Summer surface waters in the Gulf of California: Prime habitat for biological N_2 fixation

Angelicque E. White,[1] Fredrick G. Prahl,[1] Ricardo M. Letelier,[1,2] and Brian N. Popp[3]

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[1] We report significant rates of dinitrogen (N_2) fixation in the central basins of the Gulf of California (GC) during July–August 2005. Mixing model estimates based upon $\delta^{15}N$ values of particulate matter in the surface mixed layer indicate that N_2 fixation provides as much as 35% to 48% of the phytoplankton-based nitrogen demand in the central Guaymas and Carmen basins. Microscopic analyses identify the responsible genera as the N_2-fixing endosymbiont, *Richelia intracellularis*, with lesser contributions from the large nonheterocystous diazotroph *Trichodesmium*. Analyses of remotely sensed chlorophyll *a* and sea surface temperature indicate that primary production levels are elevated in regions of the GC where oceanographic conditions are ideal in summertime for the growth of N_2-fixing organisms. These findings suggest that biological N_2 fixation must be taken into account when assessing past and present nitrogen dynamics in this environmentally important region.

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1. Introduction

[2] The Gulf of California (GC) is a subtropical marginal sea important as a site of rich biological productivity and as an intermediate in the flow of terrestrial and anthropogenically derived materials to the open ocean. Wind-driven upwelling of nutrient-rich waters [*Thunell et al.*, 1996] and nutrient inputs from continental runoff [*Beman et al.*, 2005] generate strong biological productivity in surface waters during winter and spring. Diatom genera dominate the phytoplankton community during these months causing the region to become a major sink for biogenic silica [*Sancetta*, 1995] and a seasonal mediator for the net transfer of atmospheric carbon to the marine subsurface [*Thunell*, 1998]. During the summer, winds relax over the central and eastern GC promoting upper water column stratification. Phytoplankton growth in these warm, persistently stratified, central regions rapidly depletes surface waters of nutrients, leading to nitrate concentrations in the surface mixed layer (SML) that are typically below the 0.03 μmol L^{-1} detection limit set by standard autoanalyzer technology. However, summer phosphate concentrations in the SML generally exceed 0.3 μM, indicating a stoichiometric deficit of inorganic N relative to P and hence N-limited primary production.

[3] In the central GC, warm, persistently stratified surface waters in summer coupled with N-deficient but P-replete dissolved nutrient pools represent the ideal ecological conditions for the growth of N_2-fixing organisms (or diazotrophs) [*Karl et al.*, 2002]. Despite the observation of blooms of N_2-fixing organisms in the outer entrance zone to the GC (e.g., Mazatlan Bay [*Mee et al.*, 1984]) and documented episodic summer decreases in the $\delta^{15}N$ values of sediment trap particulate matter in the central basins of the GC (e.g., Carmen and Guaymas Basin) [*Altabet et al.*, 1999; *Thunell*, 1998], neither the presence of N_2-fixing organisms, nor the rate of N_2 fixation has been reported for the GC proper. Additionally, even though there is evidence that summertime primary production is N-limited, export rates of particulate nitrogen (PN) and organic carbon (POC) out of GC surface waters to the deep sea, measured in sediment traps, are not depressed in the summer months relative to the winter upwelling period [*Altabet et al.*, 1999; *Thunell*, 1998]. In this context, the potential that N_2 fixation may supplement PN export in summer has not been explored in the GC. Here we use a combination of microscopy, $^{15}N_2$ uptake experiments, analyses of the isotopic composition of particulate matter, and measurements of ambient nutrient fields to investigate diazotrophic activity in the central basins of the GC. Furthermore, we have analyzed MODIS (MODerate resolution Imaging Spectroradiometer) derived time series of surface chlorophyll *a* (chl *a*) and nighttime sea surface temperature (nSST) for the entire GC region in order to evaluate the occurrence of summer blooms and their spatial distribution, relative to our direct measures of N_2 fixation in the central GC.

2. Methods

2.1. Field Data

[4] Field sampling in the Gulf of California (GC) took place between 23 July and 12 August 2005 aboard the R/V

[1]College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA.
[2]Also at Departmento de Ecologia, Facultad de Ciencias Biologicas, Pontificia Universidad Católica de Chile, Santiago, Chile.
[3]Department of Geology and Geophysics, University of Hawaii at Manoa, Honolulu, Hawaii, USA.

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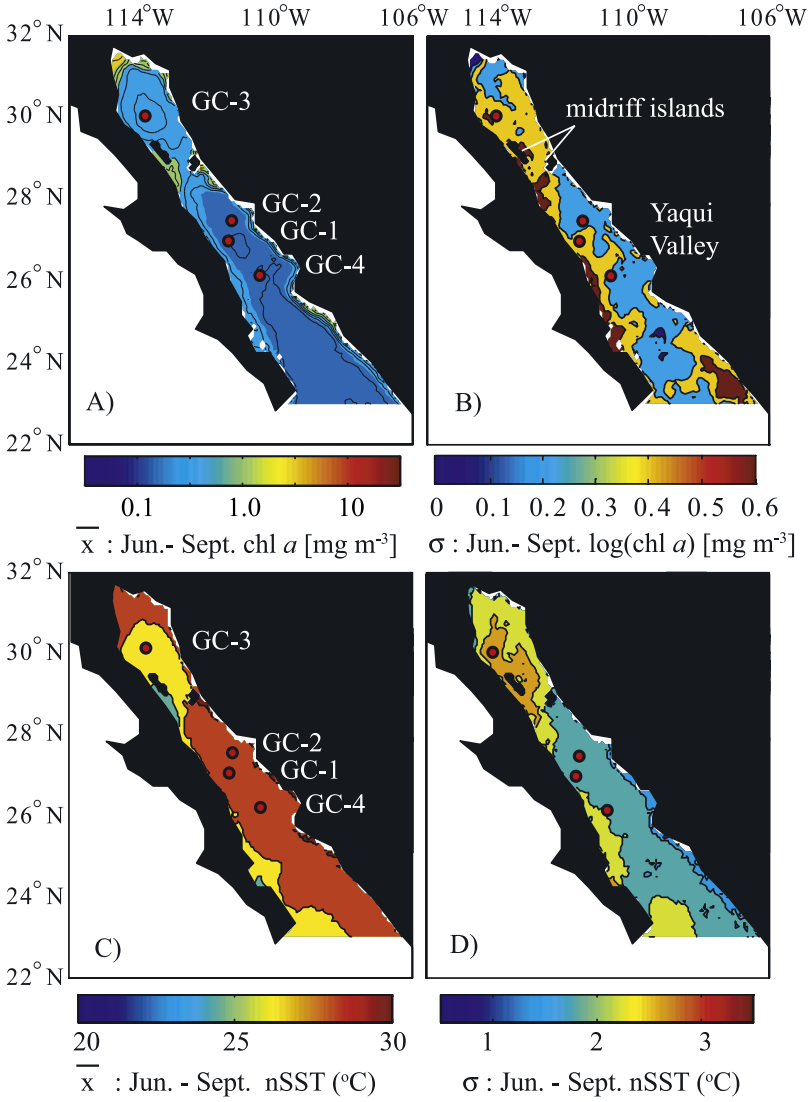

Figure 1. Mean ($\bar{x}$) and standard deviation (σ) fields for (a, b) surface chl *a* and (c, d) nighttime SST (nSST) in the GC calculated for summer months (1 June to 1 September 2002–2005). The color bar for Figure 1a is in linear units while the plot shows the distribution of log(chl *a*). Contour intervals are as follows: Figure 1a, 1.6; Figure 1b, 0.05; Figure 1c, 2.0; and Figure 1d, 0.5. The locations of the four sampling stations (GC-1:GC-4) are denoted as red circles. The midriff islands and the general location of the Yaqui valley irrigation district mentioned in the discussion are shown in Figure 1b.

