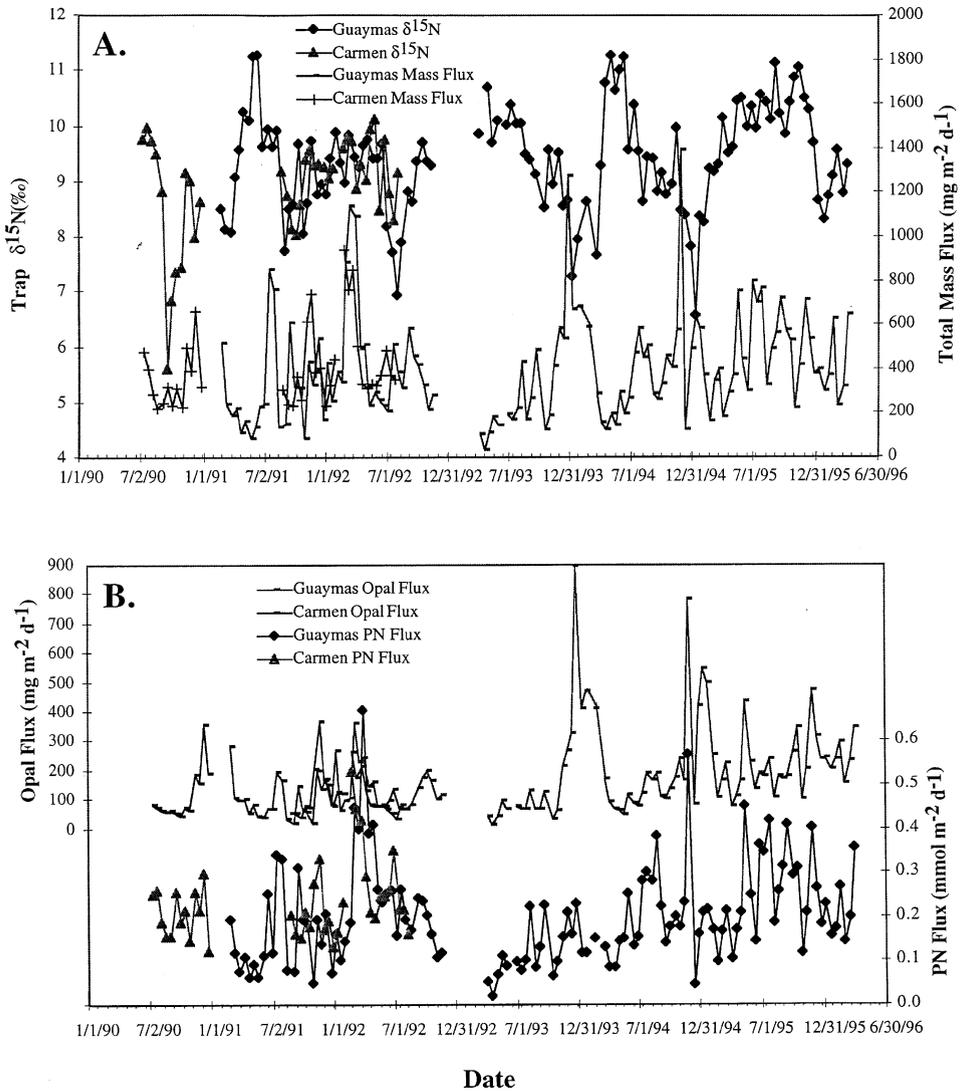
Gulf of California

Fig. 8. Gulf of California sediment trap time-series data: (A) $\delta^{15}N$ for sediment trap samples and mass flux; (B) Sediment trap time-series data for opal and PN flux.

