

Effects of dust deposition and river discharges on trace metal composition of *Trichodesmium* spp. in the tropical and subtropical North Atlantic Ocean

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Abstract

We present the elemental composition (Al, Cd, Co, Cu, Fe, Mn, Mo, Ni, V, Zn, and P) of field-collected *Trichodesmium* populations. To distinguish the effects of river discharges (Amazon and Niger Rivers) and Saharan dust deposition on metal concentrations in the colonies, samples were collected both in the western (February 2001, July–August 2001, and April–May 2003) and eastern (May–June 2003) basins of the North Atlantic. Metal composition (medians normalized to P) in *Trichodesmium* ranged from 0.011 mmol mol⁻¹ for Co to 39 mmol mol⁻¹ for Fe and varied over an order of magnitude among different locations. A comparison of metal ratios measured in the *Trichodesmium* colonies with ratios reported for the potential sources suggests that the most important sources of trace metals to the tropical and subtropical Atlantic during our sampling were the Amazon and Niger Rivers, rather than dust deposition from the Sahara.

Diazotrophs play a critical role in supporting oceanic new production and in the “global biological carbon pump” (Capone et al. 1997). Members of the genus *Trichodesmium*, recognized as one of the most important oceanic nitrogen fixers, are thought to be among the most significant cyanobacterial primary producers in the tropical

and subtropical North Atlantic Ocean (Capone et al. 1997; Mills et al. 2004). Because of the ecological importance of nitrogen fixation by *Trichodesmium*, major research efforts are currently focused on identifying and understanding the primary controls on this process, including the role of trace metals (e.g., Sañudo-Wilhelmy et al. 2001; Mills et al. 2004; LaRoche and Breitbarth 2005).

Quantification of trace metals in phytoplankton is critical to assess their biochemical status and their nutritional requirements. However, information on metal levels in natural populations is limited (e.g., Collier and Edmond 1984; Cullen et al. 2003). The main reason for this lack of data is the inherently low metal content in natural populations, complicating sample collection and analyses

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without contamination. Separation of algal biomass from associated heterotrophs and detritus in natural samples is also problematic for most phytoplankton. Therefore, most studies of trace metal composition in marine phytoplankton have been carried out in cultures growing under controlled laboratory conditions (i.e., Ho et al. 2003; Hutchins and Bruland 1995). Despite evidence of potential metal limitation of *Trichodesmium* nitrogen fixation (Sañudo-Wilhelmy et al. 2001; Kustka et al. 2003; Mills et al. 2004), concentrations of bioactive trace metals other than Fe have not been reported.

Recent studies have linked biological activity in the ocean to the transport of metals from the land (Di Tullio and Laws 1991; Prospero and Lamb 2003; Jickells et al. 2005). Atmospheric deposition of Saharan dust and river discharges from the Amazon and Niger Rivers are significant sources of metals to the Atlantic Ocean. In fact, African dust is likely to be the most important source of metals to the entire tropical Atlantic Ocean (Jickells et al. 2005). However, the relevance of river discharges such as the Amazon River, which supplies up to 20% of all of the river water input to the Atlantic Ocean (Seyler and Boaventura 2003), and the Congo and Niger Rivers, the largest rivers in Africa (Nriagu 1986), cannot be ignored.

Because of these distinct sources of trace metals to the Atlantic Ocean, mineral differences in the composition of soils and rock in South America and West Africa could be used as tracers of metal sources. For example, metal ratios in phytoplankton of the tropical and subtropical Atlantic Ocean could potentially reflect the metal composition reported for the Sahara desert or the Amazon River, Niger River, or both. Indeed, characterization and identification of the sources supplying metals to phytoplankton is essential for understanding the processes controlling phytoplankton activity.

In this study, we characterized the metal composition of natural *Trichodesmium* colonies collected in western and eastern basins of the tropical and subtropical North Atlantic and evaluated the influence of different sources. In addition, we compared the metal : P ratios obtained in the field populations of *Trichodesmium* with those reported from our laboratory experiments and in previous work with different species of marine phytoplankton (Ho et al. 2003; Quigg et al. 2003). Although our field results were within the range of the metal stoichiometry reported by Ho et al. (2003), metal : P ratios measured in the *Trichodesmium* were as variable as those reported in cultures of 15 different marine phytoplankton species. This suggests that metal variability in field-collected phytoplankton might not solely reflect the evolutionary history of the phytoplankton, but also the ambient conditions in which the colonies were collected and their prior growth history.

