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 nitrogen fixation far from the mouth and provides important pathways for sequestration of atmospheric CO2 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⁻¹ of the new production supported by NO3 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 CO2 and the implied oceanic carbon transport. Global Biogeochem Cycles 21, doi:10.1029/2006GB002751]. The enhancement of N2 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

Owning 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 CO2 (1). The flux of nitrate (NO3) from deep water to the photic zone can stimulate new phytoplankton production and export (2), but because the upwelling or diffusive flux of NO3 is accompanied by a corresponding upward flux of CO2, 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 N2 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 × 10⁶ km² 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⁻¹ [based on the NO3 + NO2 + NH4 flux of 2.5 × 10⁶ mol of N d⁻¹ reported by DeMaster and Aller (6)] and consequences to biogeochemical cycles [reviewed by DeMaster and Aller (6)]. However, none of these investigations 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). 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 NO3 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 NO3 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 NO3 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).

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 (<25 nM) and dFe (<1.8 nM) we measured in the outer plume


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(Table 1; and see Fig. 3) were much lower than the 0.8 and 2.5 μM, respectively, reported near the mouth, reflecting mixing with ocean waters, uptake by phytoplankton, and complex particle adsorption/desorption relationships that need to be investigated in the future. Aerosols are also important sources of Fe to this region (13), and there is little evidence of Fe limitation in the WTNA, with average surface concentrations exceeding the half-saturation constant for growth of coastal diatoms as well as for N₂ fixation by *Trichodesmium* (0.05–0.075 nM and 0.16 nM, respectively (14, 15). After the plume leaves the continental shelf, excess P and Si (N:P < 16 and Si:n > 6.6) supplied by the river establish an ideal niche for N₂ fixation.

The mean depth-integrated primary production rate for the coastal stations was 35 ± 5 mmol of C m⁻² d⁻¹, the lowest rate of the three station groups (Table 1). We found that colored dissolved organic matter, rather than phytoplankton, dominated (~70%) total light absorption at coastal stations, whereas phytoplankton and other particulate matter dominated (~40% each) absorption in the mesohaline stations (16), extending the conclusion of Smith *et al.* (17) that primary production on the Amazon shelf is light-limited nearshore (Fig. 2). The depth-integrated primary production rates for the mesohaline and oceanic stations were comparable with each other at ~58 mmol of C m⁻² d⁻¹. The mean depth-integrated N₂ fixation rate (μmol of N m⁻² d⁻¹) of mesohaline stations (986 ± 373, n = 34), however, was more than six times higher than that of the oceanic stations (157 ± 32, n = 39, Fig. 1) with the highest rates measured at stations dominated by *Richelia* blooms. Assuming Redfield stoichiometry in the organic matter produced, these observed rates of N₂ fixation can support only 11% of the observed total primary production (6.5 of 57 mmol of C m⁻² d⁻¹) in the mesohaline waters, whereas ~2% and <0.5% of the primary production was supported by N₂ fixation in oceanic stations and low-salinity stations, respectively. Pico- and nanoplanktonic N₂ fixers were not found to be abundant in mesohaline waters (18), and their contribution to this system is not yet well constrained.

The phytoplankton species composition at the low-salinity stations was dominated by coastal diatom species such as *Skel...
etonea costatum and Pseudonitzschia sp (19). The diatoms Hemiaulus hauckii and Rhizosolenia clevei containing the symbiotic cyanobacteria Richelia sp. (diatom diazotroph associations, 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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low-salinity stations</th>
<th>Mesohaline stations</th>
<th>Oceanic stations</th>
<th>Kruskal–Wallis P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface salinity</td>
<td>27.91 ± 0.63 (0,3,5) = 8</td>
<td>32.97 ± 0.20 (0,18,17) = 35</td>
<td>36.03 ± 0.03 (24,7,8) = 39</td>
<td>4.9 × 10⁻¹⁵</td>
</tr>
<tr>
<td>1% light depth, m</td>
<td>28 ± 4 (0,3,5) = 8</td>
<td>37 ± 3 (0,18,17) = 35</td>
<td>86 ± 3 (24,7,8) = 39</td>
<td>6.1 × 10⁻¹²</td>
</tr>
<tr>
<td>Surface dissolved iron, nM</td>
<td>1.8 ± 0.4 (0,3,4) = 7</td>
<td>1.7 ± 0.2 (0,17,8) = 25</td>
<td>1.4 ± 0.5 (17,7,2) = 26</td>
<td>0.006</td>
</tr>
<tr>
<td>Surface soluble reactive phosphorus, nM</td>
<td>52 ± 18 (0,3,5) = 8</td>
<td>30 ± 4 (0,16,15) = 31</td>
<td>37 ± 4 (19,7,5) = 31</td>
<td>0.35</td>
</tr>
<tr>
<td>Surface dissolved Si, μM</td>
<td>10.9 ± 2.7 (0,3,5) = 8</td>
<td>4.1 ± 0.7 (0,15,12) = 27</td>
<td>1.4 ± 0.1 (16,6,3) = 25</td>
<td>9.8 × 10⁻⁵</td>
</tr>
<tr>
<td>Surface biogenic silica, μmol liter⁻¹</td>
<td>0.47 ± 0.19 (0,2,5) = 7</td>
<td>0.53 ± 0.12 (0,17,12) = 29</td>
<td>0.08 ± 0.03 (12,6,3) = 21</td>
<td>4.5 × 10⁻⁶</td>
</tr>
<tr>
<td>Depth integrated Trichodesmium counts (×10⁶ trichomes m⁻²)</td>
<td>12 ± 9 (0,3,5) = 8</td>
<td>13 ± 4 (0,18,16) = 34</td>
<td>28 ± 5 (24,7,8) = 39</td>
<td>0.027</td>
</tr>
<tr>
<td>Depth integrated Richelia counts (×10⁶ heterocysts m⁻²)</td>
<td>7 ± 6 (0,3,5) = 8</td>
<td>523 ± 116 (0,18,16) = 34</td>
<td>4 ± 2 (24,7,8) = 39</td>
<td>9.2 × 10⁻⁶</td>
</tr>
<tr>
<td>Depth-integrated chlorophyll a, mg of chla m⁻²</td>
<td>14 ± 2 (0,3,5) = 8</td>
<td>22 ± 2 (0,17,17) = 34</td>
<td>26 ± 1 (21,6,8) = 35</td>
<td>0.002</td>
</tr>
<tr>
<td>Depth-integrated primary production, mmol of C m⁻² day</td>
<td>35 ± 5 (0,3,5) = 8</td>
<td>57 ± 7 (0,17,12) = 29</td>
<td>59 ± 3 (19,7,5) = 31</td>
<td>0.010</td>
</tr>
<tr>
<td>Depth-integrated N₂ fixation by Trichodesmium and Richelia, μmol of N m⁻² day</td>
<td>25 ± 17 (0,3,5) = 8</td>
<td>986 ± 373 (0,18,16) = 34</td>
<td>157 ± 32 (24,7,8) = 39</td>
<td>0.028</td>
</tr>
<tr>
<td>Surface biologically depleted DIC, μmol kg⁻¹</td>
<td>20 ± 10 (0,3,5) = 8</td>
<td>29 ± 5 (0,16,16) = 32</td>
<td>12 ± 1 (22,7,8) = 37</td>
<td>1.8 × 10⁻⁶</td>
</tr>
<tr>
<td>Shallow trap mass flux, mg m⁻² day</td>
<td>—</td>
<td>152 ± 26 (0,3,5) = 8</td>
<td>42 ± 8 (2,0,3) = 5</td>
<td>—</td>
</tr>
</tbody>
</table>

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.

Fig. 2. Vertical profiles of mean light depths, chlorophyll a concentration, C and N fixation rates, and NO₃ concentrations binned by station type, details shown in Table S2. The error bars represent standard error.
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 N2 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 (N2). 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 provided 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 pCO2 drawdown (100–130 μatm) were associated with large blooms of Richelia. Other plume stations with no prevailing diazotroph population or with Trichodesmium showed much smaller (20–40 μatm) 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...
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. *Hemialus* with N$_2$-fixing symbionts have been reported in Mediterranean upwellings 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 *Hemialus* (28). Studies in the South China Sea (29) have reported enhanced N$_2$ fixation in mesohaline waters. Tropical mesohaline waters are an important interface between terrestrial and oceanic realms. The occurrence and impact of N$_2$ 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 $^{14}$C uptake method (30) and N$_2$ fixation by both $^{15}$N uptake and C-H$_2$ reduction methods (31). Chlorophyll 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$_3$ 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 SRP was quantified by using spectrophotometric methods.

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