New *Horizon*. The general cruise path cut along the center of the gulf (~111°W) from roughly 22°N to 30°N with transect excursions for extended station sampling at four sites: GC-1 (27°01′N 111°25′W), GC-2 (27°30′N 111°20′W), GC-3 (30°6′N 113°52′W) and GC-4 (26°4′N 110°7′W) (Figure 1). Samples at each of these stations were collected throughout the upper water column with a CTD-rosette, equipped with PVC sample bottles. Nitrate and phosphate concentrations were measured postcruise following the techniques of *Strickland and Parsons* [1972] while dissolved silicate was determined according to the method of *Armstrong et al.* [1967] as adapted by *Atlas et al.* [1971]. The detection limits (and coefficients of variation) for nitrate, phosphate and silicate measurements were 0.1 μmol L^{-1} (0.2%), 0.02 μmol L^{-1} (1%), and 0.3 μmol L^{-1} (0.5%), respectively. The parameter N* was calculated from concentration data for nitrate ($[NO_3^-]$) and phosphate ($[PO_4^{-3}]$) following the formulation *of Gruber and Sarmiento* [1997],

$$N^* = \left(\left[NO_3^-\right] - 16\left[PO_4^{-3}\right] + 2.9\right)0.87. \quad (1)$$

[5] At each of the four extended sampling stations, N_2 fixation and carbon uptake rates were measured using ^{15}N-labeled N_2 and ^{13}C-labeled bicarbonate tracers. The general procedure for these measurements is described by *Montoya et al.* [1996]. Briefly, acid-washed and sterilized silicone tubing was used for transfer of samples from rosette bottles

into ~2 L, acid-cleaned and Milli-Q water rinsed polycarbonate bottles. For each incubation depth, duplicate ~2 L volumes were collected for determination of the ambient (time-zero) isotopic composition ($\delta^{15}N$, $\delta^{13}C$) of particles and volumetric concentrations of particulate organic carbon (POC) and nitrogen (PN). All incubation bottles were filled to overflowing before being carefully sealed with a septum cap (Teflon-lined butyl rubber). To each bottle, 0.5 mL of N_2 (99 atom% ^{15}N-labeled, Cambridge Isotope Laboratories) was injected using a gas-tight syringe while 0.25 mL of a 0.05 molar $NaHCO_3$ (99 atom% ^{13}C-labeled, Cambridge Isotope Laboratories) solution was added using a separate, plunger-type syringe. Sample bottles were gently mixed and attached to an in situ array for a period of 24 hours. With the exception of GC-2, bottles were incubated at five depths (~5 m, 15 m, 20 m, 25 m and 35 m) for each array deployment (GC-1, GC-3 and GC-4). At GC-2, bottles were only deployed at four incubation depths (~5 m, 15 m, 20 m and 25 m). The design of the free-floating array and the procedure used for its deployment followed that described by *Prahl et al.* [2005a]. At the end of each incubation period, suspended particles were collected by gentle vacuum filtration through a 25-mm precombusted (450°C for 12 hours) GF/F filter. Filters were immediately stored at −20°C in an onboard freezer. Once ashore, samples were acid-fumed, dried overnight at 60°C and then encapsulated in tin cups for analysis of their $\delta^{15}N_{PN}$ and $\delta^{13}C_{POC}$ composition using the methodology described by *Prahl et al.* [2005a].

[6] At select depths (~5 m, 10 m or 15 m, and 25 m) at every station, 0.5 L water samples were collected for microscopy. This entire volume was filtered onto Irgalan black-stained, 0.2 μm pore diameter Nuclepore membrane filters using gentle vacuum filtration. Each filter was then fixed in 2.5% final concentration SEM grade gluteraldehyde and mounted onto glass slides. All slides were kept frozen at −20°C in slide boxes until counts were performed. For each slide, the entire filter field was counted using UV-epifluorescence microscopy for enumeration of individual diazotrophs.

[7] Both ^{13}C and ^{14}C fixation rates were measured during this cruise. However, only ^{13}C rates are presented since these measurements are available for all stations, while ^{14}C rate measurements (from C. Dupont, Scripps) were only available for stations GC-2 and GC-3. From ^{14}C rate measurements, it was determined that dark bottle rates were 15% of light bottle rates, on average. Thus a 15% dark correction has been applied to all ^{13}C measurements. For the two stations where concurrent ^{13}C and ^{14}C rates are available, the linear regression of productivity profiles are significant with > 95% confidence (GC-2: $^{14}C = 0.83*^{13}C + 0.25$, $r^2 = 0.91$, $p = 0.04$, n = 8; GC-3: $^{14}C = 3.2*^{13}C - 1.93$, $r^2 = 0.92$, $p = 0.04$, n = 8).

[8] Volumetric $^{15}N_2$ fixation rates (nmol N L^{-1} hr^{-1}, equation (2)) were calculated according to *Montoya et al.* [1996] using the equation

$$N_2 \text{ fixation} = \frac{1}{\Delta t}\left(\frac{A_{PN_f} - A_{PN_0}}{A_{N_2} - A_{PN_0}}\right)\frac{PN_f}{V}, \qquad (2)$$

where A_{N2}, A_{PN0} and A_{PNf} are percent abundance ratios (A) for $^{15}N_2$ additions, the PN pool at time zero and the PN pool at the end of the experiment, respectively. The volume (V) for all 24-hour (Δt) incubations was 2.3 L.

2.2. Satellite Imagery

[9] Chlorophyll *a* (chl *a*) and nighttime sea surface temperature (nSST) data for the region between 22°N−32°N and 106°W−116°W were obtained from the 8-day, 9-km, level-3 MODIS data for the period from July 2002 to December 2005 (Figure 1). MODIS data were provided by NASA/Goddard Space Flight Center and accessed via http://oceancolor.gsfc.nasa.gov. In each image, black areas represent land or clouds while white is used to depict regions outside the area of interest. All statistical analyses of chl *a* are calculated from the log transformed data because this property is lognormally distributed and varies spatially and temporally across the GC by over an order of magnitude. The calculated sample mean ($\overline{x}$) and standard deviations (σ) are then converted to linear units.

[10] The residual of sea surface height (SSH) for the GC was obtained from weekly, ⅓° by ⅓° resolution, merged TOPEX/Poseidon and ERS satellite altimetry data. Gridded wind speed data was obtained from JASON-I altimetry. These altimeter products were produced by Ssalto/Duacs and distributed by Aviso, with support from Cnes (www.aviso.oceanobs.com). All data (SSH and wind speed) were spatially averaged for the central GC region (26°N−28°N, 110°W−111°W). Monthly averages of SSH anomalies represent monthly binned data for the period from October 1992 to January 2005. Wind speed data are averaged by month using data for the period of February 2004 to March 2006.

