



# Amazon River enhances diazotrophy and carbon sequestration in the tropical North Atlantic Ocean

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The fresh water discharged by large rivers such as the Amazon is transported hundreds to thousands of kilometers away from the coast by surface plumes. The nutrients delivered by these river plumes contribute to enhanced primary production in the ocean, and the sinking flux of this new production results in carbon sequestration. Here, we report that the Amazon River plume supports N<sub>2</sub> fixation far from the mouth and provides important pathways for sequestration of atmospheric CO<sub>2</sub> in the western tropical North Atlantic (WTNA). We calculate that the sinking of carbon fixed by diazotrophs in the plume sequesters 1.7 Tmol of C annually, in addition to the sequestration of 0.6 Tmol of C yr<sup>-1</sup> of the new production supported by NO<sub>3</sub> delivered by the river. These processes revise our current understanding that the tropical North Atlantic is a source of 2.5 Tmol of C to the atmosphere [Mikaloff-Fletcher SE, *et al.* (2007) Inverse estimates of the oceanic sources and sinks of natural CO<sub>2</sub> and the implied oceanic carbon transport. *Global Biogeochem Cycles* 21, doi:10.1029/2006GB002751]. The enhancement of N<sub>2</sub> fixation and consequent C sequestration by tropical rivers appears to be a global phenomenon that is likely to be influenced by anthropogenic activity and climate change.

diatom diazotroph associations | nitrogen fixation | new production | river plumes | *Richelia*

Downward vertical transport of organic carbon produced by phytoplankton, referred to as the biological pump, is a mechanism that transfers carbon from the surface to the deep ocean and regulates atmospheric CO<sub>2</sub> (1). The flux of nitrate (NO<sub>3</sub>) from deep water to the photic zone can stimulate new phytoplankton production and export (2), but because the upwelling or diffusive flux of NO<sub>3</sub> is accompanied by a corresponding upward flux of CO<sub>2</sub>, its net contribution to removal of carbon from the atmosphere is much reduced. However, the sinking flux due to new production associated with nitrogenous inputs from rivers, atmospheric deposition, and N<sub>2</sub> fixation (diazotrophy), results in the net transport of atmospheric carbon to the deep ocean (3), or “carbon sequestration” (4).

The Amazon River has the largest discharge of any river and accounts for 18% of all of the riverine input to the oceans. Between May and September, the Amazon plume covers up to 1.3 × 10<sup>6</sup> km<sup>2</sup> with a freshwater lens of salinity <35 [supporting information (SI) Table S1], which accounts for 20% of the WTNA. Our understanding of the influence of the Amazon River on the carbon cycle in the WTNA has evolved significantly since Ryther *et al.* (5) first suggested that the Amazon River depressed the productivity of the region influenced by its plume. Several studies have focused on the nutrients delivered by the river to the inner shelf, the subsequent river-supported new production of 0.6 Tmol of C yr<sup>-1</sup> [based on the NO<sub>3</sub> + NO<sub>2</sub> + NH<sub>4</sub> flux of 2.5 × 10<sup>8</sup> mol of N d<sup>-1</sup> reported by DeMaster and Aller (6)] and consequences to biogeochemical cycles [reviewed by DeMaster and Aller (6)]. However, none of these investiga-

tions studied the plume in the open ocean beyond the shelf. We undertook three field campaigns to study the influence of the Amazon River on the carbon and nitrogen cycles beyond the shelf. Samples at a total of 82 stations in the WTNA in January to February 2001, July to August 2001, and April to May 2003 (Fig. 1 and Table S2) complement earlier studies by examining the region of the plume starting 300 km north of the mouth of the river. We classified the stations into three categories based on sea surface salinity (SSS).<sup>¶¶</sup> The “low salinity” group contained all of the stations with SSS <30. Stations that had SSS between 30 and 35 were classified as “mesohaline,” whereas those with SSS >35 were classified as “oceanic.”