Methods

Sampling in the western North Atlantic Ocean was carried out on three cruises in areas within the influence of the Amazon River (Fig. 1). The samples were collected under different Amazon riverine flow conditions: rising

river discharge February 2001 (MP01), falling river discharge July–August 2001 (MP03), and highest river discharge April–May 2003 (MP08) (DeMaster and Pope 1996). Although the Congo River is the largest river in Africa, our samples were collected hundreds of kilometers north of its mouth. The river closest to our sampling locations was the Niger River (Fig. 1). Samples from the eastern North Atlantic were collected north of the Niger River in May–June 2003 (COCA-2) when river discharge is low and high dust deposition occurs (Goudie and Middleton 2001; Fig. 1).

Trichodesmium colonies were collected at a depth of ~5 m with an acid-cleaned all-plastic 100- μ m mesh plankton net. Individual colonies were removed from the acid-cleaned polyethylene net collector with a plastic inoculating loop in a class-100 clean hood. Approximately 100 colonies were stored frozen in Teflon vials and transported back to the laboratory for acid digestion. Plankton samples were also collected at some locations by filtering a volume of seawater (10–50 mL) through 0.2- μ m acid-cleaned polycarbonate filters (Millipore Isopore®). Metal concentrations (Al, Cd, Co, Cu, Fe, Mn, Mo, Ni, V, and Zn) in the *Trichodesmium* colonies and in the plankton samples were determined by inductively coupled plasma mass spectrometry (ICP-MS; ThermoFinnigan, Element 2) after acid digestion. Samples were digested in Teflon digestion vials with combined Q-HNO₃ (60%), Q-HCl (30%), and Q-HF (10%) and heated on a hot plate (for *Trichodesmium* colonies) or in a hot bath (for plankton samples) until complete digestion (Sañudo-Wilhelmy et al. 2001, 2004). **Phosphorous** was quantified spectrophotometrically according to the methods described by Gieskes et al. (1991). Metal levels were also determined by the same methodology in exponential growth phase semicontinuous laboratory cultures of *Trichodesmium* IMS101 grown in defined YBC11 medium (Chen et al. 1996), as detailed in Fu et al. (2005). To avoid any overestimation because of contamination and to have a more realistic comparison with the field samples, in laboratory cultures, we reported the intracellular metal concentrations. Intracellular levels were determined after washing *Trichodesmium* colonies with the oxalate reagent according to the protocols described in Tovar-Sanchez et al. (2003) and Tang and Morel (2006).

Aerosol samples along the western tropical Atlantic were collected on Teflon filters (Gelman Zefluor) with an all-polycarbonate high-volume dichotomous virtual impactor (Chen and Siefert 2004a). A microwave acid digestion procedure followed by ICP-MS was used to measure total trace metal levels in those aerosols filters. More details on the aerosol sample collection and analysis are described in Chen and Siefert (2004a). Aerosol samples along the eastern subtropical North Atlantic were collected with a high-volume collector (MCV: CAV-A/HF) into acid-washed polyethersulfone filters (Supor-200, Pall Gelman Sciences). To avoid contamination from the filter holder, the polyethersulfone filter was placed on an acid-washed cellulose filter (Whatman 41). Metal concentrations in the filters were also analyzed by ICP-MS after strong acid digestion as described for plankton samples.