2.3. Definition of Summer Bloom Events

[11] We calculated the summer (1 June to 1 September) mean ($\overline{x}$) and standard deviation (σ) of log-transformed chl *a* data for each grid point (~9 km resolution) using 44 mapped, 8-day composite images available for the 2002−2005 summer seasons. This data resolution was chosen to provide a general picture of chl *a* and temperature fields in the GC. Using $\overline{x}$ and σ values for the log normal chl *a* data, a z-score $[(x - \overline{x})/\sigma]$ was calculated for each grid point (x) at every 8-day summer composite. Summer bloom events are then defined when the z-score at a single location is greater than or equal to 1.0. This definition of a bloom evaluates chl *a* values relative to the temporal summer mean and standard deviation at the spatial scale of the individual grid point (~9 km). Bloom events are divided between those coinciding with nSST values of <27°C and those coinciding with nSST values ≥27°C in order to conservatively segregate those blooms that may be associated with the upwelling of colder, nutrient-rich waters from those associated with stable water column stratification favoring N_2 fixation. Nighttime temperatures are used to eliminate the diurnal variation caused by solar heating at the sea surface.

3. Results and Discussion

[12] Changes in the position of the North Pacific high-pressure center relative to the adjacent continental low result

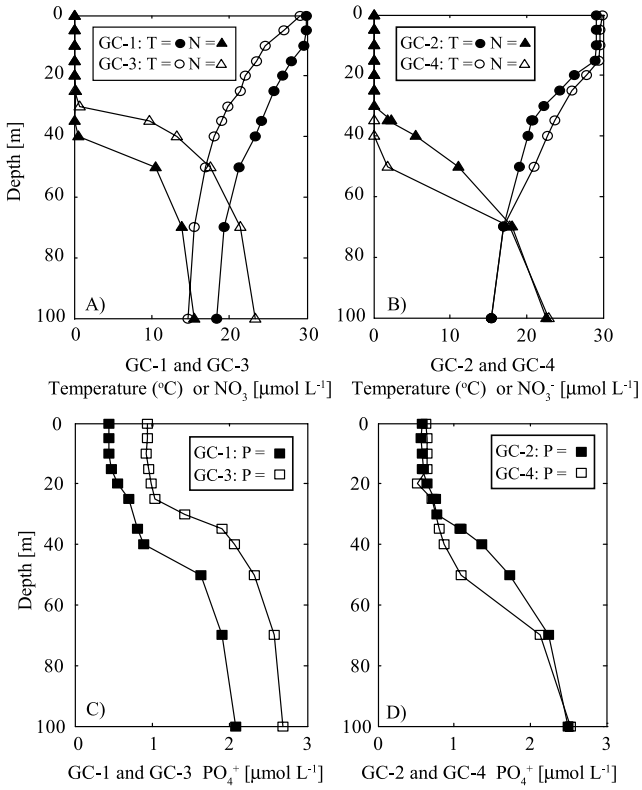

Figure 2. Depth profiles of (a, b) nitrate (NO_3^-), temperature, and (c, d) phosphate (PO_4^+) measured at stations GC-1 and 2 (Figures 2a and 2d) and GC-3 and 4 (Figures 2b and 2c). Surface waters at all stations are favorable for the growth of N_2-fixing organisms (shallow mixed layer depths, undetectable NO_3^-, and high PO_4^+ concentrations).

in seasonally reversing winds that act as the primary control on circulation and mixing throughout most of the GC [*Thunell et al.*, 1996]. In the summer, relatively weak winds from the south generate upwelling along the western margin of the GC that can be seen as regionally high mean chl *a* concentrations coupled to lower mean nighttime sea surface temperature (nSST) values along the interior of the Baja peninsula (Figures 1a and 1c). Mean chl *a* concentrations are also elevated in the waters surrounding the archipelago of midriff islands, where strong tidal mixing brings colder, nutrient-rich waters from depth to the surface. In both cases (upwelling and tidal mixing), nutrient infusions support greater concentrations of phytoplankton biomass in surface waters (Figure 1a) [*Gaxiola-Castro et al.*, 1999].

[13] The summer upwelling zones, that are highly constrained areally and characterized by higher biomass and higher variability (Figure 1b), are contrasted by the much more spatially expansive, relatively warm, lower chl *a* waters of the central to eastern GC below the midriff islands. Field data collected in August 2005 from the central GC (stations GC-1, GC-2 and GC-4) revealed shallow mixed layer depths (~15–20 m), high SST, and nitrate depletion in surface waters (Figure 2). Remote sensing products corroborate these findings. MODIS-derived nSST for the central GC are typically greater than 27°C (Figure 1c) with relatively low variability (Figure 1d) indicative of stable water column stratification. Elevated sea surface height anomalies (SSH) and low wind speeds observed throughout summer months further confirm persistent summer stratification in the central GC (Figure 3). Elevated SSH values are taken here to generally reflect thermal expansion of the central GC waters due to surface heating and thus increased stratification. In combination, field observations and remote-sensing products indicate that the central GC is characterized by warm, stratified waters having low concentrations of dissolved inorganic nitrogen in any chemical form (nitrate, nitrite or ammonium), and relatively high inorganic phosphate concentrations. Thus, throughout the central to eastern GC south of the midriff islands, the prevailing summer conditions represent ideal habitat for production of N_2-fixing organisms [*Karl et al.*, 2002].

[14] In July–August of 2005, we sampled surface waters along a latitudinal transect in the center of the GC with extended depth sampling at four stations (GC-1 and GC-2 in Guaymas Basin, GC-3 in the Delfin Basin and GC-4 in Carmen Basin) (Figure 1). Depth profiles of $^{15}N_2$ fixation showed high integrated rates of N_2 fixation only evident at stations GC-2 and GC-4 (Figure 4a and Table 1). To put these results into the context of oceanic diazotrophy, the rates measured here (GC-2 and GC-4) are comparable to that measured in the subtropical North Pacific [*Karl et al.*, 1997] and the tropical North Atlantic [*Capone et al.*, 2005], regions for which the ecological importance of biological N_2 fixation has been well documented. Using the average C:N ratio for marine plankton (6.6 as per *Redfield* [1958]), N_2 fixation accounted for as much as 4–6% of depth integrated ^{13}C fixation rates (Table 1), with the contributions as high as 10% in near surface waters (Figure 4b). In close correlation with ^{15}N rate measurements, epifluorescence microscopy indicated substantial numbers of the endosymbiont *Richelia intracellularis* occurring in association with the centric diatom *Rhizosolenia* at stations GC-2 and GC-4 (Figure 4d). Concentrations of *Richelia* were less than 100 L^{-1} in the surface mixed layer at GC-1 and GC-3. The host organism, *Rhizosolenia,* has been described as one

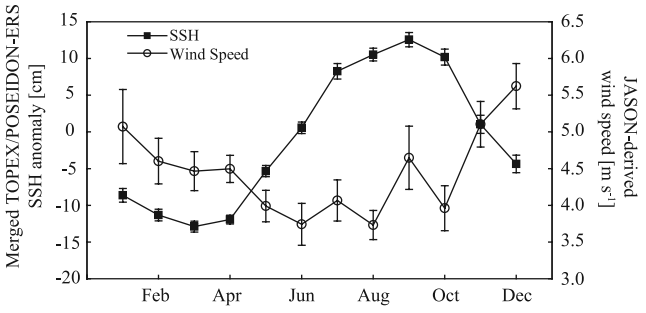

Figure 3. Monthly mean wind speed (via JASON-I altimetry) and SSH anomalies (via merged TOPEX-Poseidon and ERS altimetry) for the region of 26°N–28°N and 110°W–111°W in the central GC.

