Nitrogen fixation by *Trichodesmium* spp.: An important source of new nitrogen to the tropical and subtropical North Atlantic Ocean

Douglas G. Capone,[1] James A. Burns,[1,2] Joseph P. Montoya,[3] Ajit Subramaniam,[4] Claire Mahaffey,[1,5] Troy Gunderson,[1] Anthony F. Michaels,[1] and Edward J. Carpenter[6]

Received 6 July 2004; revised 19 January 2005; accepted 9 March 2005; published 8 June 2005.

[1] The broad distribution and often high densities of the cyanobacterium *Trichodesmium* spp. in oligotrophic waters imply a substantial role for this one taxon in the oceanic N cycle of the marine tropics and subtropics. New results from 154 stations on six research cruises in the North Atlantic Ocean show depth-integrated N_2 fixation by *Trichodesmium* spp. at many stations that equalled or exceeded the estimated vertical flux of NO_3^- into the euphotic zone by diapycnal mixing. Areal rates are consistent with those derived from several indirect geochemical analyses. Direct measurements of N_2 fixation rates by *Trichodesmium* are also congruent with upper water column N budgets derived from parallel determinations of stable isotope distributions, clearly showing that N_2 fixation by *Trichodesmium* is a major source of new nitrogen in the tropical North Atlantic. We project a conservative estimate of the annual input of new N into the tropical North Atlantic of at least 1.6×10^{12} mol N by *Trichodesmium* N_2 fixation alone. This input can account for a substantial fraction of the N_2 fixation in the North Atlantic inferred by several of the geochemical approaches.

Citation: Capone, D. G., J. A. Burns, J. P. Montoya, A. Subramaniam, C. Mahaffey, T. Gunderson, A. F. Michaels, and E. J. Carpenter (2005), Nitrogen fixation by *Trichodesmium* spp.: An important source of new nitrogen to the tropical and subtropical North Atlantic Ocean, *Global Biogeochem. Cycles*, *19*, GB2024, doi:10.1029/2004GB002331.

1. Introduction

[2] Most of the world's oceans are depleted in inorganic nitrogen at the surface. In these extensive areas, it has been traditionally thought that the level of net biological activity is sustained by the mixing of nitrate from below. This flux of "new" nitrogen in the sense of *Dugdale and Goering* [1967] into the euphotic zone supporting primary production is balanced by concomitant losses through sinking particles, vertical migration, and mixing of organic nitrogen out of the upper ocean [*Eppley and Peterson*, 1979; *Lewis et al.*, 1986; *Platt et al.*, 1992]. Although N_2 fixation was explicitly identified as a component of N input in the original formulation of the new production paradigm [*Dugdale and Goering*, 1967; *Eppley and Peterson*, 1979], it has rarely been considered in the subsequent application of this approach, perhaps owing to a paucity of quantitative information on N_2 fixation rates and diazotroph abundance.

[3] Estimates of the nitrogen demand of new production, however, have often exceeded the nitrate flux into the euphotic zone [*Jenkins*, 1988; *Lewis et al.*, 1986], and such estimates have prompted speculation about unknown or poorly quantified N inputs [*Karl et al.*, 2002; *Legendre and Gosselin*, 1989]. In the near-surface waters of the oligotrophic Bermuda Atlantic Time Series (BATS) station, total dissolved inorganic carbon concentrations (DIC) often decline through the summer despite the lack of combined nitrogen in the upper water column, implying the existence of either N_2 fixation, atmospheric inputs of nitrogen, significant deviations from Redfield stoichiometry, or some combination of these three mechanisms [*Michaels et al.*, 1994]. Large deficits exist in N budgets of the North Atlantic [*Michaels et al.*, 1996]. Analysis of oceanic nutrient fields using a parameter termed N* (or alternatively, DINxs per [*Hansell et al.*, 2004]), which quantify deviations in regeneration stoichiometry of N and P, relative to canonical Redfield values (N:P of 16:1), finds large areas of the tropical and subtropical North Atlantic with nitrate:phosphate ratios in subeuphotic zone waters exceeding the Redfield value [*Michaels et al.*, 1996; *Gruber and Sarmiento*, 1997]. Similarly, studies of the distribution

[1]Wrigley Institute for Environmental Studies and Department of Biological Sciences, University of Southern California, Los Angeles, California, USA.
[2]Now at Quileute Natural Resources, LaPush, Washington, USA.
[3]School of Biology, Georgia Institute of Technology, Atlanta, Georgia, USA.
[4]Lamont Doherty Earth Observatory of Columbia University, Palisades, New York, USA.
[5]Now at Department of Oceanography, School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, Hawaii, USA.
[6]Romberg Tiburon Center, San Francisco State University, Tiburon, California, USA.

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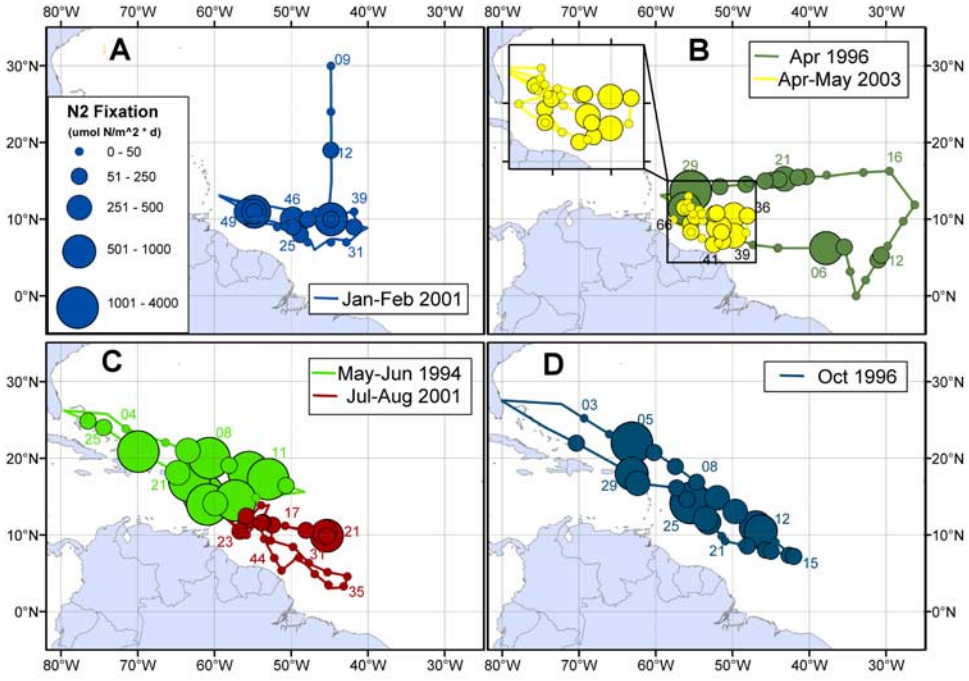

Figure 1. Cruise tracks and spatial and temporal distribution of depth-integrated nitrogen fixation by *Trichodesmium* in the tropical North Atlantic basin for the six Atlantic cruises. (a) Winter cruise aboard R.V. *Seward Johnson* in January and February 2001. (b) Spring cruises in April 1996 and April and May 2003 aboard R.V. *Seward Johnson*. (c) Summer cruises May–June 1994 aboard R.V. *Gyre* and July and August 2001 aboard R.V. *Knorr*. (d) Fall cruise aboard R.V. *Seward Johnson* in October 1996. The N_2 fixation rates for all the cruises are found in Supplemental Table 1. Circle area is proportional to the N_2 fixation rates as shown in the figure legend. Stations with no data are not shown.

of the stable isotopes of nitrogen in particulate matter [*Altabet*, 1988; *Montoya et al.*, 2002; *Mahaffey et al.*, 2003], zooplankton [*Montoya et al.*, 2002; *McClelland et al.*, 2003], and nitrate pools [*Montoya et al.*, 2002; *Brandes et al.*, 1998] in surface and near-surface waters of the oligotrophic tropics indicate significant inputs of ^{15}N-deplete N pool, presumably derived from N_2 fixation. The role of N_2 fixation in the marine nitrogen cycle has been undergoing increasing scrutiny and re-evaluation over the last decade [*Karl et al.*, 2002; *Zehr and Ward*, 2002], leading to increased estimates of its role in supporting oceanic new production.

[4] *Trichodesmium*, a filamentous, non-heterocystous cyanobacterium that is found throughout warm oligotrophic oceans [*Capone et al.*, 1997], is the most conspicuous marine N_2 fixing organism. In the North Atlantic, the most common species is *T. thiebautii*, which occurs as macroscopic aggregates containing from 100 to over 200 trichomes (filaments) or, less frequently, as free trichomes. Densities range from about 10 to over 10,000 trichomes per liter [*Carpenter et al.*, 2004; *Tyrrell et al.*, 2003] and most trichomes are found in the upper 50 m of the water column [*Carpenter et al.*, 2004; *Carpenter and Price*, 1977]. While an early analysis of N_2 fixation by *Trichodesmium* concluded that it was of relatively minor significance in the marine N cycle [*Carpenter*, 1983a], that analysis relied upon historical records of *Trichodesmium* that likely underestimated population densities [*Capone and Carpenter*, 1999].

[5] During the period 1994–2003, we made direct measurements of N_2 fixation by *Trichodesmium* during a series of six research cruises in various seasons largely in the western tropical North Atlantic Ocean from the equator to 30°N (Figure 1). This is an area of the Atlantic for which there is a relative paucity of data for biological processes in general and N_2 fixation in particular [*Lipschultz and Owens*, 1996]. We occupied a total of 154 stations. The purpose of this paper is to assess the relative importance of N_2 fixation by *Trichodesmium* in the N cycle of the upper water column using the data collected on those cruises and to relate this input to other sources of combined nitrogen to the surface mixed layer.