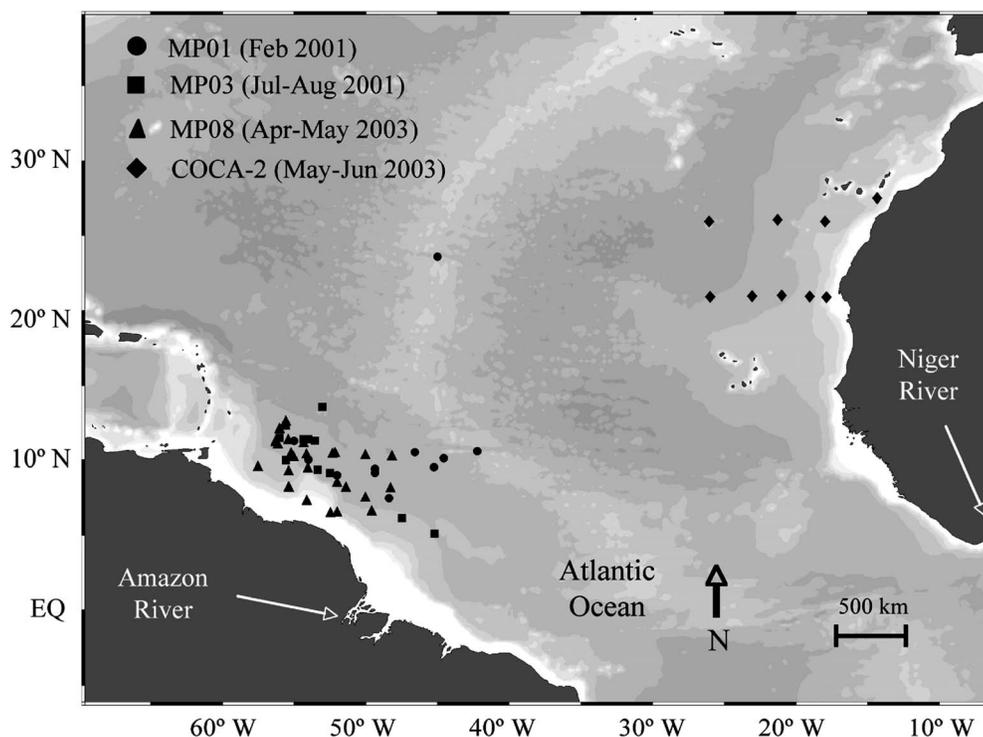


Fig. 1. Location of the sampling stations for cruises.

Results and discussion

Trace metal composition of Trichodesmium—Total metal (Al, Cd, Co, Cu, Fe, Mn, Mo, Ni, V, and Zn) and P concentrations measured in *Trichodesmium* and in other plankton taxa from the tropical and subtropical North Atlantic are presented in Web Appendix 1 (http://www.aslo.org/lo/toc/vol_51/issue_4/1755a1.pdf). Comparing element concentrations measured in all four cruises, the highest average levels of Cd ($0.85 \text{ pmol colony}^{-1}$ [col^{-1}]; $28.3 \text{ pmol } [\mu\text{g Chl } a]^{-1}$), Co ($1.3 \text{ pmol col}^{-1}$; $0.25 \text{ nmol } [\mu\text{g Chl } a]^{-1}$), Cu ($23.19 \text{ pmol col}^{-1}$; $0.76 \text{ nmol } [\mu\text{g Chl } a]^{-1}$), Mn ($41.68 \text{ pmol col}^{-1}$; $1.39 \text{ nmol } [\mu\text{g Chl } a]^{-1}$), Zn ($84.8 \text{ pmol col}^{-1}$; $2.81 \text{ nmol } [\mu\text{g Chl } a]^{-1}$), and P ($11.19 \text{ nmol col}^{-1}$; $0.38 \mu\text{mol } [\mu\text{g Chl } a]^{-1}$) were measured in colonies of *Trichodesmium* collected in January–February 2001 in the western Atlantic (MP01). The highest mean concentrations of Fe ($163.3 \text{ pmol col}^{-1}$; $12.9 \text{ nmol } [\mu\text{g Chl } a]^{-1}$) and Al ($18.70 \text{ nmol col}^{-1}$; $2.60 \mu\text{mol } [\mu\text{g Chl } a]^{-1}$) were also detected in the western basin in July–August 2001 (MP03) and in April–May 2003 (MP08), respectively.