thereby decreasing sub-euphotic zone $\delta^{15}NO_3^-$ at these times. Unfortunately the $\delta^{15}NO_3^-$ of the source of tropical/subtropical Pacific surface water that penetrates up the Gulf to our study area is not known. Another possibility is of nitrogen fixation ($\delta^{15}N$ near -1 to 0%, Hoering and Ford, 1960; Minagawa and Wada, 1986, 1971)
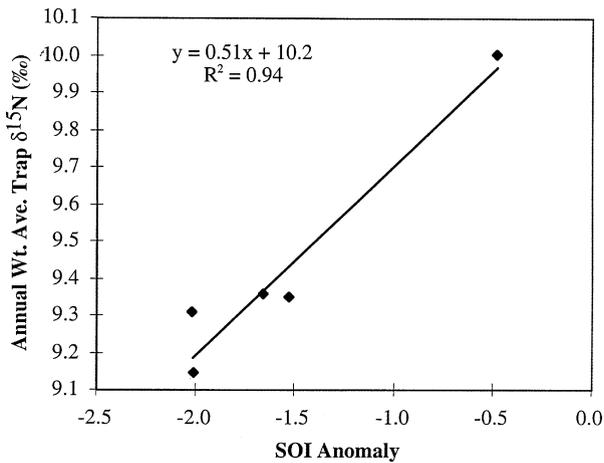
Fig. 9. Annual average $\delta^{15}N$ weighted by PN flux from the Carmen Basin sediment trap vs the annual average Southern Oscillation Index (SOI) anomaly.

occurring in the Gulf during summer stratification, when there is no prior wintertime input of NO_3^- to the euphotic zone. N fixation, however, does not appear to be responsible for the observed deviation from the denitrification trend in Fig. 7C (see above) and would have to 'turn on' only during these periods.

Whatever its origin, changes in the strength of this putative low $\delta^{15}N$ source of new nitrogen should produce interannual variations in average $\delta^{15}N$ for trap material. In fact, a modest 0.8 to 0.9‰ range in annual average $\delta^{15}N$ is observed (Table 4). Nevertheless, the highest value of 10‰ occurs in the year with the smallest annually averaged SOI anomaly (Fig. 4) as well as the highest total particulate mass and opal flux. The year with the lowest $\delta^{15}N$ annual average, 1992, also corresponds to the largest summertime $\delta^{15}N$ minima and SOI anomalies, though not the smallest particle mass flux. This year also saw the strongest input of tropical Pacific surface water to Guaymas Basin (Thunell data). Overall a positive relationship is seen between annual flux weighted average $\delta^{15}N$ and annual average SOI anomaly (Fig. 9). It appears that El Niño events lower the $\delta^{15}N$ of new nitrogen delivered to the surface waters of the Gulf of California.

Our speculation that El Niño increases Monterey Bay trap $\delta^{15}N$ is not necessarily inconsistent with this observation. Considering hydrographic changes alone, a strengthening of the California Undercurrent could co-occur with increased flow of near-surface subtropical/tropical water to the Gulf of California. Obviously, future work needs to distinguish whether these nitrogen isotopic phenomena are mediated through hydrographic changes, stimulation of nitrogen fixation, or depression of denitrification. In any event, our results do suggest El Niño modulation of key nitrogen cycle processes, which can be recorded given sufficient resolution in the sediments.

4. Inter-site comparison and conclusions

4.1. Average $\delta^{15}N$ values

Mass balance considerations require that the average $\delta^{15}N$ of new nitrogen inputs to the euphotic zone equal the average $\delta^{15}N$ of exports (Altabet and McCarthy, 1985). If it is assumed that NO_3^- transported to the euphotic zone is the source of new nitrogen and rapidly sinking particles are the sink (Eppley and Peterson, 1979), then $\delta^{15}N$ values for the two should be equivalent after taking into account any isotopic fractionation during partial NO_3^- utilization. Studies at open-ocean sites have generally confirmed this hypothesis (Altabet, 1988, 1996).

However, there are a number of possible scenarios where this perspective can break down, such as when nitrogen fixation or inputs from land via the atmosphere or rivers are significant. Terrestrial sources are a particular concern in near-shore environments, such as those studied here. Additionally, the effective time/space scales of sampling by shallow near-shore sediment traps may be too small to adequately reflect the regional average. Deuser et al. (1990) refer to a hypothetical cone of sampling extending up from the sediment trap to the surface determined by the depth of the trap, the sinking speeds of particles, and the rates of horizontal advection and mixing. This may result in a particularly acute problem for Monterey Bay and San Pedro Basin which have complex physics. The cone of sampling may intersect at times a filament of upwelled water during only a small portion of its time course for NO_3^- depletion. The result would be that the sinking particles would have $\delta^{15}N$ values skewed from the large-scale average. Our sample sites are also in basins with relatively steep slopes, and there may be some influence of sediment resuspension and lateral transport from the shelf and upper slope.