2. Materials and Methods

[6] Research cruises to various regions of the tropical North Atlantic occurred in May–June 1994 on R.V. *Gyre*, March–April and October–November 1996, January–February 2001, and April–May 2003 on R.V. *Seward Johnson*, and in July–August 2001 on R.V. *Knorr* (Table 1, Figure 1). *Trichodesmium* spp. colonies were gently collected by very slowly (~1 knot) towing a 202-μm mesh 1-m-diameter net generally from 5 to 15 m depth

Table 1. Average Areal Rate of N_2 Fixation by *Trichodesmium* spp. From Tropical Locations

			N_2 Fixation[a]			NO_3 Gradient			Estimated Diffusive NO_3 Flux, μmol N/m^2 × d	
Location	Dates	Vessel	μmol N/m^2 × d	se	n	mmol N/m^4	se	*n*	Kz = 0.11[b]	Kz = 0.37
SWR tropical North Atlantic	24 May to 18 June 1994	R.V. *Gyre*	898	±234	18	0.053	±0.009	19	46	169
Tropical North Atlantic	29 March to 25 April 1996	R.V. *Seward Johnson*	163	±58	29	0.196	±0.014	30	167	627
SWR tropical North Atlantic	12 Oct. to 4 Nov. 1996	R.V. *Seward Johnson*	300	±71	27	0.145	±0.016	25	126	402
SWR tropical North Atlantic	9 Jan. to 20 Feb. 2001	R.V. *Seward Johnson*	161	±46	24	0.230	±0.015	24	228	736
SWR tropical North Atlantic	27 June to 15 Aug. 2001	R.V. *Knorr*	59	±21	29	0.158	±0.010	28	136	504
SWR tropical North Atlantic	19 April to 20 May 2003	R.V. *Seward Johnson*	85	±23	28	0.116	±0.007	16	101	373
Grand average (weighted)			239	±38	154	0.147	±0.007	142	131	471

[a]See Supplemental Table 1 for complete data sets. Number of stations is denoted by *n*. Standard error is denoted by se.
[b]Units are cm^2/s.

where the highest densities of colonies were typically found [*Carpenter et al.*, 2004].

[7] Colonies were removed from the cod end of the net, diluted in surface seawater and isolated using a plastic bacteriological transfer loop, and carried through a filtered seawater rinse. For C_2H_2 reduction experiments, 10 colonies were then placed in each of a series of 14-mL acid-washed serum vials containing 10 mL GF/F filtered surface seawater [*Capone*, 1993]. The vials were crimp-sealed using silicone rubber closures and injected with 1 mL of instrument-grade acetylene that had been sparged through deionized water to remove trace acetone. In most assays, EDTA was added to a final concentration of 20 μM to prolong activity (J. Burns et al., Effect of EDTA additions on natural *Trichodesmium* spp. populations, submitted to *Journal of Phycology*, 2005). EDTA does not affect the initial rate of reaction, which was used to estimate nitrogenase activity. Triplicate sets of vials were prepared for assay at a range of light intensities representing 100%, 55%, 28%, 10%, and 1% of surface irradiance. Incubations were carried out on deck in an incubator filled with flowing surface seawater, typically between 26° and 28°C, and screened using neutral density filters to achieve the stated irradiances relative to the surface. Samples of the headspace were periodically removed with a gas-tight syringe and analyzed by flame ionization gas chromatography for the production of C_2H_4 from C_2H_2 [*Capone*, 1993]. For assays initiated during daylight, C_2H_4 production was generally linear for periods of 3 to 7 hours. The average variability in nitrogenase activity, given here as the standard error, was typically about 15 to 20% of the mean.

[8] We also collected *Trichodesmium* colonies from discrete depth intervals using two types of open-closing nets, a Tucker Trawl, and a Bongo Net, each of which is capable of being opened and closed at a specific depth. Samples retrieved from these depths were compared to those collected at our standard 5–15 m depth by incubation in parallel at the irradiance appropriate to the depth of collection with the opening-closing net.

[9] Direct comparisons were also made between the C_2H_2 reduction method and direct $^{15}N_2$ assimilation [*Montoya et al.*, 1996] by *Trichodesmium* colonies. Twenty to 100 colonies were placed in 310-mL glass bottles with screw cap seals with rubber septa. One hundred μL of 99 atom% ^{15}N-N_2 gas (Cambridge Isotopes) were injected to initiate the assay. Samples were incubated from 2 to 12 hours in on-deck incubators under specific level of irradiance relative to surface irradiance. Incubations were terminated by filtering samples onto pre-combusted GF/C filters that were then dried and stored until isotope ratio analysis in the laboratory.

[10] We used a CTD-rosette system to obtain water samples through the upper water column. Suspended particles were collected by gentle vacuum filtration (200 mm Hg vacuum) of 4 to 8 L of seawater through pre-combusted (450°C for 2 hours) 45 mm GF/F filters that were dried at 60°C and stored over desiccant for analysis ashore. For isotopic analysis, filters containing particle samples were trimmed, then cut into quadrants or halves that were pelletized in tin capsules. All isotopic measurements were made by continuous-flow isotope ratio mass spectrometry using a Carlo Erba elemental analyzer interfaced to a Micromass Optima mass spectrometer.

[11] Nitrate (NO_3^-) concentrations were determined by standard colorimetric techniques [*Parsons et al.*, 1984] using a Technicon or Lachat autoanalyzer. The vertical transport of NO_3^- was estimated as the product of the NO_3^- gradient at the nitracline and the diapycnal eddy (turbulent) diffusivity (K_z). Nitrate gradients used to calculate this term do not vary widely among studies within the Atlantic basin. However, there is considerable divergence, and debate, concerning appropriate values of the diapycnal eddy diffusivity (see section 3). We therefore used two values for K_z.

[12] N* was derived (according to *Gruber and Sarmiento* [1997]) using objectively analyzed 1° nutrient fields from the World Ocean Atlas 2001 (http://www.nodc.noaa.gov/OC5/WOA01/) from the North Atlantic and Ocean Data View [*Schlitzer*, 2004] as a visualization tool.

3. Results and Discussion

3.1. Nutrient Distributions

[13] Upper water column nitrate concentrations were generally below the limit of detection (<100 nM) at

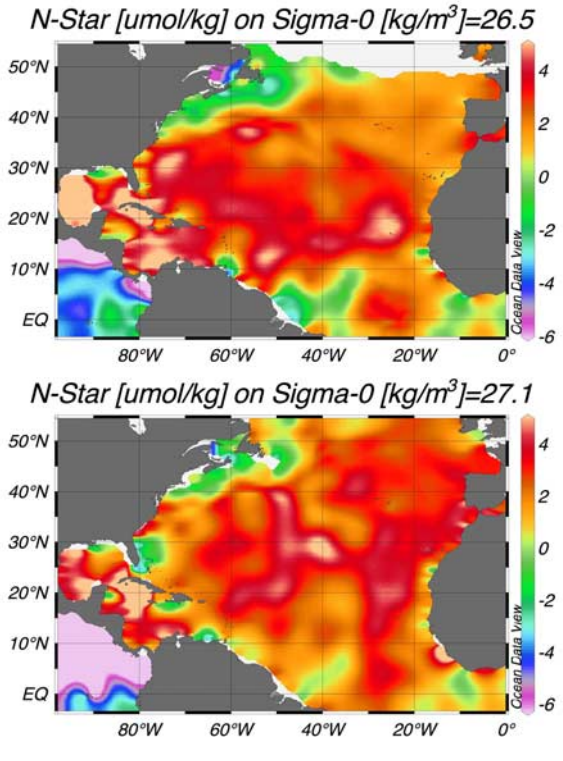

Figure 2. Distribution of N* [*Gruber and Sarmiento*, 1997] in the tropical and subtropical North Atlantic. N* was derived according to *Gruber and Sarmiento* [1997] using objectively analyzed 1° nutrient fields from the *World Ocean Atlas 2001* [*Schlitzer*, 2004] (http://www.nodc.noaa.gov/OC5/WOA01/) for the North Atlantic. (top) N* on the isopycnal surface $Sigma_T$ (σt) = 26.5 representing the Subtropical Mode (18°) Water. (bottom) N* distribution on the isopycnal surface σt = 27.1, representing the Subpolar Mode water. Figure was prepared using Ocean Data View [*Schlitzer*, 2004].

oceanic stations, but measurable at some of the Amazon plume waters during the October 1996 and April–May 2003 cruises (A. Subramaniam et al., Influence of riverine and dust inputs on diazotrophy in the western tropical North Atlantic, submitted to Nature, 2005) (hereinafter referred to as Subramaniam et al., submitted manuscript, 2005).

[14] The southwestern tropical Atlantic Ocean is an area of strong positive N* (or DINxs) anomaly (Figure 2). Both *Gruber and Sarmiento* [1997] and *Hansell et al.* [2004] observed a general DIN excess throughout the region. The high N* values are most evident on the 26.5 σ_t surface (representing the 18° water between 100 and 400 m) in the western basin and the 27.1 σ_t surface (subpolar mode water 250 to 700 m) in the eastern basin (Figure 2). Clearly defined N* maxima appear on both sides of the basin on these surfaces, with minima in the center of the gyre. There is an apparent gradient of N* between 0° and 20°N showing a general increase in the anomaly from south to north [*Gruber and Sarmiento*, 1997; *Hansell et al.*, 2004] (Figure 2). These observations imply a net source of excess N that is generally attributed to N_2 fixation throughout the southwest tropical Atlantic.

[15] Similarly, *Montoya et al.* [2002] reported minima in the $\delta^{15}N$ stable isotopic signatures in surface particulate matter and zooplankton in the southwest Sargasso Sea and southwestern tropical Atlantic. The nutrient and stable isotope data through the region will be more fully presented in a separate publication (C. Mahaffey et al., manuscript in preparation, 2005).

3.2. Rates of *Trichodesmium* N_2 Fixation

[16] Colonies of *Trichodesmium* retrieved from discrete depths in the upper 40 m yielded rates of N_2 fixation directly comparable to colonies retrieved from 10 to 20 m and incubated at a series of irradiances associated with those depths (Table 2). However, deeper samples yielded rates generally lower than those observed for colonies from the 10–20 m interval and incubated at the 10% surface irradiance level.