Surface NO<sub>3</sub> concentrations were below detection at most stations, with the highest value of 0.50 μM recorded at the station with the lowest salinity of 24. DeMaster and Pope (7) found when plotting NO<sub>3</sub> vs. soluble reactive phosphorus (SRP) concentrations for samples taken from outside the river mouth and adjacent shelf, the SRP concentration was 0.14 μM at the zero NO<sub>3</sub> intercept, implying that the Amazon is an important source of “excess” SRP (N:P < 16) to the WTNA. Using SRP concentration in the river, Devol (8) calculated that the Amazon contributed ≈30% of global riverine SRP flux to the ocean. This is very likely an underestimate because it does not include the contribution of SRP desorbed from particles once the river water mixes with oceanic waters (9). Although we do not know enough about P-uptake dynamics of the endosymbiotic diazotrophic cyanobacteria *Richelia*, *Trichodesmium* is capable of using dissolved organic P in the form of monophosphate esters and phosphonates (10) in addition to the SRP supplied by the river. The Amazon is also very likely an important source of labile Fe to WTNA. Boyle *et al.* (11) found that >90% of the dissolved Fe (dFe) in river water flocculated and precipitated in estuaries upon mixing with seawater. However, even if only 1% of the 2.5 μM dFe reported by Bergquist and Boyle (12) at Macapá was transported offshore by the plume, the surface concentrations in the offshore plume could be 25 times higher than concentrations typically observed in the WTNA. The concentrations of SRP (<52 nM) and dFe (<1.8 nM) we measured in the outer plume

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<sup>¶¶</sup>Salinity was measured by using the Practical Salinity Scale and has no units.

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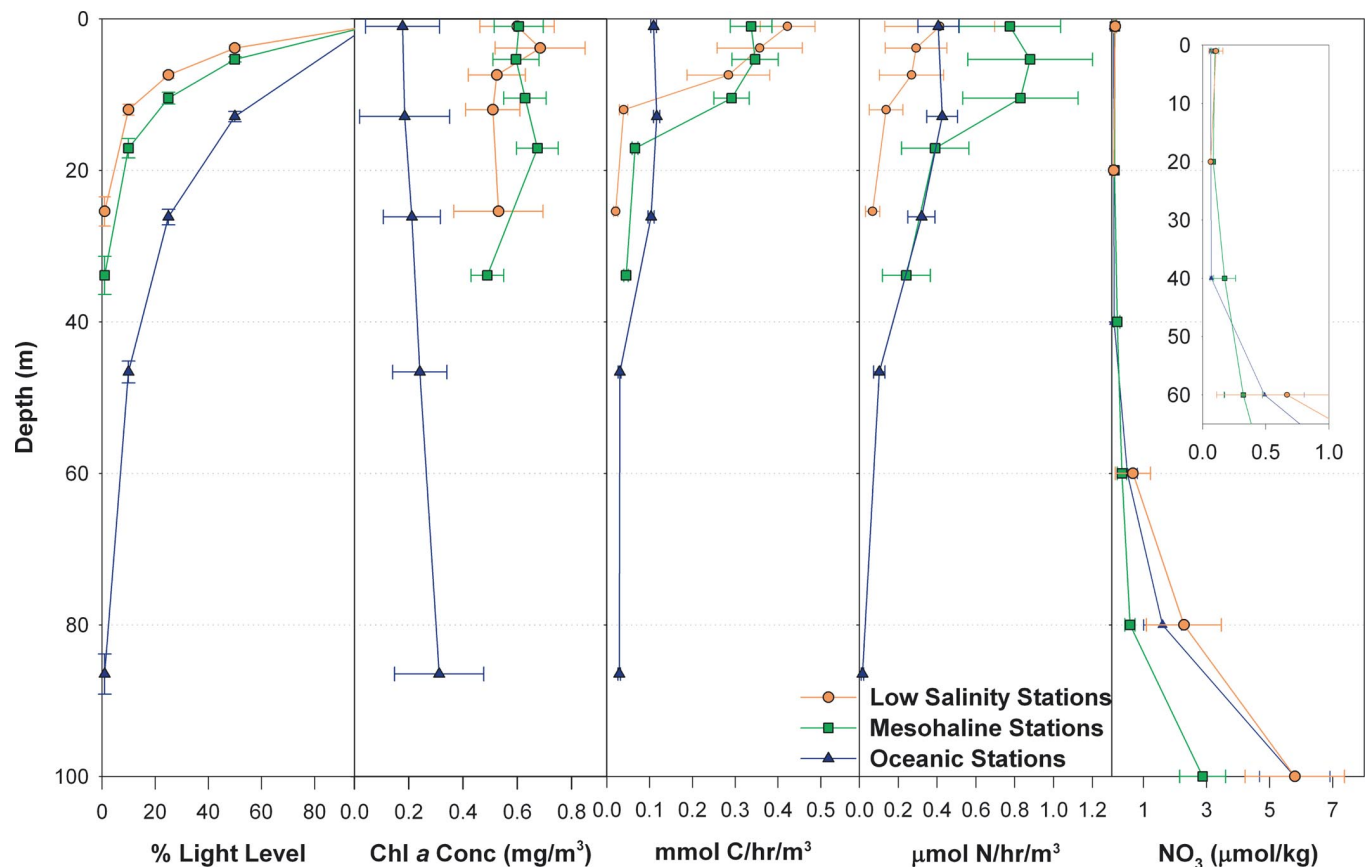
**Table 1. Forcing factors and biological response at the three station types**