Despite these potential difficulties, all three sites show a remarkable similarity between the $\delta^{15}N$ values of sub-euphotic zone NO_3^- and sinking particles (Table 3). For Monterey Bay and San Pedro Basin the values are indistinguishable, given an analytical reproducibility of better than $\pm 0.2\permil$. For the Carmen Basin, the difference observed is only $0.7\permil$. For Guaymas Basin, we have assumed that Station A is more representative than Station B due to hydrographic considerations. If non-El Niño conditions are considered more typical, the trap values and Station A $\delta^{15}NO_3^-$ are also indistinguishable (Table 4). Whatever the routes sinking particles take before being collected by the sediment traps, on average they represent the isotopic value of the presumed input. This may result from high values for horizontal advection and mixing, which would increase the surface area statistically sampled by the sediment traps (Deuser et al., 1990). The net effect is that over time they integrate the regions' new production with respect to isotopic composition.

There are a number of implications for this finding: First, sources of new nitrogen other than NO_3^- supporting export production are generally not significant. This was expected considering the importance of upwelling and wintertime convection to these systems. Since terrestrial N is generally low in $\delta^{15}N$ (Sweeney and Kaplan, 1980), it also follows that this source is an insignificant input term of particulate N to these coastal systems. This is reasonable considering their relative high productivity and

Table 4
Average $\delta^{15}N$ and flux values by year for the Guaymas Basin sediment trap Average $\delta^{15}N$ values are nearly the same whether they are weighted by N flux or not

Year	Avg. $\delta^{15}N$ (‰)	Wt. avg. $\delta^{15}N$ (‰)	Avg. total mass flux (g m^{-2} d^{-1})	Avg. opal flux (g m^{-2} d^{-1})	Avg. PN flux (mmol m^{-2} d^{-1})	Avg. SOI anomaly
91	9.3	9.3	0.31	0.10	0.15	− 1.5
92	9.1	9.1	0.45	0.13	0.25	− 2.0
93	9.6	9.4	0.31	0.15	0.12	− 1.7
94	9.3	9.3	0.41	0.20	0.18	− 2.0
95	9.9	10.0	0.48	0.24	0.25	− 0.5

low riverine inputs. These were the general conclusions of Thunell et al. (1994a) regarding organic C sources from examination of $\delta^{13}C$ data for the San Pedro Basin trap. Winter $\delta^{13}C$ values suggested, though, some terrestrial contributions, which were accompanied by large lithogenic fluxes. In contrast, terrestrial input was previously thought to be an important carbon and nitrogen isotopic endmember (Sweeney and Kaplan, 1980). Another implication is that sediment traps should record interannual variations in the $\delta^{15}N$ of sub-euphotic zone NO_3^-, as observed in the Gulf of California (Table 4). How such variations may occur in response to hydrographic and climatological modification needs to be further studied. Such phenomena would also be observed as changes in the $\delta^{15}NO_3^-$: ln $[NO_3^-]/([NO_3^-] - N^*)$ relationships (Fig. 7).