[17] Direct comparisons of the C_2H_2 reduction method with direct $^{15}N_2$ fixation showed a substantial variability among experiments (Table 3). However, while there is a relatively broad spread among experiments, the mean ratio of C_2H_2 reduced to N_2 fixed for 191 experiments was about 3.5, very close to the theoretical ratio of 3 to 4 (depending

Table 2. Comparison of Nitrogenase Activity in Freshly Collected Colonies of *Trichodesmium* Collected From a Standard Depth, or From Discrete Depths With Opening/Closing Nets

				Discrete Depth		Net From 10–20 m		
Date	Net Type	Depth, m	Irradiance Level, % of Surface	Standard Error	Number	Standard Error	Number	Ratio Surface/Depth
14 Oct.	T[a]	0–20	55%	0.31 ± 0.04	3	0.30 ± 0.07	6	0.95
15 Oct.	B[b]	20–40	28%	0.59 ± 0.06	6	0.54 ± 0.08	6	0.91
16 Oct.	B	20–40	28%	0.33 ± 0.05	6	0.46 ± 0.07	6	1.39
17 Oct.	B	20–40	28%	0.31 ± 0.06	6	0.32 ± 0.05	6	1.03
19 Oct.	B	20–40	28%	0.56 ± 0.08	3	0.63 ± 0.05	3	1.12
28 Oct.	B	20–40	28%	0.22 ± 0.04	3	0.23 ± 0.05	3	1.05
16 Oct.	B	40–60	10%	0.12 ± 0.05	3	0.14 ± 0.013	6	1.24
19 Oct.	B	40–60	10%	0.05 ± 0.02	3	0.28 ± 0.06	3	6.10
14 Oct.	T	40–60	10%	0.09 ± 0.02	3	0.34 ± 0.11	6	3.69
15 Oct.	T	40–60	10%	0.15 ± 0.02	6	0.36 ± 0.05	6	2.37

[a]Tucker trawl.
[b]Bongo net.

Table 3. Intercomparison of C_2H_2 Reduction and $^{15}N_2$ Uptake Rates in Freshly Collected Colonies of *Trichodesmium* spp.[a]

	Ratio C_2H_4/N_2	Standard Error	Number	Start, Duration	Comments (% of Surface Irradiance and EDTA Treatment)
				April 1996	
3 April	2.17	±0.43	4	11:00, 5.6 hours	10 & 55%
4 April	0.93	±0.26	4	10:00, 6 hours	10 & 55%
5 April	3.61	±1.00	6	11:00, 2 and 4 hours	55%
9 April	3.21	±0.68	2	10:20, 5.6 hours	55%
12 April	4.90	±1.63	4	10:50, 2.4 and 7 hours	28%, w/EDTA
12 April	4.31	±0.41	2	13:20, 5.3 hours	28%
19 April	1.30	±0.42	5	11:30, 3.6 and 7.4 hours	55%, ±EDTA
20 April	6.13	±2.00	4	10:50, 3.2 and 6.2 hours	55%
21 April	7.26	±0.91	15	11:00, 3.7 and 7.3 hours	55%
22 April	3.41	±0.70	12	10:00, 2, 5 and 8.6 hours	28%
24 April	1.90	±0.37	14	11:50, 2.4, 4.1 and 6.6 hours	55%
Average	3.82	±0.37	72		
				October/November 1996	
12 Oct.	2.10	±0.63	6	11:00, 2,4 and 6 hours	100%
13 Oct.	4.00	±0.93	9	11:50, 2.6 and 5.2 hours	28 and 55%
14 Oct.	4.80	±0.62	13	12:00, 2.6 and 5.2 hours	55%, ±EDTA
15 Oct.	4.20	±0.99	13	10:35, 3.1 and 7 hours	55 and 100%, ±EDTA
16 Oct.	1.60	±0.20	14	09:06, 3 and 6 hours	55 and 100%, ±EDTA
17 Oct.	2.20	±0.44	9	10:00, 4 and 7 hours	28 and 55%, ±EDTA
18 Oct.	3.30	±0.63	16	10:10, 5 hours	10, 28 and 55 and 100%, ±EDTA
19 Oct.	3.00	±0.47	16	10:20, 5 hours	10, 28 and 55 and 100%, ±EDTA
27 Oct.	4.28	±1.14	4	10:35, 5.6 hours	28 and 55%
6-Nov.	6.00	±1.15	6	11:20, 3.5 hours	28 and 55%
Average	3.42	±0.24	106		
				Grand	
Average	3.58	±0.21	178		

[a]Times are given as local time.

on the extent of nitrogenase linked H_2 production [*Postgate*, 1998]; see below). This agrees well with recent results from *Orcutt et al.* [2001], who also reported a 3:1 ratio. *Scranton* [1984] and *Glibert and Bronk* [1994] also reported ratios very close to 3. Various factors can affect the ratio between C_2H_2 reduction and $^{15}N_2$ uptake. Natural H_2 production by nitrogenase is blocked by C_2H_2; hence reducing equivalents normally lost to H_2 evolution are shunted to C_2H_2 reduction. The presence of efficient uptake hydrogenases can mitigate losses of energy through H_2 evolution [*Saino and Hattori*, 1982]. Whereas C_2H_2 reduction should in theory be a gross measure of nitrogenase activity, $^{15}N_2$ uptake into particulate matter (as most assays undertake) would miss any soluble fixed nitrogen released from the cell [*Glibert and Bronk*, 1994; *Capone et al.*, 1994] and therefore may be considered a measure of net N_2 fixation; [*Carpenter*, 1973; *Karl et al.*, 2002; *Mulholland et al.*, 2004]. Substantial release of dissolved organic or inorganic N [*Glibert and Bronk*, 1994; *Capone et al.*, 1994; *Mulholland et al.*, 1999] would increase this ratio.

[18] Colony-specific rates of N_2 fixation showed relatively low variability within cruises except for samples incubated at the lowest irradiances (Table 4). Lowest average rates occurred on the April 1996 and July–August 2001 cruises, while average rates about threefold to fourfold higher were measured during the June 1994 and October 1996 field campaigns. *Trichodesmium* biomass, as estimated by *Trichodesmium* specific Chl *a*, represented about 27% of the total phytoplankton Chl *a* and on average accounted for about 20% of the depth integrated primary production in this ecosystem [*Carpenter et al.*, 2004].

[19] The data required to fully assess depth-integrated rates of N_2 fixation by *Trichodesmium* were available for 134 stations on these six research cruises in various seasons in the tropical North Atlantic (Table 1). Assuming a cruise specific N_2 fixation rate for each irradiance depth (Table 4), we derived estimates for an additional 21 stations for which *Trichodesmium* biomass was available, expanding the total to 154 stations (Supplemental Table 1[1]). Average areal rates of N_2 fixation on the cruises, which spanned different seasons and areas, ranged from about 60 to 898 μmol N* m^{-2} d^{-1}. The average for all cruises and seasons for 154 stations was 239 μmol N* m^{-2} d^{-1} with substantial station-to-station variability (Figures 1 and 3). About 10% of the stations were essentially devoid of *Trichodesmium* (Table 1, Supplemental Table 1).

[20] At basin-wide scales, highest depth integrated rates appeared localized on the western side of the basin above 10°N (Figure 1). The greatest density of our observations was west of 40°W with one transect in April–May 1996 crossing the basin. On that cruise, there appeared to be a strong zonal trend in biomass density [*Carpenter et al.*, 2004] and activity (Figure 1). However, recent results by *Tyrrell et al.* [2003], *Mills et al.* [2004], and *Voss et al.* [2004] indicate that densities of *Trichodesmium* and rates

[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gb/2004GB002331.

Table 4. Average Colony Specific Rates of Nitrogenase Activity for Each Cruise

Percent of Surface Irradiance	Depth, m	Standard Error	Nitrogenase Activity, nmol C_2H_4 Colony h	se	se as % of Mean	Min	Max	Number of Stations *n*
			May–June 1994					
100	1		0.41	0.057	14%	0.04	0.92	21
55	17	1.0	0.44	0.069	16%	0.05	1.42	21
28	34	1.9	0.36	0.049	14%	0.04	0.76	21
10	64	4	0.36	0.052	14%	0.01	0.90	20
1	121	6.3	0.20	0.025	13%	0.00	0.49	20
			April 1996					
100	1		0.18	0.042	23%	0.04	0.30	5
55	14	2.2	0.14	0.027	20%	0.01	0.34	14
28	27	2.9	0.14	0.029	21%	0.01	0.40	15
10	49	2.9	0.09	0.024	27%	0.00	0.29	14
1	80	3.4	0.05	0.019	39%	0.00	0.20	10
			Oct. 1996					
100	1		0.44	0.055	12%	0.15	0.84	14
55	19	1.2	0.39	0.048	12%	0.15	0.93	16
28	36	2.6	0.38	0.043	11%	0.08	0.64	16
10	53	3.1	0.24	0.031	13%	0.10	0.50	13
1	82	2.6	0.07	0.017	24%	0.01	0.21	11
			Feb. 2001					
100	1		0.21	0.026	12%	0.02	0.44	14
55	15	0.9	0.24	0.026	11%	0.02	0.41	14
28	31	1.7	0.21	0.034	16%	0.01	0.50	14
10	52	1.6	0.07	0.025	35%	0.00	0.18	9
1	80	2.9	0.06	0.030	51%	0.00	0.22	8
			July–Aug. 2001					
100	1		0.17	0.027	16%	0.01	0.33	16
55	14	1.3	0.15	0.025	16%	0.01	0.37	18
28	31	2.2	0.16	0.024	15%	0.01	0.37	18
10	51	2.7	0.05	0.013	29%	0.00	0.14	14
1.0	70	5.0	0.07	0.023	35%	0.01	0.19	8
			April–May 2003					
100	1	0.2	0.12	0.03	21%	0.04	0.31	8
55	8	0.6	0.14	0.02	15%	0.04	0.30	9
28	17	1.8	0.13	0.01	9%	0.06	0.21	9
10	28	3.5	0.09	0.01	14%	0.05	0.22	8
1.0	52	5.9	0.06	0.01	17%	0.02	0.13	6

of N_2 fixation, respectively, can also be high on the eastern side of the basin. In the area above 10°N and west of 40°W, there is also evidence for some seasonality in the observed rates with lowest rates in January, increasing in the spring with maximal rates during the late summer through early fall, the period of highest upper water column stability in this region [*Coles et al.*, 2004a; *Hood et al.*, 2004].