Metal concentrations in aerosols were uncoupled from those measured in the phytoplankton because the highest mean levels were measured in April–May 2003 (MP08: Co, 9.61 pmol m^{-3} ; Fe, $10.67 \text{ nmol m}^{-3}$; Mn, $217.9 \text{ pmol m}^{-3}$) in the western basin and in May–June 2003 in the eastern basin (COCA-2: Cu, $687.7 \text{ pmol m}^{-3}$; Zn, $439.4 \text{ pmol m}^{-3}$; see Web Appendix 1). These results suggest that metal concentrations in aerosols were not good predictors of the metal content of the *Trichodesmium* colonies (r^2 between most metal concentrations in aerosols and *Trichodesmium* colonies were ≤ 0.3 , $p > 0.05$, for all

cruises). However, significant linear correlations were found for Co in MP03 ($r^2 = 0.5$, $p < 0.05$) and for Al in COCA-2 ($r^2 = 0.8$, $p < 0.05$, data not shown). This is consistent with the likelihood that atmospheric deposition is the principal source of Al to the ocean (Jickells 1995). Although atmospheric data on Co concentrations is scarce, Elbaz-Poulichet et al. (2001) estimated that the most important source of this element to the western Mediterranean basin is atmospheric deposition.

Phosphorus concentrations were also variable in the *Trichodesmium* colonies and in the total plankton (Web Appendix 1). The lowest concentrations were found in the samples collected in the eastern region in May–June 2003 (COCA-2 cruise: $0.96 \text{ nmol col}^{-1}$ and $0.14 \text{ nmol mL}^{-1}$, respectively), and the highest concentrations were measured in the western basin during high river discharge (MP01, $11.19 \text{ nmol col}^{-1}$; MP08, $82.01 \text{ nmol mL}^{-1}$; Web Appendix 1). The high levels of P measured in the western Atlantic during the MP01 and MP08 cruises is consistent with the influence of the Amazon River observed during those cruises (see the next section) because rivers are the major source of P to this region (Froelich et al. 1982). The low levels of P measured in the eastern basin near Africa are also consistent with the reports of P limitation of *Trichodesmium* (Sañudo-Wilhelmy et al. 2001) and other phytoplankton (Vidal et al. 2003) in the subtropical northeast Atlantic.

Molybdenum, Ni, and V were only measured in samples collected during two of the four cruises (MP08 and COCA-2; Web Appendix 1). Mean concentrations of those three metals in *Trichodesmium* colonies were higher in the western basin (MP08: 3.60 , 2.82 , and $15.62 \text{ pmol col}^{-1}$,