Parameter	Low-salinity stations	Mesohaline stations	Oceanic stations	Kruskal–Wallis <i>P</i>
Surface salinity	27.91 ± 0.63 (0,3,5) = 8	32.97 ± 0.20 (0,18,17) = 35	36.03 ± 0.03 (24,7,8) = 39	4.9 × 10 <sup>-15</sup>
1% light depth, m	28 ± 4 (0,3,5) = 8	37 ± 3 (0,18,17) = 35	86 ± 3 (24,7,8) = 39	6.1 × 10 <sup>-12</sup>
Surface dissolved iron, nM	1.8 ± 0.4 (0,3,4) = 7	1.7 ± 0.2 (0,17,8) = 25	1.4 ± 0.5 (17,7,2) = 26	0.006
Surface soluble reactive phosphorus, nM	52 ± 18 (0,3,5) = 8	30 ± 4 (0,16,15) = 31	37 ± 4 (19,7,5) = 31	0.35
Surface dissolved Si, μM	10.9 ± 2.7 (0,3,5) = 8	4.1 ± 0.7 (0,15,12) = 27	1.4 ± 0.1 (16,6,3) = 25	9.8 × 10 <sup>-5</sup>
Surface biogenic silica, μmol liter <sup>-1</sup>	0.47 ± 0.19 (0,2,5) = 7	0.53 ± 0.12 (0,17,12) = 29	0.08 ± 0.03 (12,6,3) = 21	4.5 × 10 <sup>-6</sup>
Depth integrated <i>Trichodesmium</i> counts (×10 <sup>6</sup> trichomes m <sup>-2</sup> )	12 ± 9 (0,3,5) = 8	13 ± 4 (0,18,16) = 34	28 ± 5 (24,7,8) = 39	0.027
Depth integrated <i>Richelia</i> counts (×10 <sup>6</sup> heterocysts m <sup>-2</sup> )	7 ± 6 (0,3,5) = 8	523 ± 116 (0,18,16) = 34	4 ± 2 (24,7,8) = 39	9.2 × 10 <sup>-6</sup>
Depth-integrated chlorophyll <i>a</i> , mg of chl <i>a</i> m <sup>-2</sup>	14 ± 2 (0,3,5) = 8	22 ± 2 (0,17,17) = 34	26 ± 1 (21,6,8) = 35	0.002
Depth-integrated primary production, mmol of C m <sup>-2</sup> day	35 ± 5 (0,3,5) = 8	57 ± 7 (0,17,12) = 29	59 ± 3 (19,7,5) = 31	0.010
Depth-integrated N <sub>2</sub> fixation by <i>Trichodesmium</i> and <i>Richelia</i> , μmol of N m <sup>-2</sup> day	25 ± 17 (0,3,5) = 8	986 ± 373 (0,18,16) = 34	157 ± 32 (24,7,8) = 39	0.028
Surface biologically depleted DIC, μmol kg <sup>-1</sup>	20 ± 10 (0,3,5) = 8	29 ± 5 (0,16,16) = 32	12 ± 1 (22,7,8) = 37	1.8 × 10 <sup>-6</sup>
Shallow trap mass flux, mg m <sup>-2</sup> day	—	152 ± 26 (0,3,5) = 8	42 ± 8 (2,0,3) = 5	—

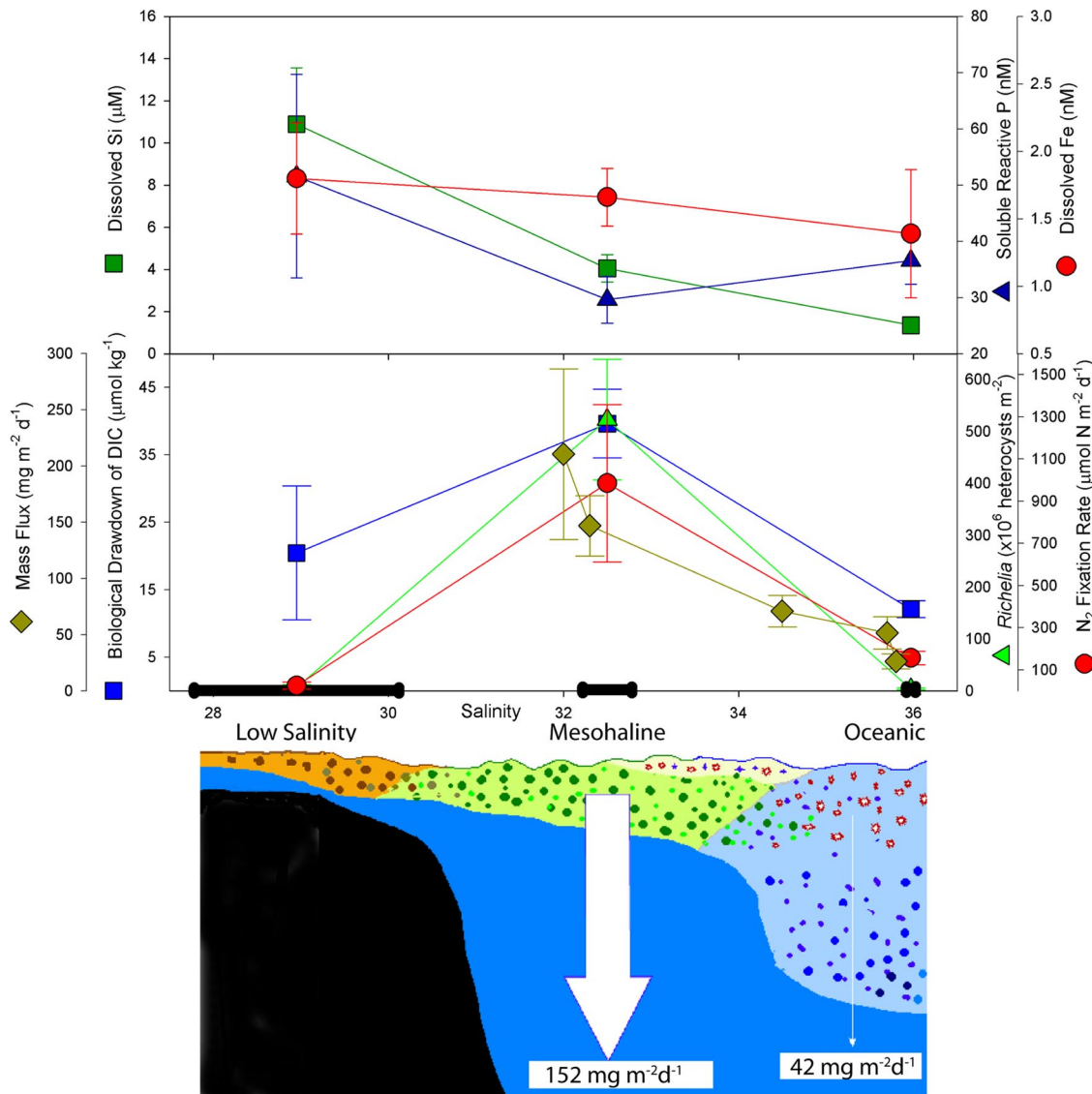
Mean measurements ± SE (number of stations from the January, April, and July cruises, respectively) = Total. The data for each station are provided in Table S2. The Kruskal–Wallis *P* value is shown for the null hypothesis that all samples are drawn from the same population.

*etionema costatum* and *Pseudonitzschia* sp (19). The diatoms *Hemiaulus hauckii* and *Rhizosolenia clevei* containing the symbiotic cyanobacteria *Richelia* sp. (diatom diazotroph associa-

tions, DDA) formed ≈28% of the biomass at the mesohaline stations, whereas they comprised <2% of biomass at the oceanic and low-salinity stations. We posit that the composition of the



**Fig. 2.** Vertical profiles of mean light depths, chlorophyll *a* concentration, C and N fixation rates, and NO<sub>3</sub> concentrations binned by station type, details shown in Table S2. The error bars represent standard error.