[21] The most extreme variability in N_2 fixation rates by *Trichodesmium* was seen in the region around 12°N, 55°W in the Amazon River plume which can extend thousands of kilometers from the coast of South America for over 6 months of the year (Subramaniam et al., submitted manuscript, 2005). Highest rates occurred in the winter and early spring when the Amazon River discharge is minimal and the plume is restricted to the coast of South America. The lowest rates occurred in the summer when the Amazon River plume covered this region with a turbid freshwater lens (Figure 1). Other diazotrophs such as diatoms with endosymbiotic cyanobacteria can be found in the silicon-rich, lower salinity waters at these times [*Carpenter et al.*, 1999; Subramaniam et al., submitted manuscript, 2005].

3.3. Comparisons With Earlier Studies

[22] Previous studies attempting to quantify directly depth-integrated rates of N_2 fixation in the North Atlantic have been limited in coverage, largely focusing on marginal seas or in the subtropics [see *Lipschultz and Owens*, 1996]. Rates of N_2 fixation by *Trichodesmium* in the subtropical North Atlantic are generally much lower (<10 μmol N m^{-2} d^{-1}) than in tropical regions (Figure 4), typically because the abundances of *Trichodesmium* are lower [*Carpenter et al.*, 2004]. Trichome specific rates of fixation tend to vary much less than areal rates (Figure 4).

[23] With regard to related studies, *Goering et al.* [1966] reported volume specific rates of N_2 fixation from two cruises off the northeast coast of South America in the early 1960s, but did not provide areal estimates. *Carpenter and Price* [1977] found a mean rate of N_2 fixation of 161 μmol N m^{-2} d^{-1} (recalculated using a 3:1 conversion ratio of ethylene to N_2) for stations in the Caribbean basin at

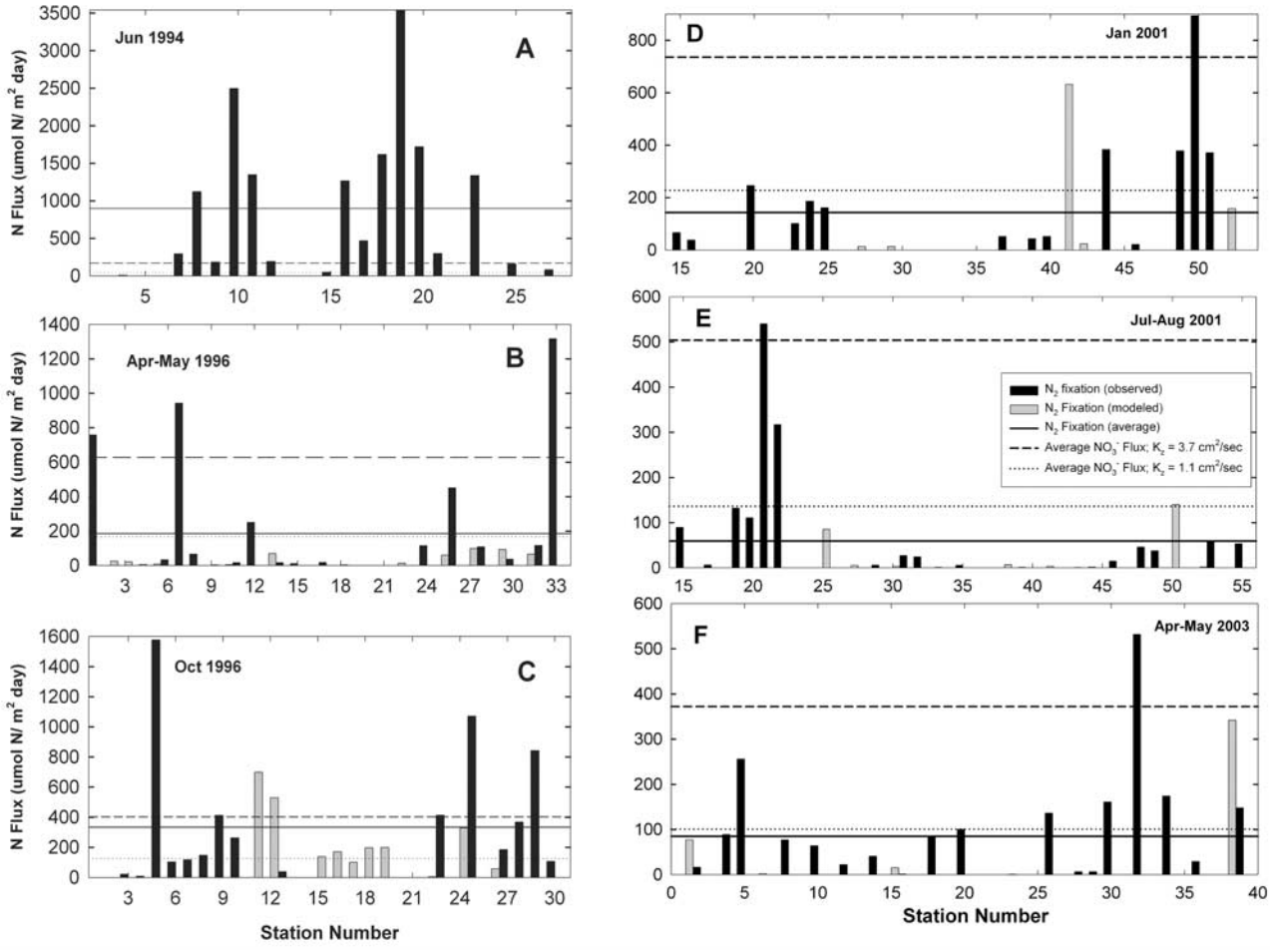

Figure 3. Areally integrated rates of N_2 fixation by *Trichodesmium* for cruises during (a) June 1994, (b) April 1996, (c) October 1996, (d) January–February 2001, (e) July–August 2001, and (f) April–May 2003. Lighter bars indicate stations for which biomass data were available but where cruise average rates of colony specific N_2 fixation were assumed. For the April–May 2003 cruise (Figure 3f), stations above 40 were not included in the graph, as rates were minimal.

various times of year. *Carpenter and Romans* [1991] postulated rates of N_2 fixation for *Trichodesmium* of 710 to 3600 μmol N m^{-2} d^{-1} (Table 5) based on the high abundances of *Trichodesmium* encountered in the tropical portion of a transect through the Atlantic and an assumed rate of N_2 fixation taken from observed doubling times in the literature. Some of the assumptions and extrapolations used in that analysis were subsequently questioned by *Lipschultz and Owens* [1996], who produced a much smaller estimate for the contribution of *Trichodesmium* in the same region using existing literature values for *Trichodesmium* biomass and N_2 fixation (Table 5). Our direct measurements establish areal rates intermediate between the results of these two studies.

3.4. ^{15}N Stable Isotope Budgets

[24] Stable isotope data provide additional insight into the relative importance and spatial extent of N_2 fixation in the tropical North Atlantic (Figure 5). The isotopic composition of suspended particles in the mixed layer reflects the relative importance of N_2 fixation and upwelled NO_3^- as sources of N supporting primary production [*Montoya et al.*, 2002]. In April 1996, we found a clear gradient in upper water column $\delta^{15}N$ across the basin at 15°N–18°N with the lowest values reflecting the largest inputs via N_2 fixation in the western portion of the basin. For the April cruise as a whole, the mean $\delta^{15}N$ of particles in the upper 100 m of the water column was 2.2 ± 1.5‰ (mean ± SD, n = 20 profiles), which implies that N_2 fixation contributed roughly 36% of the total N demand in the water column at the time of sampling. In contrast, our October 1996 cruise to the western tropical North Atlantic showed uniformly lower $\delta^{15}N$ values in the upper water column, with a mean of 0.07 ± 1.2‰ (mean ± SD, n = 20 profiles). On that cruise we also encountered an extensive bloom of the diatom *Hemiaulus hauckii* containing the diazotrophic endosymbiont cyanobacterium, *Richelia intracellularis*, and measured extremely high rates of N_2 fixation at many stations [*Carpenter et al.*, 1999]. The data from this cruise imply that roughly 68% of the upper water column N demand was met by N_2 fixation