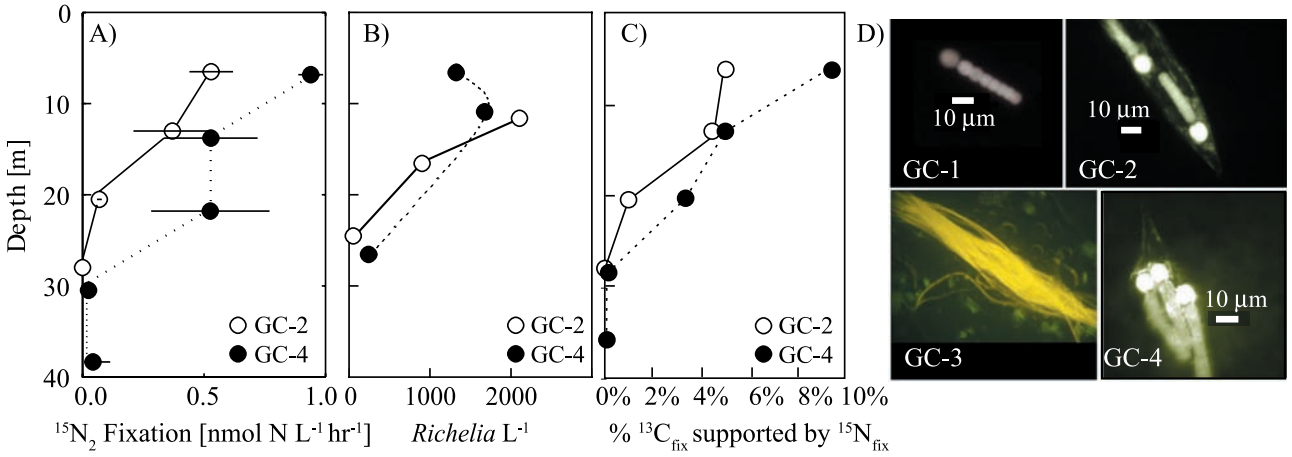

Figure 4. (a) Results of measurements of $^{15}N_2$ fixation rate assays from 24-hr free-floating incubations show significant N_2 fixation occurring in Guaymas (GC-2) and Carmen (GC-4) basin. (b) Depth distributions of *Richelia* heterocysts L^{-1} for stations GC-2 and GC-4. (c) The percentage of ^{13}C fixation that can be accounted for by $^{15}N_2$ fixation as a function of depth. N_2 fixation rates were converted to C fixation rates using measured values for the POC:PN ratio. (d) Select epifluorescence images from each station. Free trichomes of *Richelia intracellularis* (GC-1), *Richelia-Rhizosolenia* symbioses (GC-2 and GC-4) and *Trichodesmium* spp. (GC-3) were observed at all stations, however abundance of N_2-fixing organisms was greatest at GC-2 and GC-4.

of the most abundant and common taxa in the GC during summertime [*Kemp et al.*, 2000; *Gárate-Lizárraga et al.*, 2003], yet to our knowledge, symbioses with *Richelia* have never been reported for this region. Species of the N_2-fixing genus *Trichodesmium* were also observed at each of the stations; however these organisms were not found in abundances greater than 36 filaments L^{-1} or 2 colonies L^{-1}. *Trichodesmium* has only previously been described in the lagoons of the eastern GC [*Gilmartin and Revelante*, 1978] and in the outer entrance zone of the GC [*Mee et al.*, 1984].

[15] In July of 2004, on a previous cruise to the GC, abnormally high $\delta^{13}C$ values of POC were observed in the SML at our Guaymas basin station (GC-2, $\delta^{13}C = -15.0$ to -15.5‰, Figure 5). These surface values are consistent with the isotopic signature documented for colonial forms of *Trichodesmium* spp. isolated from the subtropical Atlantic, whose $\delta^{13}C$ content is surprisingly enriched (-15.2 to -11.9‰) relative to typical marine phytoplankton [*Carpenter et al.*, 1997]. Further isotopic analyses of a normal alkane (nC17), observed in the SML at GC-2 in July 2004 and known to be a dominant hydrocarbon in *Trichodesmium* [*Carpenter et al.*, 1997], also showed anomalously high values ($\delta^{13}C$ of nC17 = -13‰, [*Prahl et al.*, 2005b]) suggesting that the $\delta^{13}C$ values specific to *Trichodesmium* was ~-10 to -9‰ in surface waters in July 2004. High $\delta^{13}C_{POC}$ values were not observed in the summer of 2005 (Figure 5), consistent with low abundances of *Trichodesmium*.

[16] The $\delta^{15}N$ of particulate nitrogen (PN) reflects the isotopic composition of the nitrogen source used by biota as well as the biological fractionation that occurs during uptake and assimilation of this element. In the absence of appreciable N_2 fixation or terrestrial inputs of fixed N, the average $\delta^{15}N$ values measured in the particulate pool should reflect the $\delta^{15}N$ of subsurface nitrate when there is complete utilization of nitrate in the mixed layer. In the central GC, subsurface nitrate has been preferentially ^{15}N-enriched as a consequence of denitrification acting along the path of its circulation through the Eastern Tropical Pacific, resulting in its isotopically heavy $\delta^{15}N$ signal (~11‰, depth 100–300 m [*Altabet et al.*, 1999]). If N_2 fixation were occurring in surface waters of the GC, the biological input of atmospheric N_2 (~0‰ [*Carpenter et al.*, 1997]) would lead to very significantly reduced values of $\delta^{15}N_{PN}$. Along our 2005 cruise transect, surface water samples were

Table 1. Integrated (0–36 m) Rates of $^{15}N_2$ Fixation and ^{13}C Fixation at Each of the Four Sampling Stations[a]

Station	Integrated $^{15}N_2$ Fixation, µmol N m^{-2} d^{-1}	Integrated ^{13}C Fixation, mmol C m^{-2} d^{-1}	Percent of C Fixation Accounted for by N Fixation, %	Surface $\delta^{15}N$ of PN, ‰
GC-1	20	41	0.3	9.4
GC-2	132	15	5.8	5.7
GC-3	23	114	0.1	10.5
GC-4	250	48	3.4	8.6

[a]The Redfield C:N ratio of 6.6 was used to calculate the percent of C fixation that could have been supported by these measured N_2 fixation rates. Surface $\delta^{15}N_{PN}$ measurements were taken from depths of ~5 m.

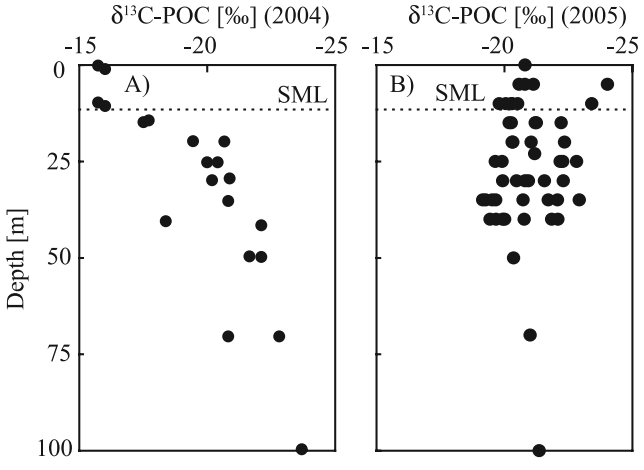

Figure 5. Isotopic analyses of $\delta^{13}C$ composition of particulate organic carbon (POC) indicate transitions in community structure at the Guaymas Basin station (GC-2). (a) In July 2004, $\delta^{13}C$-POC values were highly enriched in the surface mixed layer (SML, dashed line), transitioning to more typical values (−21.5‰) at depth. In contrast, (b) the $\delta^{13}C_{POC}$ data in the summer of 2005 from all stations were relatively more uniform with depth (∼−21.5‰) and showed no apparent enrichment in the SML.

collected at ∼0.5° latitude intervals from the ship's flow-through seawater system for analysis of the $\delta^{15}N_{PN}$ composition of suspended particulate materials. PN with relatively low $\delta^{15}N$ values (5.8−7.1‰) was observed in the Northern Guaymas and Carmen basins (Figure 6a). These findings suggest that N_2 fixation (∼0‰) has contributed significantly to the standing stock of phytoplankton-derived PN in the surface waters of the central GC.