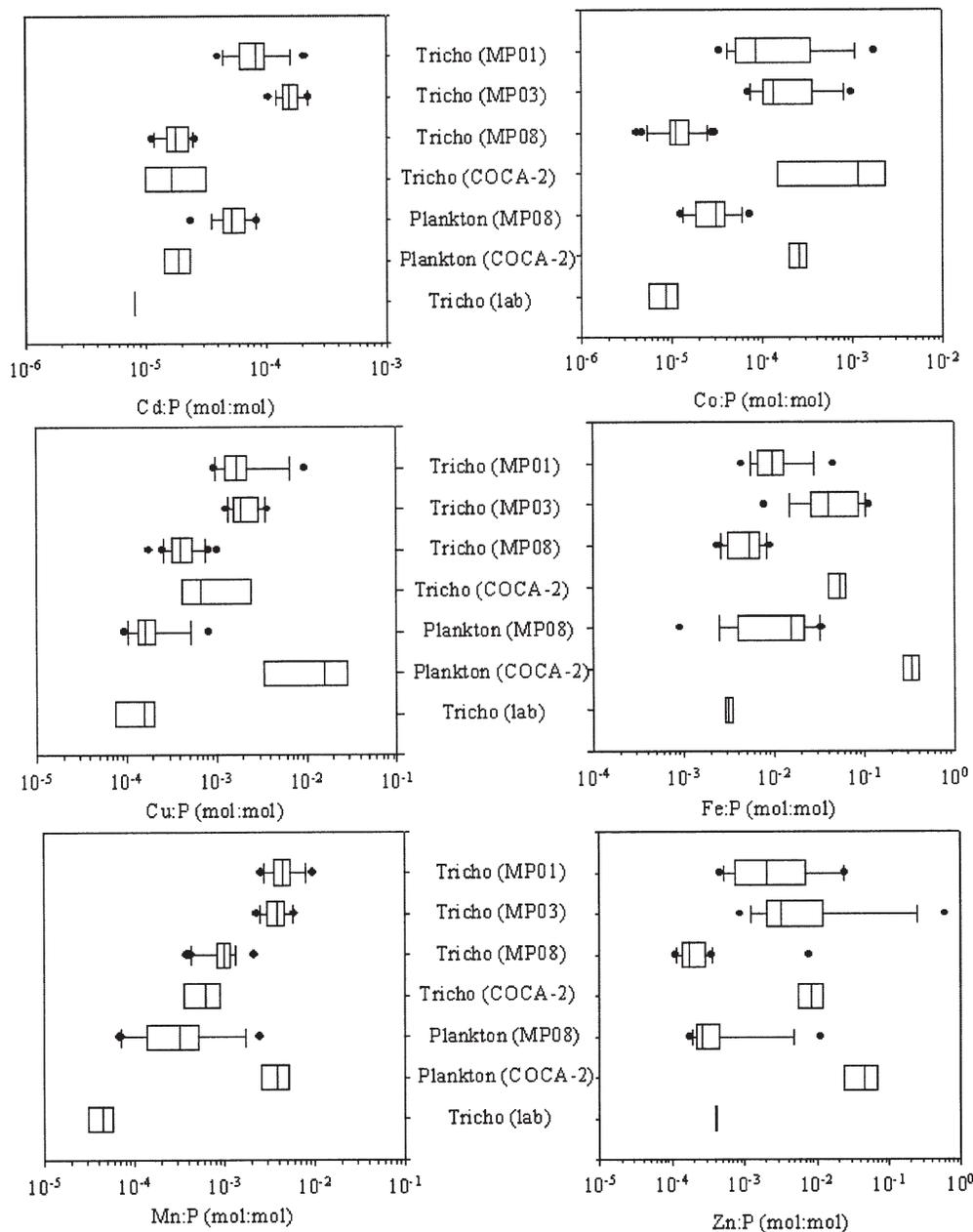


Fig. 2. Total metal : P composition of *Trichodesmium* along the tropical and subtropical Atlantic Ocean (Tricho: MP01, MP03, MP08, and COCA-2); plankton collected in MP08 (dominated principally by *Richelia intracellularis* and *Pseudo-nitzschia*); plankton collected in COCA-2 (dominated principally by the picocyanobacteria *Synechococcus* and *Prochlorococcus* and by unidentified pico- and phytoeukaryotes); and intracellular Me : P of *Trichodesmium* grown under laboratory conditions (“Tricho (lab)”), diatoms, coccolithophores, red dinoflagellates, and green algae from Ho et al. (2003). Comparison of metal composition in different natural field-collected population of *Trichodesmium* indicates different composition according to spatial and temporal distribution.

respectively) than in the eastern region of the North Atlantic (COCA-2: 0.53, 1.16, and 0.32 pmol col⁻¹, respectively). Unfortunately, we do not have enough information to establish the cause of this strong spatial gradient in those metal concentrations.

The metal composition of *Trichodesmium* and other plankton taxa (normalized to P) measured in the tropical and subtropical North Atlantic Ocean are presented in

Fig. 2 and Table 1. Significant variability in the metal quotas was observed in the different colonies, ranging from a factor of five for Cu to a factor of 20 for Zn. This result suggests that, in addition to the taxonomic variability reported by Ho et al. (2003) in 15 phytoplankton species, variability is also high within a single species when samples are collected at different times and locations. For example, although median Cd : P and Mn : P ratios in the eastern

Table 1. Elemental metal composition (mmol) normalized to P (mol).

Metal	Composition (mmol mol ⁻¹)				
	<i>Trichodesmium</i> field colonies	<i>Trichodesmium</i> laboratory cultures	Plankton*	Plankton	
				Western Atlantic†	Eastern Atlantic‡
Cd	0.15–0.016	0.008	0.54–0.068	0.053	0.019
Co	0.19–0.011	0.012	0.19	0.031	0.26
Cu	1.9–0.4	0.16	0.52–0.18	0.16	16
Fe	39–5.4	3.2	7.5–3.6	16	330
Mn	4.4–0.62	0.04	1.6–0.34	0.33	3.8
Zn	3.2–0.17	0.41	3.0–0.80	0.27	46

* Natural plankton assemblages, suspended particulate material, and cultured phytoplankton (Ho et al. 2003).