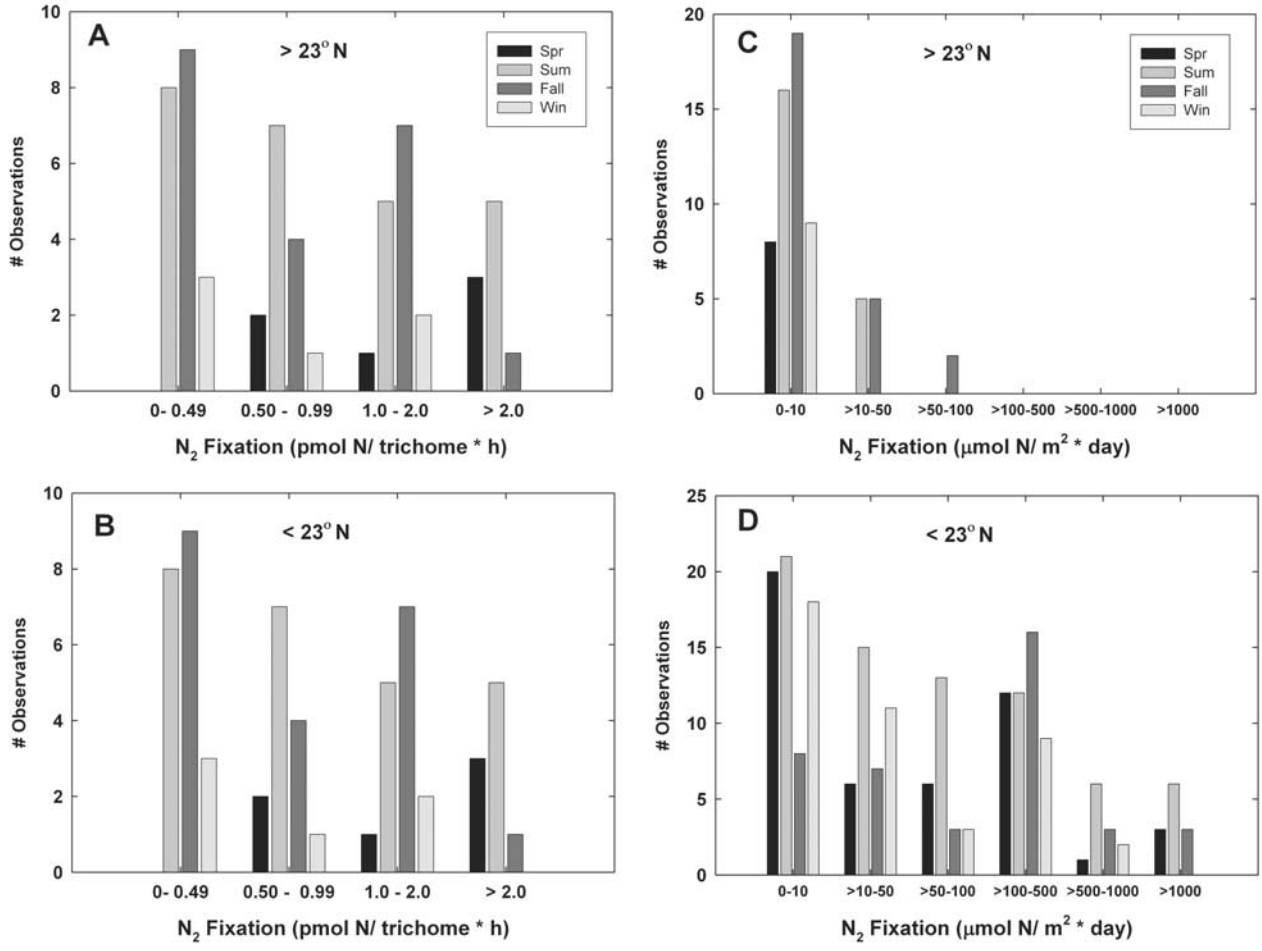

Figure 4. Histograms of rates of N_2 fixation by Trichodesmium on a (a, b) trichome specific and (c, d) areal basis for the North Atlantic tropics (Figures 4b and 4d) and subtropics (Figures 4a and 4c). Data used are presented in Supplemental Tables 2 and 3.

in these waters. The isotope data thus corroborate the conclusions from the direct measurements and confirm a major role for N_2 fixation in supporting primary production in the North Atlantic. It is important to note that isotope-derived estimates of the contribution of N_2 fixation to the N supply to the surface ocean represent an upper bound or maximum potential based upon the choice of end-member source $^{15}N/^{14}N$ values [*Mahaffey et al.*, 2005].

3.5. Comparison With Vertical Nitrate Flux

[25] The vertical flux of nitrate from below the thermocline through eddy diffusion and turbulent mixing has generally been considered the main source of new nitrogen in highly stable non-upwelling open-ocean regions. Eddy diffusivities for open ocean systems have been estimated by various approaches and typically fall in the range from 0.1 to 0.5 $cm^2\ s^{-1}$ [*Michaels et al.*, 1996; *McCarthy and Carpenter*, 1983] [cf. *Jenkins*, 1988]. Some experimental evidence over the last several decades has suggested that the effective K_zs in highly oligotrophic may be at the lower end of this range in the perennially stratified tropics [*McCarthy and Carpenter*, 1983]. *Ledwell et al.* [1993, 1998] derived K_z values of $0.11 \pm 0.2\ cm^2\ s^{-1}$ at a site 1200 km west of the Canary Islands during an extended (several months) SF_6 tracer experiment. A recent study by *Zhang et al.* [2001] at 46°N 20.5°W using SF_6 injected just below a relatively shallow (20 m) mixed layer reported an eddy diffusion coefficient of about $1.0 \pm 0.3\ cm^2\ s^{-1}$, while a similar study by *Law et al.* [2001] at 59.10°N 20.15°W reported a value of $1.95\ cm^2\ s^{-1}$ (Table 6).

[26] In order to provide a context for evaluating the impact of N_2 fixation, we estimated vertical NO_3^- flux at each station using both a widely employed value for vertical eddy diffusivity (K_z) in oligotrophic waters [*Lewis et al.*, 1986; *Michaels et al.*, 1996; *Karl et al.*, 1992] and a lower value of K_z recommended by *Oschlies* [2002b, 2002a] for these waters (see Table 6 and section 2). This resulted in an average nitrate flux for each cruise of from 169 to 736 μmol N $m^{-2}\ d^{-1}$ and 46 to 228 μmol N $m^{-2}\ d^{-1}$, respectively (Tables 1 and 6, Figures 1 and 2).

[27] Our values largely fall within the range of values reported in the literature for the tropical Atlantic (Table 6). As might be expected, studies in temperate locations with shallow thermoclines and strong NO_3^- gradients report

Table 5. Direct and Indirect Estimates of Pelagic N_2 Fixation in the Atlantic Ocean

Location/Domain	Comment	Areal Estimates Average μmol N/m^2 × d	se	Number of Stations or Observations	Domain Area, km^2 × 10^6	Areally Integrated Annual N_2 Fixation, mol N × 10^{12}	Reference
		Direct					
Trichodesmium/tropical regions							
Caribbean, 12°N–22°N	AR, 3:1[a]	161	±20	12	na	na	*Carpenter and Price* [1977]
North Atlantic	AR, 3:1	239	±38	154	17.8–28.0	1.6–2.4	this study
Richelia/Hemiaulus							
SW North Atlantic, 7°N–27°N	AR, 3:1	3110	±1315	14	unknown	unknown	*Carpenter et al.* [1999]
		Extrapolation					
North Atlantic	extrap	na		na	unknown (19)	unknown 0.09	*Carpenter* [1983a]
North Atlantic	extrap	710–3600		na	7–19	2–25	*Carpenter and Romans* [1991]
North Atlantic	extrap	160–430		na	7–19	1.1	*Lipschultz and Owens* [1996]
		Geochemical					
North Atlantic	N*, residence time	500–2500		na	7–19	3.7–6.4	*Michaels et al.* [1996]
North Atlantic, 10°N–50°N, 10°W–90°W	Integrated N*, N:P	197 (315)[b]		na	28	2 (3.2)[b]	*Gruber and Sarmiento* [1997]
Atlantic 40°N–40°S	C_t inventory	111		na	49	2.0[c]	*Lee et al.* [2002]
Atlantic 40°N–0°	C_t inventory, assume all North Atlantic	180–270		na	20–30	2.0	*Lee et al.* [2002]
North Atlantic, 15°N–25°N, 25°W–75°W	Excess nitrate	70–208 (105–312)[b]		na	6.1	0.15–0.46 (0.23–0.69)[b]	*Hansell et al.* [2004]
North Atlantic	^{15}N isotope mass balance[d]	850		na	17.8–28.0	5.5–8.7	this study

[a]Acetylene reduction method for N_2 fixation using a conversion ratio of 3:1.
[b]Assuming an N:P ratio of 45 for diazotrophs rather than 125 as originally computed by *Gruber and Sarmiento* [1997].
[c]Assuming a C:N ratio of 7:1 for biomass.
[d]Assuming an average C fixation rate of 17 mmol C m^{-2} d^{-1}, a C:N ratio of 7:1 and an input by N_2 fixation accounting for 38% of total N demand as noted on our April 1996 cruise.