[17] Vertical profiles of $\delta^{15}N_{PN}$ and the parameter N* are shown in Figure 7. When N_2 fixation was not observed (i.e., GC-3, Figure 7c) and in winter months (GC-2, Figure 7a), values of $\delta^{15}N_{PN}$ (10−13‰) are indicative of nitrate-supported growth ($\delta^{15}N_{NO3}$ ∼11‰ [*Altabet et al.*, 1999]). Conversely, when nitrogen fixation rates are high (e.g., summer 2005, GC-2, Figure 7b), $\delta^{15}N_{PN}$ profiles show a shift toward much lighter values in the surface mixed layer (SML). This trend is consistent with biological N_2 fixation contributing significantly to PN in the SML. N* profiles are also consistent with the occurrence of significant N_2-fixation in the warm, persistently stratified surface waters south of the midriff island in summer (Figure 7b) but not in warm, stratified surface waters to the north in summer (Figure 7c) or in the cold, more deeply mixed waters to the south in winter (Figure 7a). Waters throughout the GC that underlie the euphotic zone and are capable of being upwelled, display an N* of ∼−12 (Figure 7). This value is much more negative than that characteristic of deep waters throughout most of the ocean (N/P ∼15, N* = +1.7) owing to the impact of denitrification as the open ocean source water passes through the oxygen minimum zone of the Eastern Tropical Pacific and circulates into the GC. Primary productivity in GC surface waters will reduce the nutrient content of any upwelled water but without changing its N* signature if the autotrophic process removes dissolved nitrate and phosphate in Redfield proportions (i.e., 16:1). However, contributions from N_2 fixation, an autotrophic process, which removes only dissolved phosphate and perhaps even adds nitrate, would shift the −12 value positively. Such positive shifts of

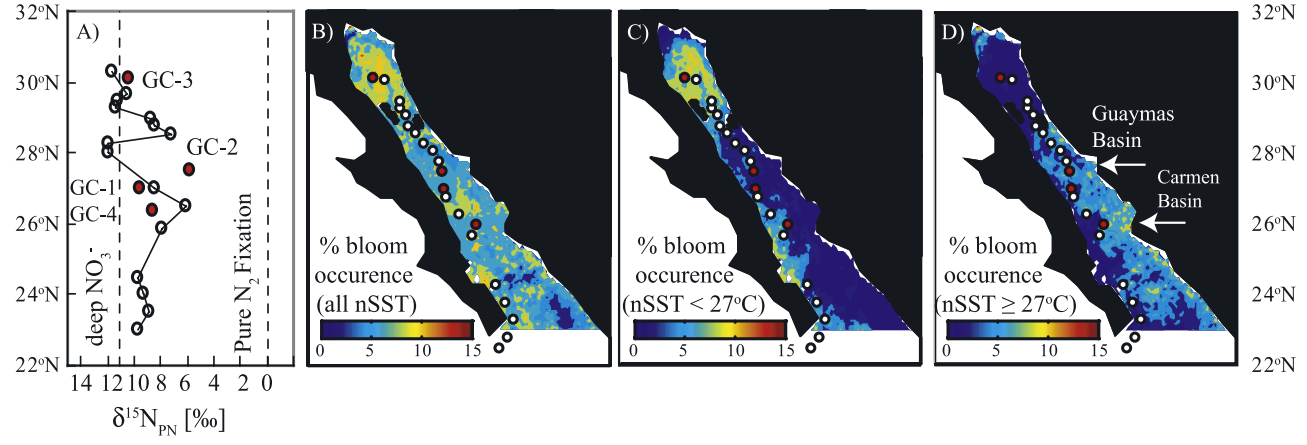

Figure 6. (a) The $\delta^{15}N$ values for PN samples from the surface mixed layer as a function of latitude for all transect (open circles) and extended station (solid circles, GC-1, GC-2, GC-3, and GC-4) locations. The dashed lines indicate the $\delta^{15}N$ value expected for deep water nitrate (∼11‰ [*Altabet et al.*, 1999]) and measured in PN at the bottom of the photic zone for these sites, and the $\delta^{15}N_{PN}$ value expected for pure N_2 fixation (0‰). (b−d) Percentage of the total number of summer MODIS chl *a* composites (8-day) having a z-score greater than 1 (e.g., a bloom) and having (Figure 6b) any retrieved nSST value, (Figure 6c) nSST < 27°C, and (Figure 6d) nSST ≥ 27°C. The location of transect (open circles) and extended station sampling sites (solid circles) are overlain on all bloom maps.

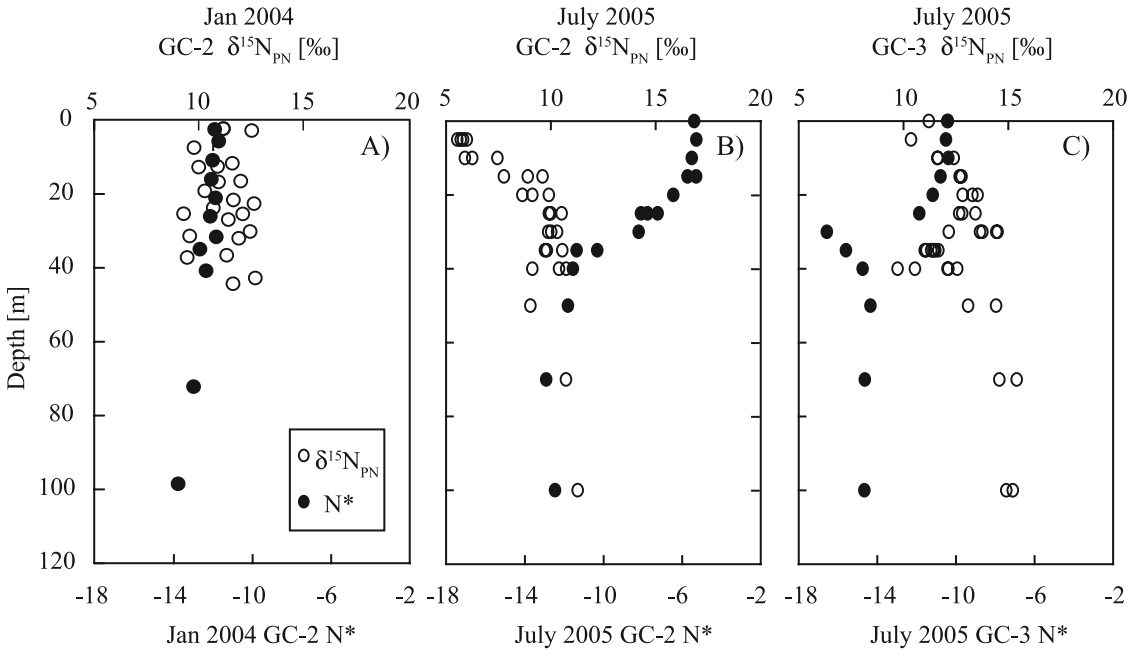

Figure 7. Vertical profiles of the stable isotopic composition of particulate nitrogen ($\delta^{15}N_{PN}$) and the parameter N* (= ([NO_3^-] − 16 [PO_4^{-3}] + 2.9)0.87 [*Gruber and Sarmiento*, 1997]) for GC-2 sampled in (a) January and (b) July 2005 and (c) for GC-3 in July 2005.

any significance were only apparent in the N* profiles for surface waters from the GC south of the midriff islands in summer.