† Natural plankton dominated principally by *Richelia intracellularis* and *Pseudo-nitzschia*.

‡ Natural plankton dominated principally by picocyanobacteria *Synechococcus* and *Prochlorococcus* and by unidentified pico- and nanophytoeukaryotes.

basin (COCA-2 cruise, 0.016 and 0.62 mmol mol⁻¹, respectively) were lower than those measured in the western basin (0.16 mmol mol⁻¹ in MP03 and 4.4 mmol mol⁻¹ in MP01, respectively), Co : P, Fe : P, and Zn : P ratios in the eastern basin were higher (1.1, 53, and 8.6 mmol mol⁻¹, respectively). These results suggest that metal : P ratios in field populations of *Trichodesmium* are highly variable both in space and time in response to different environmental forcing.

The metal : P ratios measured in the total plankton samples were not significantly different from the ratios measured in the *Trichodesmium* colonies for most of the metals analyzed (Fig. 2; Table 2). The only exceptions were Cu, Fe, and Zn in the eastern Atlantic, where the ratio variability was higher (ranging from a factor of 20 for Fe to almost 200 for Zn).

To evaluate whether our field results were consistent with other studies, we compared (Table 1) the elemental composition of *Trichodesmium* and plankton collected in the north Atlantic with those reported for other natural plankton assemblages, suspended particulate materials, and cultured phytoplankton species compiled by Ho et al. (2003). We also compared those elemental ratios to intracellular trace metal ratios found in cultured *Trichodesmium* colonies. This analysis shows that metal quotas in natural populations of *Trichodesmium* were within the range of previously reported values from both laboratory and field (Table 1). Metal quotas in the lab cultures were closer to the lower end of the range of values found in field samples. This suggests that a significant portion of the total

metal concentrations measured in the natural *Trichodesmium* colonies could be in the extracellular pool.

Sources influencing the composition of metals in Trichodesmium—To identify the external sources of metals influencing *Trichodesmium* metal composition in the different regions of the tropical and subtropical north Atlantic Ocean, Mn : Al and Fe : Al ratios in the colonies were compared with the same metal ratios reported for Saharan dust (Chester et al. 1984) and the major rivers emptying into these ocean basins: the Amazon (Aucour et al. 2003; Seyler and Boaventura 2003) and the Niger (Picouet 1999; Fig. 3). In addition, to determine the importance of atmospheric deposition during our sampling, we compared the metal ratios measured in the colonies with those measured in aerosols collected during our cruises. We used Al, Fe, and Mn as terrigenous tracers because they are all enriched in the earth's crust (average abundance in the continental crust: Al, 8.23%; Fe, 5.63%; Mn, 0.19%; Taylor

Table 2. The quantitative contribution (range, mean) of the different studied sources to the trace metal composition of *Trichodesmium* colonies. The model used two end members: Saharan dust and river (Amazon River was used in the model for the western basin and Niger River for the eastern basin).

Source	Source contribution (%)			
	MP01	MP03	MP08	COCA-2
Amazon River	51–100, 76	0–17, 8	98–100, 99	—
Niger River	—	—	—	63–64, 64
Sahara dust	0–49, 24	83–100, 92	0–2, 1	36–37, 37