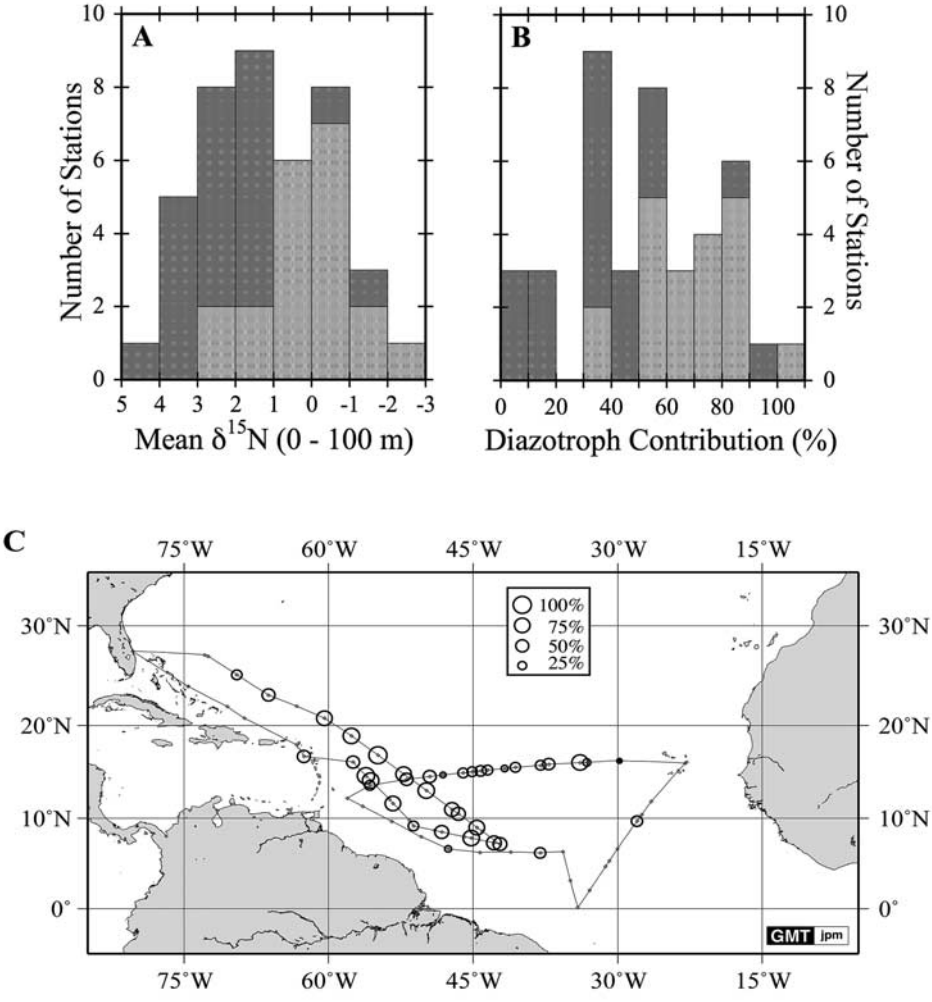

Figure 5. Nitrogen isotopic index to the contribution of diazotrophs to particulate nitrogen (PN) in the upper 100 m of the water column. (a) Mean $\delta^{15}N$ of suspended particles in the upper 100 m of the water column from cruises SJ9603 in April 1996 (dark bars) and SJ9612 in October 1996 (light bars). Means are weighted by PN concentration and depth interval represented by vertically stratified bottle samples. Note reversed horizontal ($\delta^{15}N$) axis. (b) Contribution of diazotroph N to PN in the upper 100 m of the water column from cruises SJ9603 in April 1996 (dark bars) and SJ9612 in October 1996 (light bars). Diazotroph contribution estimated using an isotopic mixing model [*Montoya et al.*, 2002]. Each bar represents the number of stations with a diazotroph contribution greater than or equal to the minimum and less than the maximum boundary for that interval. Hence the rightmost bar represents one station for which 100% of the nitrogen input could be accounted for by N_2 fixation. (c) Spatial distribution of estimated diazotroph contribution to upper water column PN. Area of circles is proportional to the diazotroph contribution. Stations without PN profiles marked with small diamonds. Chart was prepared with GMT [*Wessel and Smith*, 1998].

considerable diapycnal fluxes of nitrate [*Zhang et al.*, 2001; *Law et al.*, 2001]. Interestingly, both of these studies were in anticyclonic warm core rings. *Jenkins* [1988] and *Jenkins and Doney* [2003] also estimated a very high flux (up to 2301 ± 712 μmol N m^{-2} d^{-1} in the latter study) of nitrate in the Sargasso Sea near Bermuda based on the ^3H excesses in the upper mixed layer and a "flux gauge technique" describing a nutrient spiral in the North Atlantic.

[28] In the more permanently stratified oligotrophic tropics, estimates of diapycnal flux are considerably lower (Table 6). For instance, *Lewis et al.* [1986] reported a mean flux of 139 μmol N m^{-2} d^{-1} for a station somewhat south (28.5°N) but much farther east (23°W) of the *Jenkins* [1988] study. A recent model by *Oschlies* [2002b] explains some of the apparent discrepancies between the nitrate flux estimates of *Lewis et al.* [1986]

Table 6. Some Estimates of Vertical NO_3^- Flux Into the Euphotic Zone of the Tropical Atlantic Ocean

Location	NO_3^- Gradient, mmol/m^4	K_z, cm^2/s	se	N Flux, μmol N/m^2 × d	Error	*n*	Comment	Reference
				>30°N				
Sargasso Sea 32°10 N, 64°30 W	0.02–0.03	[7.6][a]		1644	548 (sd)		^{3}He excess	*Jenkins* [1988]
Sargasso Sea 31°50 N, 64°10 W	0.03	0.4		100-			Fickian	*Michaels et al.* [1996]
Subtropical North Atlantic 45°N–50°N, 15°W–20°W	n/a	n/a		274			Convective model	*Williams et al.* [2000]
Subtropical North Atlantic 46°N, 20.5°W	0.48	1.0		4150			SF_6 tracer	*Zhang et al.* [2001]
North Atlantic 59.10°N, 20.15°W	0.107	1.95		1250			SF_6 tracer	*Law et al.* [2001]
				<30°N				
Oligotrophic east Atlantic 28.5°N, 23°W	0.045	0.37 (0.006–2.3)		139 (2.7–1035)	2–890 (95% CI)		tked/bfm[b]	*Lewis et al.* [1986]
Oligotrophic east Atlantic 26°N 28°W	0.03	0.11		27-			SF_6 tracer	*Ledwell et al.* [1993]
Central Atlantic 34°S to 27°N	0.092	0.29	±1.2	380	±180 (se)	14	tked/bfm[b]	*Planas et al.* [1999]
Central Atlantic 3°N to 27°N	0.152	0.58	±2.9	838	±344 (se)	6	tked/bfm[b]	*Planas et al.* [1999]
Tropical/subtropical North Atlantic 25°N–30°N, 70°W–75°W	n/a	n/a		137			convective model	*Williams et al.* [2000]
Tropical/subtropical North Atlantic	n/a	n/a		137			er/cecm[c]	*Oschlies* [2002b]
Tropical Atlantic	0.05–0.023	0.11		46–228			Fickian	this report
Tropical Atlantic		0.37		169–736			Fickian	this report

[a]Apparent K_z back-calculated from *Jenkins* [1988] assuming a NO_3 gradient of 0.25 mmol m^{-4}.
[b]Turbulent kinetic energy diffusion/buoyancy frequency model.
[c]Eddy-resolving coupled ecosystem circulation model.

and *Jenkins* [1988]. The site of the *Jenkins* [1988] measurements was at the southern edge of the region of higher nitrate flux, while *Lewis et al.*'s [1986] site was in a region of lower nitrate flux, thus showing that both measurements are valid for their respective regions [*Oschlies*, 2002b].

[29] The average rate of N_2 fixation ranges from 50% to 180% of our contemporaneous estimates of the concurrent diapycnal flux of nitrate. The lower value of K_z used for these waters (see Table 6) diminishes the estimate of vertical input of NO_3^- and, correspondingly, increases the relative importance of N_2 fixation. The regions where we find our highest N_2 fixation rates by *Trichodesmium* spp. (898 μmol N m^{-2} d^{-1} noted during the early summer of 1994 in the southwestern region of the subtropical gyre) are where the *Oschlies* [2002b] model predicts the very lowest nitrate fluxes (0–27 μmol N* m^{-2} d^{-1}). This relationship is also apparent in the modeling results of *Hood et al.* [2004] and *Coles et al.* [2004a, 2004b].

[30] Consistent with *Oschlies* [2002b], the observed vertical NO_3^- gradients were on average also weaker on the June 1994 cruise than on subsequent cruises (Table 4). The resultant estimates of diapycnal nitrate flux of 46 to 169 μmol N* m^{-2} d^{-1} are thus lowest on this cruise. On the June 1994 cruise, the rate of N_2 fixation was typically 5–20 times higher than the estimated flux of nitrate into the euphotic zone. Over all the cruises, the rates of N_2 fixation we observed for *Trichodesmium* overlap substantially with current estimates of diffusive and turbulent vertical nitrate flux in these systems, implying that N_2 fixation in the North Atlantic is of roughly equal importance to nitrate as a source of new production.

[31] More recently, model and climatological evidence suggests that mesoscale eddies may be responsible for an additional, stochastic injection of nitrate from the deep to the surface ocean. Estimates of eddy-induced nitrate supply derived in the Sargasso Sea near Bermuda range from 0.19 ± 0.1 to 0.35 ± 0.1 mol N m^{-2} yr^{-1} [*McGillicuddy and Robinson*, 1997; *McGillicuddy et al.*, 1999; *Siegel et al.*, 1999], which equates to a potential daily supply of 520 to 958 μmol N m^{-2} d^{-1}. However, mesoscale eddy events are both spatially and temporally diverse, and the instantaneous nitrate supply may be much higher than 1000 μmol N m^{-2} d^{-1} during an event. The biogeochemical role of eddies in fuelling export production of organic matter, or potentially altering plankton community structure remains debated [*McGillicuddy et al.*, 2003; *Sweeney et al.*, 2003; *Oschlies*, 2002a]. Major anticyclonic rings routinely transit the western tropical Atlantic [*Johns et al.*, 1990; *Fratantoni and Glickson*, 2002].

3.6. Comparison With Geochemical Estimates

[32] Geochemists have historically argued that phosphorus rather than nitrogen availability is the key factor controlling marine productivity on long timescales [*Tyrrell*, 1999] such that N_2 fixation is only important in ameliorating short-term deficits of combined nitrogen. This viewpoint assumes that the Redfield ratio is a fixed constraint on the production of oceanic biomass and that the dynamics of the N and P cycles are such that the biota will always adjust oceanic N inventories to match P inventories through a combination of N_2-fixation and denitrification. However, new approaches indicate substantial variability in the N:P ratios of biomass and that the rates of N_2 fixation could be much higher than required to maintain steady state Redfield stoichiometry [*Michaels et al.*, 2001]. Our data speak directly to the controversy between the historical viewpoint and the emerging contention that rates of diazotrophy are large and cannot be ignored on a basin or global scale.

[33] Our mean rate of *Trichodesmium* based N_2 fixation, 239 μmol N* m^{-2} d^{-1} (Table 1) derives from

observations from 154 stations over all seasons, a relatively robust sampling compared to earlier efforts. Our sampling area (defined by the polygon that includes all of our stations with N_2 fixation determinations) encompassed a region of about 9×10^6 km^2. Applying our spatially and seasonally averaged rate to this area yields an input of 0.8×10^{12} mol N* yr^{-1}. As noted above, the greatest density of our stations was in the western portion of the basin, but recent results from the eastern flank also indicate high densities of *Trichodesmium* [*Tyrrell et al.*, 2003] and comparable rates of N_2 fixation [*Voss et al.*, 2004]. The N* distributions across the basin (Figure 2) would also suggest that N_2 fixation is generally important across a relatively wide area of the tropical and subtropical North Atlantic.

[34] In order to compare our results with recent geochemical estimates, we have scaled our rates over appropriate portions of the North Atlantic basin. We used seasonally averaged sea surface temperatures (SST) greater than or equal to 25°C or 20°C (17.8 and 28×10^6 km^2, respectively) of the North Atlantic and Caribbean as a proxy for warm oligotrophic waters likely to be inhabited by substantial populations of *Trichodesmium* [*Carpenter*, 1983b]. The areas derived from these limits are about 2 and 3 times that of the area in which we undertook cruises and made our observations. Scaling to these areas yields annual estimated rates of N_2 fixation of from 1.6 to 2.4×10^{12} mol N* yr^{-1} (Table 5).