[18] Regenerated N sources (1.5−2.0‰) [*Altabet*, 1988] or DON (1 to 2‰) [*Abell et al.*, 1999] may also contribute to some portion of the recorded $\delta^{15}N$ signal. So, while we cannot unequivocally identify which N source may be responsible for the relatively light PON found in the central GC basins, our observations of very large numbers of organisms actively fixing N_2 coincident with the regions of low $\delta^{15}N$ values, less negative N* and significant measured rates of N_2 fixation, lead us to conclude that N_2 fixation has driven these isotopic diversions. Using a simple two end-member mixing model assuming a light (0‰) and a heavy (11‰) isotopic source of N, representing respectively N_2 fixation and a supply of deep nitrate, we estimate that N_2 fixation can account for as much as 35−48% of the $\delta^{15}N$ signature associated with standing stock in the central GC basins.

[19] *Altabet et al.* [1999] have reported summer minima (5.5−6.6‰) in the $\delta^{15}N$ of PN settling into sediment traps deployed in the Guaymas and Carmen basins between 1990 and 1996. These minima are similar in magnitude to our measured $\delta^{15}N$ values for suspended PN in the SML of these same basins. This observation, particularly when considered in perspective with the N* results described above, clearly underscores the potential for the export of primary production derived from N_2 fixation to depth. The summer-derived particulate material reaching the sediment may then record the net effect of surface N_2 fixation and water column denitrification. *Altabet et al.* [1999] considered this possibility, however they concluded that the episodic summer $\delta^{15}N$ minima could not be driven by N_2 fixation for the reason that the recorded trap $\delta^{15}N$ minima were intermittent over their ∼6-year record, thus requiring that N_2 fixation would have to "turn on" only during certain periods.

[20] In other marginal seas such as the Arabian [*Capone et al.*, 1998] and the Red Sea [*Post et al.*, 2002], blooms of large N_2 fixers such as the genera we have described (i.e., *Richelia* symbioses, *Trichodesmium*) are known to occur episodically under stratified summer conditions. Given that biological N_2 fixation requires a high light environment and that diazotrophs are at a competitive disadvantage in the presence of nitrate, it is expected that N_2 fixation would be enhanced in the GC only during summer months when highly stratified, dissolved inorganic nitrogen-poor conditions are common.

[21] Shifts in the diazotrophic community structure may further help to explain the interannual variability observed in these sediment trap $\delta^{15}N$ values. Specifically, whereas *Trichodesmium* are strongly buoyant, nonbiomineralized organisms typically resistant to sedimentation, *Richelia-Rhizosolenia* symbioses are packaged in a relatively heavy silica shell, potentially facilitating more rapid export from the SML. Thus material derived from *Richelia*-supported diatom blooms in summer may be more likely to reach the depth of sediment traps (∼650 m) and result in $\delta^{15}N_{PN}$ minima than that derived from *Trichodesmium* supported blooms. A logical extension of this problem is to investigate whether or not summer blooms occur in the GC, and if so, are they spatially consistent with our findings of N_2 fixation in the central GC.

[22] To examine the spatial and temporal patterns of phytoplankton biomass in the GC, we have calculated summer (period from 1 June to 1 September) maps for the

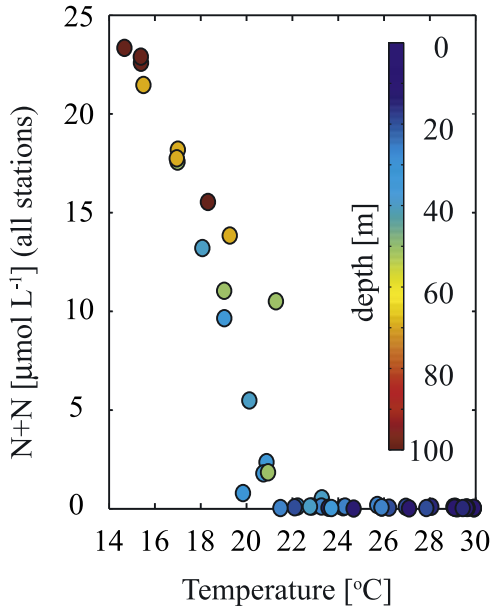

Figure 8. Nitrate plus nitrate (N + N) concentrations as a function of water temperature for samples collected from all stations in July–August of 2005. Symbol color corresponds to sample depth. N + N concentrations are typically below the detection limits of standard autoanalyzer technology at temperatures greater than ~22°C.

mean ($\bar{x}$) and standard deviation (σ) of the 9-km, 8-day resolution MODIS-derived chl *a* in the region of 22°N–32°N, 116°W–106°W. From these maps, all 9-km pixels within any one 8-day composite (x) with a z-score ($[x - \bar{x}]\ \sigma^{-1}$]) greater than one were defined as a bloom event. Over the four summer periods in the 2002 to 2005 timeframe, we found that, on average, summer bloom events occur in ~10% of the individual time series. Spatially, these events are concentrated primarily in the northern GC with patches occurring in the central regions (Figure 6b). We also analyzed the 9-km, 8-day resolution MODIS-derived nighttime sea surface temperature (nSST) in order to discern the temperature characteristics coincident with summer blooms. Average chl *a* concentrations during these bloom events are 0.79 mg m^{-3}, roughly twice the regionally averaged, mean summer chl *a* concentration (0.38 mg m^{-3}). The average nSST coinciding with summer bloom events is 27.0°C.

[23] In the north and along the western margin of the GC, where upwelling and strong mixing, respectively, are common in summer, we would expect that the majority of the defined bloom events would be associated with lower nSST. Conversely, if biological N_2 fixation were supporting phytoplankton blooms, we would expect these blooms to occur in persistently warm, highly stratified, nitrate-poor surface waters. It is also conceivable that summer blooms occurring in warmer waters on the east side of GC could be driven by anthropogenic inputs of N via riverine sources (as per *Beman et al.* [2005]). This latter possibility seems unlikely, however, as peak irrigation events are isolated to winter and spring months [*Beman et al.*, 2005]. *Gaxiola-Castro et al.* [1999] report that nitrate is nondetectable in surface waters having temperatures greater than 24°C. Our own summer data (Figure 8), show that dissolved inorganic nitrogen in the form of either nitrate, nitrite or ammonium form is essentially undetected above 22°C, with all sampled locations having N-depleted surface waters. Thus, in order to evaluate these blooms most conservatively, we chose 27°C as a threshold temperature to indicate the transition between conditions favorable for upwelling of waters enriched in nitrate to the SML, supporting classical phytoplankton blooms, from those bloom events presumed favorable for N_2 fixation.