**Fig. 3.** Changes along the river plume as it moves offshore. (*Top*) Changes in surface nutrient concentrations as a function of salinity for each of the station types; the values and statistics are presented in Table 1. Error bars denote standard error; the thick horizontal line on the x axis indicates the mean salinity  $\pm 1$  S.E. for each group of stations. (*Middle*) Changes in biological response and mass flux from floating sediment traps at 200 m presented as in A. (*Bottom*) A schematic of changes along the plume; the arrows showing the mean mass flux for the mesohaline, and oceanic stations. The brown particles represent coastal phytoplankton species; the dark green represents DDA; the red represents *Trichodesmium*; and the blue represents particles typical of oligotrophic oceanic phytoplankton. Phytoplankton chlorophyll, *Trichodesmium*, and *Richelia* concentrations are given in Table 1. Water below the euphotic zone is depicted in solid dark blue, and the 1% light depths are given in Table 1.

phytoplankton community changes along the Amazon River plume from the mouth to the open ocean in response to changing nutrient availability (Fig. 3). At the low-salinity stations, there is enough P, Si, and combined N at the surface to support coastal diatom species, and there is very little  $N_2$  fixation. As the combined N is assimilated and the plume is mixed with low-nutrient ocean waters, diazotrophs become significant sources of new nitrogen (Table 1 and Fig. 1). Diatom hosts of *Richelia*, the dominant diazotroph at the mesohaline stations, require the Si and P found in the river plume, but N is supplied by fixation of dinitrogen ( $N_2$ ). Farther “downstream,” where river-associated Si and SRP are depleted, the species composition transitions to that typical of oligotrophic tropical oceans, and the dominant diazotroph is *Trichodesmium*.

The change in phytoplankton community structure affects the efficiency of the biological pump. Although new nitrogen pro-

vided by any marine diazotroph increases the availability of fixed nitrogen in the ocean and leads to carbon sequestration, the actual pathways and time scales of sinking of organic matter through the upper ocean and into the deep sea can vary for the different diazotrophs (20). We found a significant correlation between biologically depleted DIC in the plume (Fig. 1) and the vertically integrated cell abundance of *Richelia* ( $r = 0.6$ ;  $n = 77$ ,  $P < 0.01$ ). The six surface samples with the greatest net seasonal biological  $pCO_2$  drawdown (100–130  $\mu atm$ ) were associated with large blooms of *Richelia*. Other plume stations with no prevailing diazotroph population or with *Trichodesmium* showed much smaller (20–40  $\mu atm$ ) seasonal biological drawdowns (21). These conclusions were further supported by a multivariate statistical approach: A principal-components analysis (Table S3) generated four axes that explained 74% of the system variability. Axis 1 (35%) signified the physical river–ocean gradient, Axis 2

(19%) denoted the mesohaline DDA population, Axis 3 (13%) represented *Trichodesmium* population, and Axis 4 (7%) correlated with total integrated primary production and dFe. The key result was that the largest nonconservative changes in DIC were associated with high *Richelia* abundance and high N<sub>2</sub> fixation on Axis 2 (Fig. S1).

The DDA drawdown of DIC corresponded to greater particulate export. Sedimentation rates (mg m<sup>-2</sup> d<sup>-1</sup>) derived by using floating sediment traps at 200 m were nearly fourfold higher at our mesohaline stations (152 ± 26, eight samples from three deployments) compared with oceanic stations (42 ± 8, 5 samples from two deployments, Wilcoxon rank sum  $P = 0.003$ , Fig. 3). The isotopic composition of N in the material collected in the floating trap can be used to infer the potential origin of the material found in the traps. Particulate nitrogen in waters dominated by both *Trichodesmium* and the diatom *Hemiaulus* containing the endosymbiont *Richelia* is known to be significantly depleted in <sup>15</sup>N (22), with δ<sup>15</sup>N values typically being <0‰. At our mesohaline station (3–23, shown in Fig. 1) dominated by DDAs, the δ<sup>15</sup>N of the trap material was -1.5‰, suggesting that the DDA contributed strongly to the vertical flux. The high particulate export by DDAs has also been observed deeper in the water column. In the subtropical Pacific, Scharek *et al.* (23) reported a 500- to 1,250-fold increase of intact DDA cells at 4,000 m in late July/early August. They calculated that these DDAs had settling rates of 100–200 m d<sup>-1</sup> with little remineralization along the way. Deuser *et al.* (24) observed that total material flux into a deep trap (3200 m) deployed just east of Barbados (13°13' N, 57°41' W) ranged between 100 and 200 mg m<sup>-2</sup>d<sup>-1</sup> when the Amazon River plume passed over it but was only 35–60 mg m<sup>-2</sup>d<sup>-1</sup> during the winter months, analogous to our mesohaline and oceanic conditions, respectively.

One important consequence of the rapid sinking of diatoms is the significant transport of atmospheric C to the deep ocean by this process. Using a 6.6 C/N stoichiometry and the mean N<sub>2</sub> fixation rate for mesohaline stations dominated by DDAs, we derive a C-fixation rate of 6.5 (±2.5) mmol of C m<sup>-2</sup> d<sup>-1</sup> for diazotrophs in the waters influenced by the Amazon plume. Combining this with satellite-based monthly estimates of the areal extent of the plume with salinity between 30 and 35, we calculate that the carbon sequestration due to diazotrophy in mesohaline waters can be as high as 1.7 ± 0.7 Tmol of C (20 ± 8 Tg of C) annually. Added to the estimate for new production based on river nitrate, we get a total Amazon-supported new production of 2.3 Tmol of C per yr<sup>-1</sup>. Despite differences in relevant temporal and spatial scales, the mesohaline number agrees well with the independent net community production estimate of 1.2 ± 0.4 (25) or 1.3 ± 0.5 (26) Tmol of C (15 ± 6 Tg of C), calculated from the drawdown of DIC in the plume and 1.3 Tmol of C (15 Tg of C) derived by using a mass flux of 150 mg m<sup>-2</sup>d<sup>-1</sup> and by assuming that 40% of total sinking material is organic carbon (Table S1) and suggests that this biological pump is highly efficient.

Our work shows that the Amazon River plays an important role in enhancing primary production far beyond the continental shelf by supporting diazotrophs and thereby providing a significant source of new N. Although the Amazon represents the largest riverine input to the tropical ocean, there are numerous other tropical rivers that deliver large volumes of water with “excess” P and Si to this biome. Carbon sequestration by DDAs associated with excess nutrients supplied by tropical river plumes may be a globally significant phenomenon. *Hemiaulus* with N<sub>2</sub>-fixing symbionts have been reported in Mediterranean sapropels related to hypermonsoonal periods of enhanced runoff of the Nile River (27). In the Eastern Tropical Atlantic, up to 95% of the cells at a station south of the Congo River mouth were *Hemiaulus* (28). Studies in the South China Sea (29) have reported enhanced N<sub>2</sub> fixation in mesohaline waters. Tropical mesohaline waters are an important interface between terrestrial and oceanic realms. The occurrence and impact of N<sub>2</sub> fixation in these waters is sensitive to changes in hydrological cycles, fertilizer, and land use and must be understood.

### Methods Summary

The abundances and depth distribution of the diazotroph population at each station was determined as described by Carpenter *et al.* (30). The euphotic depth was estimated from spectral downwelling irradiance measured by using a free-falling spectroradiometer. Measurements of C and N fixation, chlorophyll a concentrations, and phytoplankton biomass were integrated through the euphotic zone to determine the areally integrated rates reported in Table 1 and in Table S2. Carbon fixation was determined by <sup>14</sup>C uptake method (30) and N<sub>2</sub> fixation by both <sup>15</sup>N uptake and C<sub>2</sub>H<sub>2</sub> reduction methods (31). Chlorophyll a concentrations were measured by using an HPLC (32). Fe concentrations were determined by AAS (MP01, MP03) or ICP-MS (MP08) after preconcentration with APDC/DDDC organic extraction (34). SRP was quantified spectrophotometrically (35). Si and NO<sub>3</sub> were determined by using standard calorimetric techniques on a Bran and Luebbe AA3. Total dissolved inorganic carbon and alkalinity were measured by using standard methods (33), and biological drawdown calculated as described by (26). Please see SI Text for detailed description of methods.

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