[35] There are several published estimates of N_2 fixation in the North Atlantic basin based on different geochemical approaches. *Michaels et al.* [1996] undertook a comprehensive analysis of nutrient pools and fluxes in the North Atlantic using the GEOSECS, TTO, and BATS data sets, including introduction of the N* parameter. They examined gradients in N* along isopycnal surfaces and the residence times of these water masses and derived a basin-scale estimate of $3.7–6.4 \times 10^{12}$ mol N* yr^{-1}. This translates to rates of from 500 to 2500 μmol N* m^{-2} d^{-1} over their domain. N* based estimates represent the net balance between N sources and sinks and would reflect sources of N_2 fixation other than *Trichodesmium* as well as reflecting any reductions in the nitrate pool which would result from denitrification (thought to be minor in the North Atlantic water column).

[36] Subsequently, *Gruber and Sarmiento* [1997] derived an N* estimate for the North Atlantic of 2.0×10^{12} mol N yr^{-1} using a more extensive data set and a more refined method (Table 5). The *Gruber and Sarmiento* [1997] N* analysis produced an areal rate of 197 μmol N* m^{-2} d^{-1}. In order to derive their N* based estimate of N_2 fixation, *Gruber and Sarmiento* [1997] assumed an N:P ratio for diazotrophs much greater than the canonical Redfield ratio of 16:1 to account for the positive N* anomalies. They chose a value of 125:1 gleaned from a report of the N:P ratio of bloom material from Station ALOHA in the Pacific [*Karl et al.*, 1992]. However, at least for *Trichodesmium*, the reported N:P values are typically closer to 40 to 50 [*Carpenter*, 1983b; *Letelier and Karl*, 1996]. As discussed by *Gruber and Sarmiento* [1997], their high estimate of the diazotroph N:P ratio provides a conservative estimate for the rate of N_2 fixation. Recalculating their N_2 fixation rates in the North Atlantic assuming an N:P ratio of 45 yields a rate of about 300 μmol N* m^{-2} d^{-1} and an annual input of 3.2×10^{12} mol N yr^{-1} [*Gruber and Sarmiento*, 1997, Figure 18].

[37] Our isotopic measurements provide yet another avenue for estimating the rate of N_2 fixation in the North Atlantic. For our isotopic budget calculation, our goal was simply to assess the relative contributions of deep water nitrate and N_2 fixation in supporting the production of particulate organic matter in the mixed layer. The $\delta^{15}N$ of deep water nitrate (about 4.5 to 4.8 ‰ in the Atlantic) provides a strong isotopic contrast with the N (−1 to −2‰) fixed by *Trichodesmium* [*Montoya et al.*, 2002]. We used conservative values for these end-members (−2‰ for diazotroph N and 4.5‰ for deepwater nitrate) and the isotope budget approach of *Montoya et al.* [2002] to estimate the contribution of N_2 fixation to the upper ocean N budget.

[38] The rate of primary production in the tropical and subtropical North Atlantic is not well constrained in the literature, with estimates ranging between about 17 and 83 mmol C* m^{-2} d^{-1} [*Carpenter et al.*, 2004]. Even the lower end of this range implies a total nitrogen demand of about 2.4 mmol N* m^{-2} d^{-1}, assuming a Redfield C:N ratio of 7:1 in the organic matter formed. Our isotopic mass balance calculations show that during our April 1996 cruise through the central tropical Atlantic, about 36% of the standing stock PN in the upper water column was derived from diazotrophic activity. This in turn suggests a lower limit for total N_2 fixation in this region of about 850 μmol N* m^{-2} d^{-1} based on the total N demand for these waters. These rates reflect processes occurring on the timescale of turnover of mixed layer PN, and are somewhat higher than the estimates based on N* distributions in the North Atlantic, which likely integrate on a longer timescale. On the basis of a similar approach using isotopic budgets as well as other data (including limited direct determinations), *Karl et al.* [1997] have similarly concluded that N_2 fixation accounts for about one half the new nitrogen input at the Hawaiian Ocean Time series (HOT) Station ALOHA in the Pacific. Scaling our isotopic mass balance based estimates to the same areas used for the *Trichodesmium* exercise yields values of 5.5 to 8.7×10^{12} mol N yr^{-1}, at the high end of the geochemical estimates (Table 5). As for N*, this temporally and spatially integrative estimate would include the contribution from all diazotrophs.

[39] *Lee et al.* [2002] have recently analyzed and integrated the annual decrease in inorganic C (C_t inventory) in nitrate-depleted waters and concluded that 0.2×10^{15} Pg C yr^{-1} of the new production in the Atlantic from 40°N to 40°S was supported by nitrogen sources other than subeuphotic zone supplies of NO_3^- (Table 5). This amounts to 2.0×10^{12} mol N* yr^{-1} assuming a C:N ratio in biomass of 7, and implies an areal rate of N_2 fixation of 111 μmol N* m^{-2} d^{-1}. The most intense negative dissolved inorganic carbon anomalies occurred in the North Atlantic. If we assume that the full amount of the integral calculated by *Lee et al.* [2002] for the Atlantic Ocean largely occurred over the $20–30 \times 10^6$ km^2 of the tropical

North Atlantic, this would amount to daily areal rates in the range of 180 to 270 μmol N* m^{-2} d^{-1}, in very reasonable agreement with our observations for *Trichodesmium* alone.

[40] *Lee et al.* [2002] noted that at the BATS station, their inferred rates of N_2 fixation are much greater than those reported for BATS by *Orcutt et al.* [2001]. However, as noted above, N_2 fixation at BATS is limited to a very brief season, and the excess N detected at that station is likely formed to the south. Furthermore, the C_t method, as with N* and N isotope budgets, provides a spatially and temporally integrated estimate of N cycle dynamics, compared to direct biological estimates such as those provided here. *Lee et al.* [2002] also noted that the more recent data based on direct measurements from the marine tropics [*Capone et al.*, 1997] were concordant with their analysis.

[41] In contrast to these four studies, a recent examination of the excess nitrate in the subtropical and tropical North Atlantic has come to a more modest conclusion about the basin-scale significance of N_2 fixation. Taking an approach similar to the *Gruber and Sarmiento* [1997] N* analysis, *Hansell et al.* [2004] used a portion of the data set from the WOCE program in the 1990s and estimated the rate of N_2 fixation using the same high value for the N:P ratio of organic matter produced by diazotrophs as did *Gruber and Sarmiento* [1997]. They found the region of excess nitrate creation in the North Atlantic (and therefore where N_2 fixation was putatively occurring) to be only about 6.1×10^6 km^2 or about one fifth the area reported by *Gruber and Sarmiento* [1997]. This yielded a basin wide value of only 0.15 to 0.5×10^{12} mol N* yr^{-1} (Table 5). Interestingly, the areal rates of N_2 fixation over their domain are only somewhat lower than our mean (Table 5).

[42] The *Hansell et al.* [2004] estimate for the area of the basin with active nitrate creation (6.1×10^6 km^2) is less than the area of our operations (9×10^6 km^2). Using a more realistic N:P value and extrapolating their areal rate to the area where seawater temperatures are 25°C or above would gives a basin estimate of about 2×10^{12} mol N yr^{-1}, more in line with the other geochemical studies.

[43] One other component of the dichotomy between the *Hansell et al.* [2004] study and the earlier N* studies may be the different data sets and interannual variability forced by the North Atlantic Oscillation (NAO). *Hood et al.* [2001] first suggested that the interannual variability in N_2 fixation noted at BATS may derive from climatic variation forced by the NAO. *Bates and Hansell*'s [2004] recently proposed that N_2 fixation intensity may vary up to sixfold over the NAO cycle. However, the N* approach should smooth out some of the interannual variability for the parts of the signal in waters with multiannual residence times. The key open question seems to be the areal extent of N_2 fixation.

[44] Thus four discrete geochemically based estimates of N_2 fixation using three distinct approaches (N*, Ct inventories, and N isotope budgets) in the North Atlantic range from 2 to 9×10^{12} mol N yr^{-1}. In contrast, *Hansell et al.* [2004] suggest values at least tenfold smaller. Our direct measurements, derived by methods fully independent of these geochemical measurements, support the higher values. *Trichodesmium* N_2 fixation alone can account for a substantial fraction of the activity inferred in three of these studies and our own stable isotope mass balance.

3.7. Modeling N_2 Fixation in the Atlantic

[45] It is only relatively recently that N_2 fixation has been explicitly represented in ecosystem and biogeochemical models, and several recent efforts have focused specifically on the North Atlantic basin. *Hood et al.* [2001] exploited the BATS data set, including observations of *Trichodesmium* abundance [*Orcutt et al.*, 2001] in a one-dimensional model. *Hood et al.* [2004] and *Coles et al.* [2004a] built further on their work at BATS (above), and developed a climatologically forced coupled, 3-dimensional, biological-physical model for the tropical North Atlantic basin, including a dynamic representation of *Trichodesmium*. The model captures and predicts the seasonal and spatial distribution of *Trichodesmium* in the basin. While there was a good correlation between the model derived distribution and seasonality and direct observations of *Trichodesmium* [see *Hood et al.*, 2004, Table 1], the model output also revealed persistently high *Trichodesmium* biomass and rates of N_2 fixation in the Gulf of Guinea off of Africa, a region where there are few direct observations of diazotrophs [*Dandonneau*, 1971]. Thus, while benefiting greatly from direct field observations, these complex biological-physical models can also generate testable predictions which can be used to validate the model and to guide future field campaigns to investigate new and unexplored regions of N_2 fixation.

[46] While it has been assumed that the basin scale spatial extent of *Trichodesmium* is largely controlled by temperature (>22–25°C [*Carpenter et al.*, 1992], model output also suggested that the depth and duration of winter mixing have a stronger control [*Hood et al.*, 2004]. Going one step further, *Hood et al.* [2004] were able to capture the succession of phytoplankton species linked to the physical supply of nitrate. Model output describing a temporal progression from diatoms, to *Trichodesmium* in response to the drawdown of nitrate by diatoms, to *Trichodesmium* supported flagellate growth, exemplifies the impact of N_2 fixation on the plankton community.