[24] Given that 90% of the water-leaving radiances used to derive estimates of ocean color originate from within the first optical depth [*Gordon and McCluney*, 1975] (defined as the depth at which irradiance decreases by e^{-1}) we estimate that MODIS data should be representative of chl *a* concentrations within the top ~10–15 m of the water column during typical summer conditions (Figure 9). For stations GC-1: GC-4, we calculate the first optical depth as 8 m, 15 m, 12 m and 10 m, respectively. These limits are well above the depth of the chl *a* maximum (Figure 9) and the position of the top of the nitracline (30–40 m or 2–3 optical depths, Figure 2). Thus, from the observed vertical distribution of chl *a* and dissolved nitrogen in the central GC, it is unlikely that MODIS-derived estimates of chl *a* corresponding to surface waters with temperatures greater

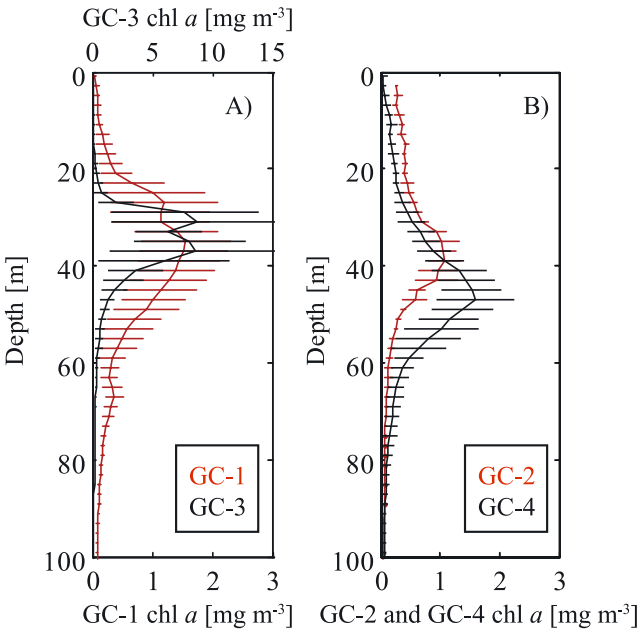

Figure 9. Chlorophyll *a* concentrations derived from a CTD mounted fluorometer as a function of depth. Data from multiple casts were averaged by 2-m increments. Error bars represent the standard deviation of these 2-m binned chl *a* concentrations. The first optical depth (the depth at which surface irradiance is decreased by e^{-1}) was equivalent to 8 m, 15 m, 12 m, and 10 m for stations GC-1, GC-2, GC-3, and GC-4, respectively.

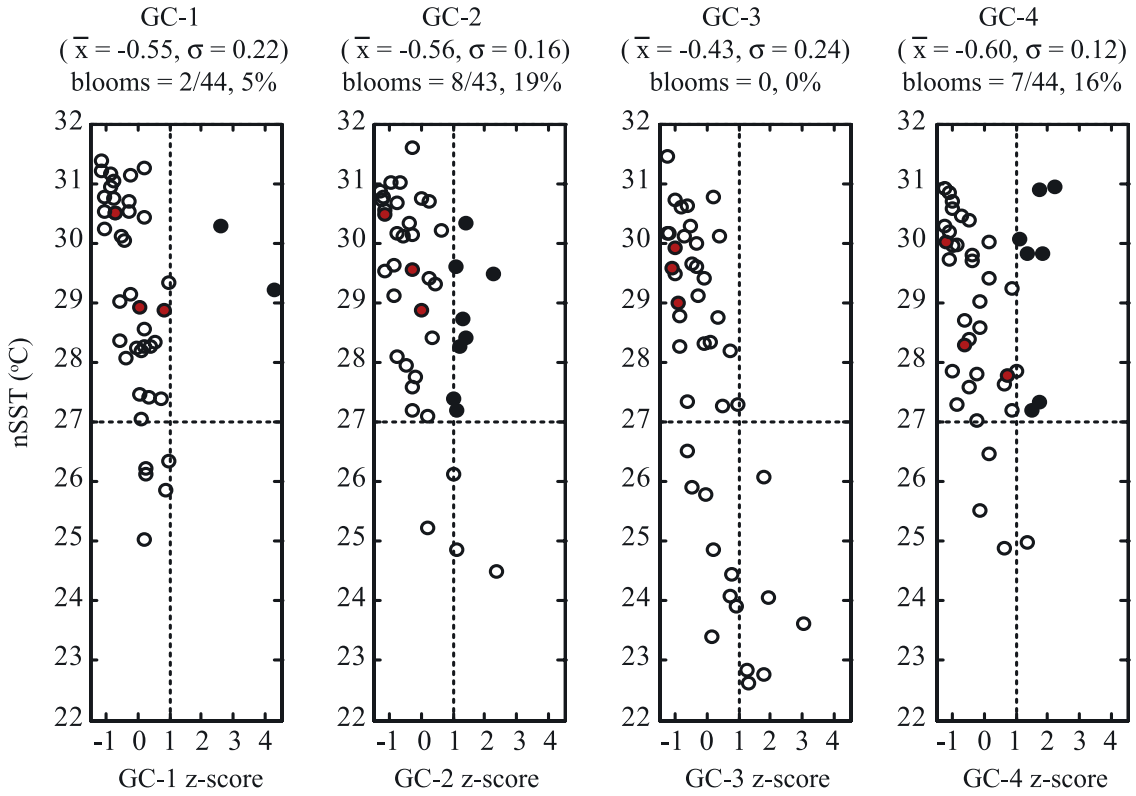

Figure 10. The z-score calculated for each 8-day summer composite at each station location versus the nSST for the same 9-km pixel of an 8-day composite. Bloom events defined to be consistent with biological nitrogen fixation (nSST > 27°C) are noted as solid circles. At this resolution, blooms were not evident in the ±8 day period (n = 3) corresponding to our sampling dates (red circles). The overall $\overline{x}$ of summer log(chl a), the σ and the percentage of bloom events relative to the total number of cloud-free composite summer images are noted in the title of each graph.

than 22°−24°C are associated with the deep chl *a* maxima or the nitracline. Hence we presume that increases in chl *a* in these regions are driven by the biological fixation of atmospheric N_2. (Figure 10)

[25] Figures 6b−6d present spatial maps for the percentage of 8-day summer composites (total summer n = 203,786, bloom n = 15,249) that are defined as a bloom event (Figure 6b) as well as those same blooms segregated according to the nSST threshold of 27°C (Figures 6c and 6d). Blooms co-occurring with nSST < 27°C (n = 7574, $\overline{x}$ chl *a* = 0.91 mg m^{-3}, $\overline{x}$ nSST = 24.7°C) are spatially consistent with wind-driven upwelling along the western GC boundary and tidal mixing around the archipelago in the northern GC. Conversely, those blooms occurring in waters with nSST ≥ 27°C (n = 7675, $\overline{x}$ nSST = 29.3°C, $\overline{x}$ chl *a* = 0.68 mg m^{-3}) coincide with environmental conditions presumed favorable for biological N_2 fixation (i.e., warm, stratified, nitrate poor). These analyses indicate that (1) summer blooms occur regionally in ∼7.5% of the cloud-free MODIS data record for summer periods from 2002 to 2005, (2) approximately half of the summer GC is characterized by nSST > 27°C, thus approximately half of the defined bloom events that occur coincide with nSST > 27°C, and (3) these presumed N_2 fixation supported blooms may result in an approximately twofold increase in chl *a* and presumably primary productivity above the regional summer mean.

[26] The bloom dynamics of locations coinciding with the four field sampling stations have also been analyzed. These station-specific analyses indicate that bloom occurrences having nSST ≥ 27°C occur in 5%, 19%, 0% and 16% of the MODIS data record at GC-1, GC-2, GC-3 and GC-4 locations, respectively. These findings are consistent with our field data showing that the lowest $\delta^{15}N$ values for PN in the SML, the highest N* and the highest measured integrated rates of N_2 fixation were found at stations GC-2 (5.7‰, 132 μmol N m^{-2} d^{-1}) and GC-4 (8.5‰, 250 μmol N m^{-2} d^{-1}) (Table 1). Bloom events were not detected in the ±8 day timeframe corresponding to our sampling dates. However, z-scores for chl *a* concentration were elevated at GC-1 (z-score = 0.82) and GC-4 (z-score = 0.75) in the 8-day composite preceding our sampling dates.