Second, our results show that the sediments provide an accurate paleoceanographic record for $\delta^{15}NO_3^-$. Denitrification is the principal modifier of subsurface $\delta^{15}NO_3^-$ and is responsible for our observed values of $> 8‰$ (Cline and Kaplan, 1975; Liu and Kaplan, 1989) as compared to an open-ocean average of 4.6‰ (Sigman, 1997). Our observations confirm the interpretation of the downcore record from the Gulf of California (Pride et al., 1998), the Mexican Margin in the ETNP (Ganeshram et al., 1995), and the Arabian Sea (Altabet et al., 1995) in terms of climatically linked variations in denitrification. These records, which all show large reductions in $\delta^{15}N$ and hence denitrification during the last glacial period, also suggest variability in the ocean's fixed nitrogen content that would have impacted the carbon cycle through its influence on productivity. $\delta^{15}N$ values are high (ca. 8‰) in Monterey Bay and San Pedro Basin, even though they are not zones of active water column denitrification. It has been suggested that the ETNP supplies ^{15}N-enriched NO_3^- to the subsurface waters of these areas (Liu and Kaplan, 1989), thereby accounting for this observation. Further study is needed, though, on the influence of isotopic signatures by the interplay of denitrification in the ETNP, the advective field, and mixing with other water masses. Such an approach is also likely to lead to an understanding of the El Niño-related variations in $\delta^{15}N$. Given that, downcore $\delta^{15}N$ records from this region should reveal past changes in this regime at a variety of time scales.

Surficial sediments at our study sites have $\delta^{15}N$ values very similar to that of the sinking flux (Table 3). All are within 1.7‰ of each other. This is in contrast to findings from deep-sea depositional environments, where a consistent enrichment of about 4‰ is observed between sinking PN and core top sediment (Altabet, 1996). The presence of suboxic overlying water cannot be solely responsible for apparent lack of diagenetic effects on sediment $\delta^{15}N$. The Monterey Bay site has oxic bottom water, but sediments are actually 1‰ lower in $\delta^{15}N$ than the trap material. Pride et al. (1998) has shown the same $\delta^{15}N$ values for core top materials in the Gulf of California taken within the suboxic zone and below it in oxic deep waters. All our sites do have surface sediment %N 2–10 times higher than the carbonate-rich sediments of the Equatorial Pacific, which we have previously studied (Altabet and Francois, 1994; Altabet, 1996). We have observed that relatively small differences in %N observed for deep-sea sediments do not appear to influence the magnitude of the diagenetic enrichment in ^{15}N. Nevertheless, the much better preservation of organic N at our coastal margin sites has evidently prevented this enrichment from occurring. We can conclude that sediment records will directly reflect the $\delta^{15}N$ of past inputs from the water column (and hence subsurface NO_3^-) as long as the level of preservation of organic N observed at the core top is maintained down core.

4.2. Time-series $\delta^{15}N$

Our combined time-series $\delta^{15}N$ data set for the eastern North Pacific margin shows a number of departures from previous open-ocean observations. Variations in $\delta^{15}N$ are not overall tightly coupled to upwelling/convective events and maxima in PN flux (Figs. 3, 6 and 8). Here the distinction between these margin sites and the open-ocean with regard to time/space scales of events may be responsible, particularly if the flux entering the trap samples at a larger time/space scale than the scale of upwelled filaments. Complexities in the processes that transform surface productivity into sinking particles are suggested by the observation that peaks in mass and opal flux are more closely coupled to $\delta^{15}N$ minima than PN flux, the phase that actually carries the ^{15}N signal. Pilskaln et al. (1996) showed good correlation between primary productivity and sinking POC flux during non-El Niño conditions but not during El Niños. This difference associated with the presence or absence of diatom blooms results from a shift in the efficiency of export of POM from the euphotic zone to deeper layers.

From a paleoceanographic perspective, using sediment $\delta^{15}N$ to detect seasonal upwelling/convection and flux events is pertinent only where the sedimentary record is capable of resolving this time scale. In the Gulf of California, this possibility is afforded by the lack of bioturbation and the presence of laminations where the OMZ impinges on the basin sides. At first glance, observation of seasonal $\delta^{15}N$ minima in the sedimentary record would have an ambiguous interpretation, being the result of wintertime injection of NO_3^- to surface waters or the undetermined summertime events occurring during strong El Niño years (Fig. 8). In the Gulf of California, diatoms bloom only during the wintertime convection/upwelling events. When the opal accumulation record is considered, the cause of $\delta^{15}N$ minima would easily be distinguished, and a record of wintertime convective input of nutrients as related to

climate can be obtained. Recently, methods have been developed to isolate diatom frustules from sediments for nitrogen isotopic measurements (Sigman, 1997). Diatom $\delta^{15}N$ would provide a confirming record of wintertime nutrient injection.

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