[47] The intensity of N_2 fixation predicted by the basin model using observed densities [*Coles et al.*, 2004a] is comparable to recent direct estimates for *Trichodesmium* (for which it is tuned), but about 25% of geochemical estimates which would include the contribution of other diazotrophs [*Gruber and Sarmiento*, 1997]. In order to approach geochemical derived estimates of N_2 fixation (Table 1), *Coles et al.* [2004a] found that *Trichodesmium* biomass must be increased beyond that observed.

[48] Ecosystem models have also been used to investigate factors that limit N_2 fixation in the world's oceans. Employing a global marine ecosystem mixed-layer model, *Moore et al.* [2002b, 2002a] explored a wide variety of marine ecosystems, including N, P, and Fe-limited systems, in which diazotrophs, as well as other phytoplankton, were represented. Direct field data regarding the temperature constraints, growth rates, grazing and non-grazing mortality, photo-physiology, Fe requirements, and elemental

stoichiometry of diazotrophs, as well as atmospheric dust deposition model studies, were used to parameterize these complex models. *Moore et al.* [2002a] found that these models were able to reproduce the seasonality and biomass of diazotrophs at BATS and, largely in agreement with direct observations [*Wu et al.*, 2001] and other projections [*Berman-Frank et al.*, 2001; *Sañudo-Wilhelmy et al.*, 2001] described P limitation at BATS and in parts of the southwest North Atlantic.

[49] Most recently, using monthly climatological satellite data of sea surface chlorophyll concentrations (from SeaWiFS) and sea surface height (from TOPEX/Poseidon altimeter), *Coles et al.* [2004b] reported an anomalous summertime maximum in phytoplankton biomass in a region of highly stratified, nutrient-deprived water in the southwest tropical North Atlantic. Employing a climatological forced biological-physical model with a dynamic representation of *Trichodesmium*, *Coles et al.* [2004b] were able to simulate this chlorophyll maximum in the western tropical Atlantic, which was absent when *Trichodesmium* were omitted from the model. The authors concluded that N_2 fixation (*Trichodesmium* specifically in their model) was responsible for this summertime phytoplankton bloom in an otherwise nutrient-starved region. Model and satellite derived estimates of N_2 fixation were 192 μmol N m^{-2} d^{-1} and 220 μmol N m^{-2} d^{-1} [*Coles et al.*, 2004a], comparable to both direct and geochemical observations (Table 5).

3.8. Remaining Unknowns

[50] As mentioned above, our direct estimates should still be viewed as conservative as they do not capture the contribution by *Trichodesmium* blooms, which can result at times in greatly amplified input of nitrogen to the upper water column [*Capone et al.*, 1998] or any contribution from other diazotrophs such as coccoid cyanobacteria, heterotrophic bacterioplankton, or cyanobacterial endosymbionts. The diazotrophic cyanobacterium, *Richelia intracellularis*, has long been known to occur as an endosymbiont of the diatoms *Hemiaulus hauckii*, *H. membranaceus*, and some *Rhizosolenia* spp. [*Zehr et al.*, 2000]. On our October 1996 cruise, we encountered a bloom of this organism off the northeast coast of South America that was spatially extensive, covering about 2500 km along a linear cruise track [*Carpenter et al.*, 1999]. The rates of N_2 fixation were among the highest noted in any marine ecosystem (Table 5; we recorded rates of 19,000 μmol N* m^{-2} d^{-1} at one station) and our N isotope balance for that cruise suggests that more than half of the local N demand was met by N_2 fixation (see above). We again found extensive populations on the cruises in July/August of 2001 and in April/May 2003 in this same region. These symbioses are likely an important contributor to the total N fixed in this region. However, the spatial and temporal extent of these blooms is poorly constrained, and it is difficult to incorporate their input into basin scale budgets at present.

[51] Coccoid cyanobacteria and bacterioplankton also contribute to marine N_2 fixation. *Zehr et al.* [2001] have amplified nifH sequences from coccoid cyanobacteria and α and γ proteobacteria in samples from oligotrophic surface waters of the North Atlantic and North Pacific [*Zehr et al.*, 1998] and more recently found expression of nitrogenase in populations of coccoid cyanobacteria and eubacteria in the upper water column of Station ALOHA north of Hawaii. Quantifying the magnitude of their input is a current challenge, and the magnitude of the contribution of this diazotrophic component remains to be rigorously and broadly evaluated. Several recent studies of $^{15}N_2$ uptake have reported a wide range of rates of N_2 fixation by small cells (<10–20 μm). At Station ALOHA near Hawaii, N_2 fixation rates by small cells are measurable but low relative to rates reported here for *Trichodesmium* [*Karl et al.*, 1997; *Dore et al.*, 2002; *Montoya et al.*, 2004]. At other sites in the North Pacific and near Australia, rates of N_2 fixation by small cells often exceed the rates reported for *Trichodesmium* [*Montoya et al.*, 2004]. Preliminary observations in the tropical North Atlantic have found lower rates ranging from trace to about 100 μmol N* m^{-2} d^{-1} (D. G. Capone et al., manuscript in preparation, 2005). Thus we may soon be able to close some of the gap between the geochemical measurements and directly determined rates of N_2 fixation by these other components of the diazotrophic community. In addition to N_2 fixation, other N inputs, such as atmospheric deposition of DON, have also been poorly quantified in the past [*Duce*, 1986; *Cornell et al.*, 1995], and more accurate assessment of their contribution to the oceanic N cycle will help further rectify current discrepancies in basin scale and oceanic N budgets [*Galloway et al.*, 2004].

[52] The controls on oceanic N_2 fixation remain to be fully determined. Clearly, for an organism such as *Trichodesmium*, there are important prerequisites for N_2 fixation with respect to the physical environment. Upper water column stability and a relatively shallow mixed layer are crucial for organisms that have a high compensation point and require minimal turbulence [*Carpenter and Price*, 1976] and relatively high light conditions [*Carpenter*, 1983b; *Carpenter et al.*, 1993; *Hood et al.*, 2004].

[53] With respect to chemical constraints, the extensive areas of positive N* anomalies in the North Atlantic roughly correspond to regions which receive substantial dust input from aeolian deposition [*Michaels et al.*, 1996; *Gruber and Sarmiento*, 1997; *Gao et al.*, 2001]. The recognition that photosynthetic diazotrophs have a higher cell quota for iron [*Berman-Frank et al.*, 2001; *Kustka et al.*, 2003] has led to the general hypothesis that iron enrichment resulting from dust deposition in the tropical North Atlantic is responsible for enhanced levels of diazotrophy in the upper water column of this system [*Karl et al.*, 2002; *Capone*, 2001]. Phosphorus is also present at extremely low concentrations in the tropical North Atlantic [*Wu et al.*, 2000] and can be a limiting factor [*Sañudo-Wilhelmy et al.*, 2001, 2004]. The frequent occurrence of dense populations of these organisms in areas of uniform, widespread phosphate depletion [*Carpenter*, 1983a; *Carpenter et al.*, 2004] indicates that the local controls on this process are still not well understood [*Karl et al.*, 2002].

3.9. The Shifting Paradigm

[54] Our results demonstrate directly the importance of oceanic N_2 fixation and should promote the ongoing paradigm shift in how the community conceptualizes the nitro-

gen cycle of the tropical Atlantic Ocean. Although efforts are currently underway to incorporate N_2 fixation as an explicit term in ocean biogeochemical models in order to assess its importance in global carbon dynamics [e.g., *Tyrrell*, 1999; *Hood et al.*, 2000, 2004; *Coles et al.*, 2004a], many N-based ecosystem models for the tropical North Atlantic continue to overlook this important process, focusing solely on nitrate flux from deep waters as a source of new nitrogen to the euphotic zone [*Oschlies and Koeve*, 2000; *Christian and Murtugudde*, 2003]. *Oschlies* [2002b] found that although his model can reproduce nitrate fluxes extremely well, it underpredicts primary production in the southern subtropical gyre. One process he notes that he had not taken into account in his model is N_2 fixation.

[55] Accurate determination of oceanic N_2 fixation may also be critical for estimating biological removal of inorganic C from the upper layers of the ocean. New production dependent upon N_2 fixation can effect a net removal of DIC from the euphotic zone, in contrast to production dependent upon NO_3^- from depth, which co-diffuses with inorganic carbon in Redfield proportions [*Eppley and Peterson*, 1979; *Karl et al.*, 2002; *Michaels et al.*, 2001]. The assumption that vertical NO_3^- flux is the sole, or even predominant source of new N in tropical oligotrophic systems should be discarded, and models that are based on this assumption should be used with great caution: If they obtain good matches with the data, it may be for the wrong reason. Tropical ocean nitrogen and carbon cycles can only be understood if N_2 fixation is included as a major source of new nitrogen to the upper water column.

[56] **Acknowledgments.** The authors gratefully acknowledge the sustained support of the Biological Oceanography Program of the Ocean Sciences Division, U.S. National Science Foundation. The latter three cruises were undertaken as part of the NSF Biocomplexity in the Environment Program. We also extend our thanks to the Captains and crews of the R.V. *Gyre*, *Seward Johnson*, and *Knorr* and to the numerous students, postdoctoral associates, and support staff who contributed to this effort. We particularly thank Janet Barnes, Pilar Heredia, Genevieve Aldridge, Michael Neumann, Chris Payne and Dennis Guffey. This is LDEO contribution LDEO 6747.

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J. A. Burns, Quileute Natural Resources, P. O. Box 187, 401 Main Street, LaPush, WA 98350-0187, USA.

D. G. Capone, T. Gunderson, and A. F. Michaels, Wrigley Institute for Environmental Studies and Department of Biological Sciences, University of Southern California, Los Angeles, CA 90275, USA. (capone@usc.edu)

E. J. Carpenter, Romberg Tiburon Center, San Francisco State University, Tiburon, CA 94920, USA.

C. Mahaffey, Department of Oceanography, School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, HI 96822, USA.

J. P. Montoya, School of Biology, Georgia Institute of Technology, Atlanta, GA 30332, USA.

A. Subramaniam, Lamont Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA.