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Patterns of nitrogen fixation along 10°N in the tropical Atlantic

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[1] Nitrogen fixation supports new production in the oligotrophic oceans and removes dinitrogen and carbon dioxide from mixed layer waters. N-fixation rates have been estimated in various ways but measurements are still too rare and factors limiting N-fixation are not yet fully understood. Here we present data from a transect along 10°N through the tropical Atlantic on the Meteor Cruise 55 where N-fixation rates between 3.7 and 255 μmol $N*m^{-2}*d^{-1}$ were recorded. The highest rates occurred off Africa in the eastern tropical North Atlantic (ETNA), and in the Amazon River plume in the West and contributed to 1–12.2% of the N-demand of primary production. N-fixation rates correlated with dissolved Fe concentrations, which were 20–280 times greater than the estimated demand. High atmospheric Fe inputs combined with the shallow nutricline make the ETNA a favourable environment for N-fixers. *INDEX TERMS:* 4855 Oceanography: Biological and Chemical: Plankton; 4875 Oceanography: Biological and Chemical: Trace elements; 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; 9325 Information Related to Geographic Region: Atlantic Ocean; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615). **Citation:** Voss, M., P. Croot, K. Lochte, M. Mills, and I. Peeken (2004), Patterns of nitrogen fixation along 10°N in the tropical Atlantic, *Geophys. Res. Lett.*, *31*, L23S09, doi:10.1029/2004GL020127.

1. Introduction

[2] Cyanobacteria of the genus *Trichodesmium* occur throughout the tropical and subtropical ocean and are responsible for the majority of marine N-fixation [*Capone et al.*, 1997]. Global estimates of marine N-fixation aim to contribute to the understanding of biological productivity, and are based on nutrient fields from previous experiments [*Deutsch et al.*, 2001; *Gruber and Sarmiento*, 1997]. Both conclude that N-fixation is higher than measured rates and contributes new N to the oceans; especially where dust/Fe input from land is high. Iron is the essential micronutrient necessary for nitrogenase, the enzyme that fixes dinitrogen and has been hypothesized to limit N-fixation [*Falkowski*, 1997]. Since iron is supplied via atmospheric deposition [*Martin et al.*, 1994], and N-fixation is an energy demanding process it is advantageous for diazotrophs to dwell near the surface [*Capone et al.*, 1997]. Whether *Trichodesmium* is limited by dissolved phosphorus, iron, or co-limited by Fe and P is controversial. According to *Sanudo-Wilhelmy et al.* [2001] phosphorous limitation occurs in the central Atlantic where iron is supplied in excess.

[3] Here we studied the regional variability of N-fixation, and evaluated environmental conditions that may support growth of N-fixing organisms, along 10°N in the Atlantic Ocean. The cruise took place in autumn when the intertropical convergence zone has its northernmost extension providing rain and dust input along the transect [*Kremling and Streu*, 1993; *Perry et al.*, 1997]. Previous measurements of *Trichodesmium* sp. abundance were higher in the western tropical North Atlantic (WTNA) than in the ETNA [*Carpenter*, 1983; *Carpenter et al.*, 2004], but low $\delta^{15}N_{PON}$ values, indicative of N-fixing organisms, have been recorded as far east as 20°W [*Mahaffey et al.*, 2003]. Nutrient concentrations however, were expected to be higher in the east where upwelling occurs off Guinea, Africa. We therefore expected higher N-fixation rates along the western part of the transect than in the east.

2. Material and Methods

[4] The Meteor cruise 55 (M55) took place October 12th–November 17th, 2002 from 56.6°W to 17°W along 10°N with a 7 day excursion to the equator at app. 25°W (Figure 1). We collected water samples throughout the upper water column (5 m, 15 m, 40 m/50 m, 60 m/80 m and 100 m) with a CTD-rosette, equipped with Niskin bottles and at some stations with a bucket from the surface. Nutrients (NO_2, NO_3, PO_4, SiO) were measured with an auto-analyser on board after *Grasshoff et al.* [1983]. At 16 stations N-fixation and CO_2 uptake rates were measured with the tracers $^{15}N_2$ and $^{13}CO_2$. The general procedure for that is described in *Montoya et al.* [1996]. Briefly, samples were incubated in 1 L glass bottles, filled to overflowing without screening. To each bottle 200 μl of a 0.1 molar $^{13}CO_2$ stock solution (99.9% $NaH^{13}CO_3$, Campro Scientific) was added before being sealed with a Teflon backed butyl septum cap. With a gas-tight syringe 1 ml of $^{15}N_2$ gas (99% $^{15}N_2$, Campro Scientific) was added to each bottle. Bottles were incubated for 6–7 hours in boxes on deck under neutral density screens approximating the in-situ light levels (100%, 50%, 20%, 6%, 1% light intensity and dark) and cooled with circulating surface seawater. Four bottles were incubated from each depth and 2 were combined on one filter resulting in replicate filters for each depth. Incubations were stopped by gentle vacuum filtration through precombusted GF/F filters, which were rinsed with freshly filtered seawater, and immediately dried at 60°C. Filters were stored dry at room temperature. In three experiments (St. 15, 18, 22, and, 38) only 2 light intensities were incubated and therefore no depth integrated fixation rates were calculated. Prior to analysis, the filters were fumed with HCl for 2 hrs, and dried again. Concentrations of particulate organic nitrogen (PON) and carbon (POC) were measured with a CE1108 elemental analyser connected to a Finnigan Delta S isotope ratio mass spectrometer. Calibra-

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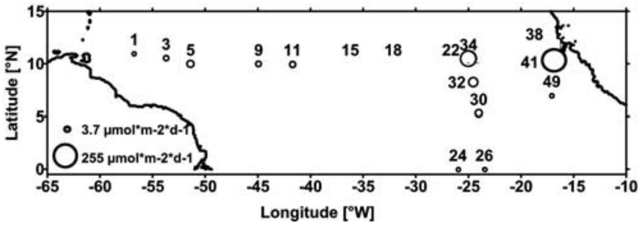

Figure 1. Station map and nitrogen fixation (circles). Circle size is linearly proportional to the N-fixation rate. At stations 15, 18, 22, and 38 no surface values were measured and no depth integration carried out.

tion of isotopically enriched substances was made with IAEA standards 310 for nitrogen (50‰ and 200‰) and 309 for carbon (100‰ and 550‰). Daily fixation rates (N_2 and CO_2) were extrapolated to the light period assuming a linear relationship between light intensity and fixation using the ship's continuous light measurements.

[5] Samples for iron determination were obtained using 8 L trace metal clean GoFlo bottles attached to a plastic hydrowire. Both dissolved (filtration through a 0.2 µm Sartorius cartridge filter) and total (unfiltered) iron samples were collected. Samples were extracted using the established dithiocarbamate solvent technique with analysis by graphite furnace atomic absorption [*Croot et al.*, 2004]. The integrated iron concentrations and N-fixation rates were calculated by the trapezoidal rule. Where iron and N-fixation rates were not available from the same station neighbouring stations were combined, if hydrographic variability was low.

3. Results and Discussion

[6] There was considerable variability in N-fixation, between 56.6 and 17°W, with lower rates in the WTNA and at the equator than towards the African coast (Figure 1). Integrated N-fixation rates varied from 3.7 to 255 μmol*m^{-2}*d^{-1}. This gives a 0.01 to 0.1 mol N*m^{-2}*y^{-1}, assuming N-fixation occurs year round, and is comparable to the mean flux estimate of *Gruber and Sarmiento* [1997] (0.072 mol N*m^{-2}*y^{-1}). We grouped the stations into WTNA (Stations 3–11) equatorial (Stations 24 and 26), and ETNA (Stations 30–49). A conservative mean input through N-fixation is 24 ± 18 μmol*m^{-2}*d^{-1} and 140 ± 78 μmol*m^{-2}*d^{-1} in the WTNA and ETNA, respectively. These data are in the same range as those compiled by *Capone et al.* [1997], where rates vary between a few to 278 μmol*m^{-2}*d^{-1}, with the highest numbers and amounts of trichomes [*Carpenter et al.*, 2004] measured in Caribbean waters. Our rates were low in the western part of the transect which was south of the Caribbean and possibly not influenced by *Trichodesmium* sp. rich Sargasso Sea waters. The only western station with elevated rates was station 5 (10.0°N, 51.4°W), characterised by a surface salinity below 31.2 and linked to the Amazon River [*Körtzinger*, 2003]. Heterotrophic ciliates, small zooplankton, aggregates of phytoplankton with *Trichodesmium* and *Rhizosolenia,* containing the N-fixer *Richelia* sp., were observed. The N-fixation rate at St.5 was 56 μmol N*m^{-2}*d^{-1}, considerably lower than that measured by *Carpenter et al.* [1999].

[7] Our rates are the furthest east measurements of N-fixation in the tropical Atlantic and slightly higher than reported in *Mills et al.* [2004] from the same cruise. They support the view that N-fixation is highest in the ETNA, and that the equator is a minimum. The standing crop of trichomes was low between 40°W and 25°W [*Carpenter et al.*, 2004], where *Montoya et al.* [2002] on the same transect found varying contributions of diazotrophs to the PON pool (4–40%). N-fixation, converted to C-uptake rates via Redfield equivalents, contributes 1.5–6.7% and 5.8–12.2% of primary production in the WTNA and ETNA, respectively, which is in the same order of magnitude as 11% for *Trichodesmium* sp. in Oct. 1996 [*Carpenter et al.*, 2004].

[8] Increased N-fixation rates towards the African coast were recorded in an area heavily impacted by atmospheric deposition of dust [*Croot et al.*, 2004]. Total Fe in the water column during M55 was between 0.2 and 6.8 nmol L^{-1} in the upper 100 m, while the dissolved fraction was roughly half. We found a significant relationship between N-fixation and dissolved iron inventories (overall exponential but app. linear at low iron inventories, Figure 2). Individual measurements, however, did not show the same correlation, indicating the importance of mixing processes and/or vertical migration. Additionally, P and Fe may be co-limiting and the P is supplied from the same dust source as the Fe [*Mills et al.*, 2004].

[9] The Fe demand of N-fixers was calculated after conversion of N-fixation rates via Redfield stochiometry into C-uptake rates and assuming 28 μmol Fe per mol of fixed C for phototrophic diazotrophs [*Kustka et al.*, 2002]. The Fe demand varied between 0.67 and 46.5 nmol*m^{-2}*d^{-1}. Based on this, dissolved Fe concentrations were 20–280 times greater than seem necessary to meet the N-fixation requirements. Field estimates give higher Fe requirements by a factor of 3–5 [*Kustka et al.*, 2003]. *Berman-Frank et al.* [2001] found maximal Fe:C ratios of 450 ± 242 μmol:mol in Australian waters, that suggest only a 1 to 17 fold surplus of dissolved Fe at our stations. Likewise, the

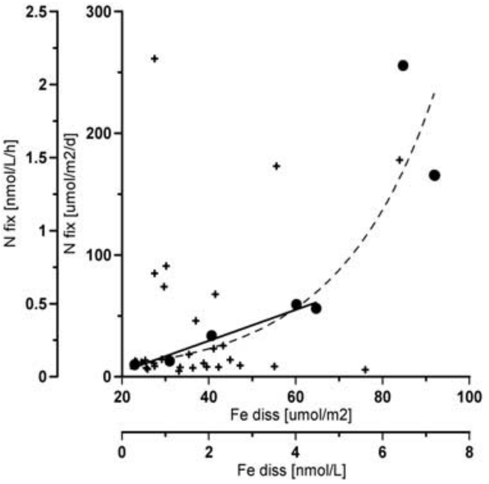

Figure 2. Relationship between N-fixation rate and Fe$_{\mathrm{diss.}}$, integrated over the upper 100 m (●). Exponential: n = 7, r^2 = 0.94, significant <0.001; linear: n = 5, r^2 = 0.96, sig. <0.005 and single measurements of N-fixation rates over Fe$_{\mathrm{diss.}}$ (+). Note there are fewer stations than in Figure 1 because Fe data were not always available.