[27] In summary, these analyses suggest that N_2 fixation supported blooms most commonly occur in the central GC (specifically, GC-2 and GC-4), albeit the presence of high concentrations of N_2-fixing organisms does not always result in significant increases in satellite-derived chl *a*.

[28] Both satellite analyses (Figure 6d) and direct measurements (e.g., measured N_2 fixation at GC-2 but not at GC-1) suggest spatial patchiness of N_2 fixers in the central and

eastern GC. One potential explanation for this perceived patchiness is that N_2 fixation may turn "on" and "off" in response to an external input of aeolian-supplied limiting nutrients, such as iron. During the summer months in the GC, convective thunderstorms deliver large inputs of terrigenous material, primarily derived from the Sonoran desert [*Baumgartner et al.*, 1991]. These iron-rich aeolian inputs may act to stimulate patches of diazotrophic growth throughout the central GC. Support for this hypothesis lies in the work of *Kemp et al.* [2000] who analyzed laminated sediment cores from Guaymas basin and found that Rhizosolenid diatoms are commonly concentrated at the top of the summer terrigenous lamina. While *Richelia* are not preserved in these laminated sediments, it would be intriguing to extract organic matter from the Rhizosolenid diatom tests in these sediment layers for the analysis of $\delta^{15}N$ composition (as per *Robinson et al.* [2005]) in order to determine whether these sediment strata are also associated with ^{15}N-depleted PN and enhanced N_2 fixation.

4. Conclusions

[29] Our composite analyses have provided evidence that significant rates of N_2 fixation occur in the GC, with satellite proxies confirming increases in primary productivity in the warm, persistently stratified, nitrate-poor, phosphate-replete waters of the central and eastern margins. Rate measurements were reinforced by microscopic analyses showing high concentrations of *Richelia intracellularis* at stations GC-2 and GC-4. While the measured N_2 fixation rates and diazotroph abundances were substantial, the net influx of biologically usable N to the system is probably not sufficient to alleviate nitrogen limitation imposed by the low N:P composition (<10 mol N:mol P) for dissolved nutrients introduced from depth to surface waters. Similarly, even though nitrate concentrations in the SML were below detection limits, the measured $\delta^{15}N_{PN}$ values did not reflect the full signal for N_2 fixation (~0‰), rather surface $\delta^{15}N_{PN}$ values indicated only an ~40% contribution from N_2 fixation to the isotopic composition of standing particulate matter. In terms of daily primary production, $^{15}N_2$ fixation rates accounted for as much as 10% of ^{13}C fixation rates. These composite results indicate that (1) N_2 fixation rates may have been higher prior to our measurements such that the $\delta^{15}N_{PN}$ values reflect the integrated history of diazotrophy at each station and that (2) the predominant fraction of summer production is likely supported by microbial recycling of N sources and/or utilization of dissolved organic N. Alternatively, given that *Rhizosolenia* has a reputed ability to migrate vertically in the water column [*Villareal et al.*, 1996] and that the summertime SML is quite shallow (15–20 m), *Rhizosolenia* may acquire additional N via vertical migration to the depths of the nutricline. Additionally, given that the GC is clearly a N-limited system in summer months, it may be the case that C and N growth is uncoupled [*Goldman et al.*, 1979] and as a consequence C production rates are in excess of the requirements for phytoplankton growth. Despite these unanswered questions, it is now apparent that N_2 fixation plays a significant role in the summer ecology of the GC. Additionally, the remote sensing approach we have advanced in this study, while it may not be capable of confirming the occurrence of N_2 fixation, could also be applied to other regions where biogeochemical indicators of N_2 fixation (low $\delta^{15}N$ values or high N* [*Gruber and Sarmiento*, 1997]) coincide with seasonally warm stratified conditions (e.g., Mediterranean Sea [*Ribera d'Alcalá et al.*, 2003] and the eastern Tropical Pacific [*Sigman et al.*, 2005]) in order to estimate the spatial and temporal extent of N_2 fixation associated events.

[30] Our findings are also in line with a growing body of work suggesting that seasonal N_2 fixation occurs in parts of the surface ocean proximate to regions of intense subsurface denitrification [*Deutsch et al.*, 2007; *Westberry and Siegel*, 2006; *Sigman et al.*, 2005; *Brandes et al.*, 1998; *Capone et al.*, 1998]. While the GC itself is not renowned as a site of localized denitrification, the California Undercurrent brings a supply of suboxic, denitrifying waters from the eastern tropical North Pacific, which intrude into the central GC at depths of 500–1000 m [*Liu and Kaplan*, 1989]. Denitrification, the microbial process by which N electron acceptors (NO_3^-, NO_2^-) are reduced to N_2 to facilitate organic matter degradation, is energetically favorable in low O_2 environments. Hence denitrification occurs in oxygen minima zones where aerobic respiration of biological material raining from sunlit surface waters has depleted dissolved oxygen levels. Locally, the intensity of denitrification influences the concentration of inorganic N and thus decreases the N:P ratio of dissolved nutrients that are delivered to surface waters via upwelling. Given that nitrogen fixation is favored by a low N:P ratio [*Karl et al.*, 2002], upwelling of denitrified waters, if followed by stratification and Redfield-type nutrient drawdown, can prime surface waters for nitrogen fixation and thus lead to potential feedbacks (positive and negative) for export production, the maintenance of the suboxic conditions that favor denitrification [*Sigman et al.*, 2005] and the magnitude of dissolved N:P ratios that are generated in the denitrification zone. In addition to the GC, geographical coupling of N_2 fixation and denitrification has also been strongly suggested to occur in the Arabian Sea [*Brandes et al.*, 1998; *Capone et al.*, 1998] and the eastern tropical Pacific [*Westberry and Siegel*, 2006; *Sigman et al.*, 2005].

[31] In the central GC, the coherence between the $\delta^{15}N$ values measured in our study and previous reports of summer $\delta^{15}N_{PN}$ minima [*Altabet et al.*, 1999] occurring in sediment trap records for Carmen and Guaymas basins, support N_2 fixation as a mechanism for the net export of particulate material. Episodic fluxes of materials derived from N_2 fixation would provide organic matter to fuel denitrification in subsurface waters and dampen the impact that this process has on the magnitude of ^{15}N-enrichment in residual nitrate. In combination with this effect, passage of such ^{15}N-depleted material through the O_2 minimum zone to the sediment record would attenuate the $\delta^{15}N$ of PN that we now tie simply to denitrification intensity. Given the implications of the phenomenon we now identify on global and regional N budgets and the paleoceanographic interpretation of sediment records, further study of the GC region and other locales (e.g., the Arabian Sea and the ETP) where

N_2 fixation and denitrification may be tightly coupled seems necessary and clearly warranted. Potential results from this effort would almost certainly help to refine our current understanding of the past and present marine nitrogen cycle.

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R. M. Letelier, F. G. Prahl, and A. E. White, College of Oceanic and Atmospheric Sciences, Oregon State University, 104 COAS Administration Building, Corvallis, OR 97331, USA. (awhite@coas.oregonstate.edu)

B. N. Popp, Department of Geology and Geophysics, University of Hawaii, Honolulu, HI 96822, USA.