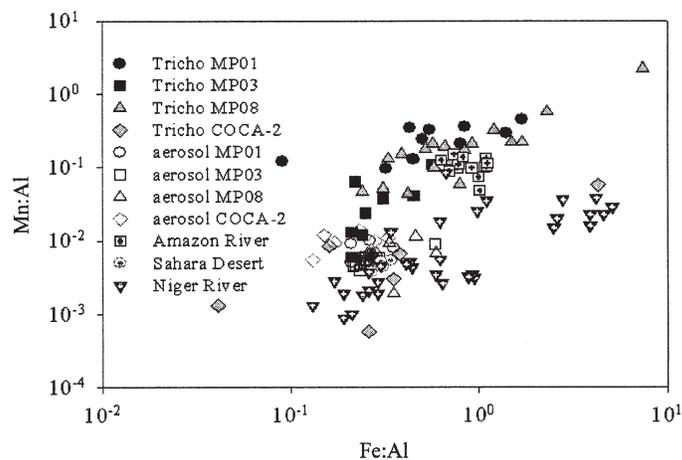


Fig. 3. Manganese and Fe composition normalized to Al in water (dissolved fraction) from Amazon and Niger Rivers, Saharan dust (concentration in aerosols), and *Trichodesmium* (total composition) and aerosol deposition collected in the four cruises along the tropical and subtropical Atlantic Ocean. Similar composition of *Trichodesmium* from the western (MP01, MP03, and MP08) and eastern (COCA-2) regions with waters from the Amazon and Niger Rivers, respectively, indicate these two sources as principal suppliers of metals to *Trichodesmium*.

1964). Metal normalized to Al has previously been used as an effective tool to identify the influence of terrestrial inputs on plankton composition (Caetano and Vale 2003).

In the western tropical Atlantic, the metal ratios in the *Trichodesmium* colonies collected in February 2001 (MP01) and April–May 2003 (MP08) cruises clustered with the metal composition of the Amazon River (Fig. 3), suggesting that the river was the principal supplier of metals to *Trichodesmium* during those times. Metal ratios measured in the colonies during July–August 2001 (MP03) seem to reflect a mixture of two sources: the Amazon River and Saharan aerosols (Fig. 3). These results are consistent with the seasonal fluctuations of the external sources of metals to the tropical Atlantic. For example, maximum dust deposition in the western Atlantic occurs during July–August (Prospero and Lamb 2003), just preceding the period of low Amazon River discharge (August–October; Aucour et al. 2003). Sample collection in the other 2 cruises (MP01 and MP08, February–April) coincided with the period of high Amazon river flow (Aucour et al. 2003). The lowest salinities were also measured during those two cruises, consistent with the high river discharge (Web Appendix 1).

Despite the geographic proximity to the African coast and the high concentrations of metals measured in the aerosols collected along the COCA cruise in the eastern Atlantic (Web Appendix 1), metal ratios in *Trichodesmium* did not reflect the atmospheric source (Fig. 3). As for the western Atlantic, the metal composition in the colonies was consistent with the metal ratios reported for the major riverine source (the Niger). These results suggest that phytoplankton preferentially use metals delivered by the rivers rather than those derived from atmospheric deposition. This hypothesis is consistent with the low solubility of metals from soil dust (i.e., for Fe < 1%; Jickells and Spokes 2001) and with the demonstrated influence of African rivers on the biogeochemistry of the tropical Atlantic Ocean (Da Cunha et al. 2005). In contrast, most of the metals delivered by the Amazon and Niger plumes should consist of truly soluble metal species because of the coagulation and removal of riverborne humic colloids.

Aerosols collected in the western and eastern basins during our cruises had similar metal compositions and reflected the Saharan source (Fig. 3). This is consistent with previous observations showing that dust from North Africa influences the entire tropical Atlantic all year (Prospero and Lamb 2003).

The proportional contribution of each source (Amazon and Niger Rivers and Saharan dust) influencing the metal composition of *Trichodesmium* was calculated with a mixing model described in detail by Phillips and Gregg (2003) and the data presented in Fig. 3. This analysis showed that the Amazon and Niger Rivers contributions during the MP01, MP08, and COCA-2 cruises were substantial (51–100%, 98–100%, and 64%, respectively; Table 2). In the western Atlantic during the MP03 cruise, 83–100% of the metal composition could be attributed to Saharan dust.

Metal composition of natural populations of *Trichodesmium* in the tropical and subtropical Atlantic Ocean was

highly variable and seems to reflect the different ambient conditions in which the samples were collected. The Me : Al ratios measured in *Trichodesmium* in the western and eastern regions of the North Atlantic reflected inputs from the Amazon and Niger Rivers, respectively. Our results thus suggest both that metal content of *Trichodesmium* in nature might be far more variable than is suggested by laboratory culture studies and that the importance of riverine-derived metal sources relative to dust inputs could have been underestimated in past studies and needs to be re-evaluated in future work.

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