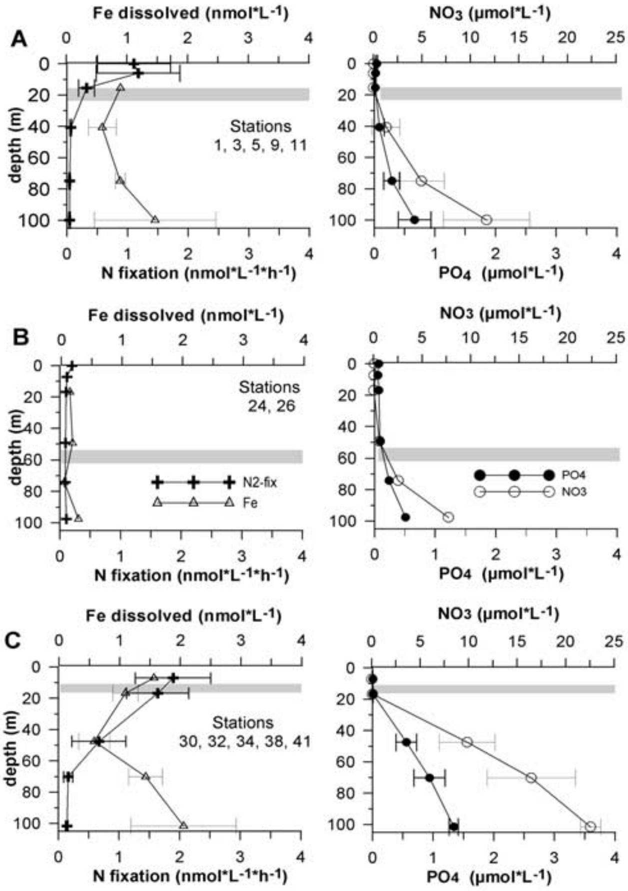

Figure 3. Vertical profiles of nitrogen fixation, dissolved iron, nitrate and phosphate concentrations for stations grouped into western Atlantic (A), equator (B), and eastern Atlantic (C). Note some depths are means: A: 80 m ± 12 m, C: 48 m ± 10 m and 70 m ± 10 m. The mixed layer depth (hatched area) is defined as the local maximum in the buoyancy frequency.

bioavailable fraction, (assumed to be iron hydroxy species as determined by voltammetric speciation measurements), is approximately 2–3 orders of magnitude less than the dissolved fraction (P. Croot, manuscript in preparation, 2004). The Fe concentrations we measured may therefore be in the required range or even limiting for N-fixation when the uncertainty in Fe quotas and availability of Fe are considered.

[10] N-fixation rates were always highest in the surface and rapidly decreased with depth. Only the easternmost stations had high fixation rates, even below the mixed layer (Figure 3). Maximal rates of 3.1 nmol $N^*L^{-1}{}^*h^{-1}$ (surface), and 2.2 nmol $N^*L^{-1}{}^*h^{-1}$ (50 m), were recorded. This is untypical for the chain forming *Trichodesmium* sp. that is positively buoyant, and inhabits surface waters [*Capone et al.*, 1997]. Similarly, these deeper N-fixation rates were measured at relatively high NO_3 concentrations (Figure 3c). Investigations of the inhibitory effects of NO_3 on the diazotrophic activity of *Trichodesmium* sp. have been contradictory; from complete inhibition of N-fixation [*Ohki et al.*, 1991] to no difference in the forms of nitrogenase present [*Chen et al.*, 1996]. The increased N-fixation rates at depth may result from unicellular cyanobacterial and heterotrophic diazotrophs, both detected along the M55 cruise track (R. Langlois and J. LaRoche, personal communication, 2004). *Falcon et al.* [2004] measured significant contribution from unicellular bacterioplankton at depths of 100 m in the WTNA. In the Pacific they clearly contribute to the N- input at 25% of surface irradiances [*Zehr et al.*, 2001]. Thus, our high rates at depth (20% light level) may be connected to unicellular diazotrophs.

[11] Alternatively, the N-fixation at depth may be related to the high DIP concentrations. Surface nutrients (NO_3, PO_4) were always below detection limit (Figure 3, except Si at St. 5), but the depth of the nutricline decreased considerably from app. 100 m in the west to app. 40 m in the east. An investigation by *Tyrell et al.* [2003] suggested a shallow nutricline combined with high dust inputs favours *Trichodesmium* abundance off West Africa. Phosphate concentrations at the easternmost stations averaged 0.5 μmol^*L^{-1} at 40 m, and 0.5 nmol Fe^*L^{-1}. At the western stations, and along the equator, PO_4 concentrations were much lower, and Fe concentrations equal or less (Figure 3). The P content of *Trichodesmium* colonies is the key-limiting nutrient for N-fixation in the Atlantic [*Sanudo-Wilhelmy et al.*, 2001], and *Wu et al.* [2000] imply that the low concentration of DIP limit N-fixation in the tropical North Atlantic. Thus the higher DIP concentrations at depth may contribute to the increased diazotrophic activity in our study. Independent measurements on the Meteor 55 cruise found N-fixation in the ETNA was co-limited by P and Fe, and stimulated by Saharan dust [*Mills et al.*, 2004]. Thus, the high N-fixation rates at depth must have had a Fe supply, most likely atmospheric deposition of dust. It seems possible that DIP input through the thermocline, in combination with atmospheric inputs of Fe (and P) play substantial roles in stimulating N-fixation rates, even at depth, in the ETNA.

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