

## COMMENT

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### Influence of river discharge in the tropical and subtropical North Atlantic Ocean

The recent article by Tovar-Sanchez *et al.* (2006; hereafter referred to as TS2006), presents a new comprehensive dataset of trace metal concentrations in *Trichodesmium* sp. populations and aerosol samples from the western tropical (MP01, MP03, and MP08 samples) and eastern subtropical (COCA2 samples) Atlantic Ocean. In TS2006, the authors considered the atmospheric deposition of Saharan dust as probably the main source of trace metals for the surface tropical Atlantic, together with the riverine input of trace metals to the coastal ocean. TS2006 determined the trace metal composition in aerosol samples and *Trichodesmium* sp. colonies in both the eastern and the western tropical Atlantic, and used additional published data for riverine upstream concentrations of dissolved and particulate trace metals. The riverine and aerosol metal ratios were used to infer the sources of these metals in *Trichodesmium* sp. colonies in the tropical and subtropical Atlantic Ocean. TS2006 found that trace metal ratios measured in some samples of *Trichodesmium* sp. colonies (Mn:Al and Fe:Al) were more similar to the dissolved riverine trace metal ratios than to the aerosol metal composition, and concluded that the Amazon and Niger Rivers are seasonally the most important sources of trace metals for *Trichodesmium* sp.

Although the new data presented in TS2006 are relevant for the characterization of metal composition in aerosol and phytoplankton, we present here seven fundamental points explaining why we fundamentally disagree with their conclusions.

*Northeastern subtropical Atlantic Ocean circulation, riverine freshwater input, and riverine and dust Fe inputs*—In TS2006, there is a dramatic mismatch between the localization of the COCA2 samples in the northeast tropical and subtropical Atlantic Ocean (20–30°N, 25–15°W) and the Niger River outflow (4°N, 6°E). The COCA2 samples are from a region under influence of the Canary Current, flowing south off the northwest African coast (Fig. 1), and are also influenced by the Mauritanian Upwelling (Babin *et al.* 1996).

The continental freshwater runoff to the Atlantic Ocean from the African continent between 20°N and 30°N (Sahara Desert) is negligible (Vorosmarty 2002). According to the runoff maps of Doell and Lehner (2002) and Korzoun *et al.* (1977), the riverine freshwater input to the area of the COCA2 stations is 3.9 km<sup>3</sup> yr<sup>-1</sup>. This is reflected by the reported average salinity for COCA2 stations (36.59), which is not representative of an area under riverine freshwater influence (Fig. 2).

In an ocean biogeochemistry model study, Cotrim da Cunha *et al.* (2007) estimated a riverine dissolved Fe input to the Atlantic of 3.14 10<sup>-4</sup> Gg Fe yr<sup>-1</sup> for the region above. Fe input via dust to this area is 0.65 Gg Fe yr<sup>-1</sup>, according to Tegen and Fung's (1995) dust model data and considering that dust is composed of 3.5% Fe and that only 2% is immediately soluble (Jickells and Spokes 2001). The possible contribution of riverine Fe to the COCA2 site is more than three orders of magnitude lower than that from dust deposition. High salinity, low continental freshwater runoff, and influence of Fe deposition from dust in the COCA2 sampling area are shown in Fig. 2. Therefore, it is improbable that *Trichodesmium* sp. metal composition at COCA2 stations was influenced by riverine inputs at any season of the year.

*Western tropical Atlantic Ocean and the Amazon River plume*—We concede that the Amazon River may be a source of metals for phytoplankton in the western tropical Atlantic during the high water discharge period (May–August, according to Moreira-Turcq *et al.* 2003).

In TS2006, the western tropical Atlantic *Trichodesmium* sp. samples (MP01, MP03, and MP08) covered oceanic and coastal locations in each one of the sampled periods. Presumably, *Trichodesmium* were exposed to different trace metal regimes between the different locations. Yet *Trichodesmium* data are put together for each sampled period, assuming that oceanic phytoplankton was influenced by riverine trace metal inputs. This is reflected by the variable salinity values of each MP sample group. Based on a graphic representation of log-transformed Fe:Al vs. Mn:Al ratios, TS2006 concluded that MP01 (Jan–Feb 2001, average salinity 36.18) and MP08 (April–May 2003, average salinity 34.35) *Trichodesmium* samples had higher riverine influence than did MP03 (Jul–Aug 2001, average salinity 31.55) *Trichodesmium* samples.

This statement cannot be reconciled with either the average salinity data or the metal ratios for phytoplankton and aerosol samples. Cooley and Yager (2006) collected water samples concomitantly (MP01 and MP03) to TS2006. They state that because Amazon plume waters cannot be identified by geographic characteristics, the plume-influenced stations were identified by their low surface salinities (<35) and shallow haloclines (<10 m), according to the definition of Lentz and Limeburner (1995). It seems contradictory to argue that MP01 and MP08 samples had higher riverine influence when average water sample salinities at MP01 and MP08 were 36.18 and 34.35, respectively, compared to 31.55 at MP03.

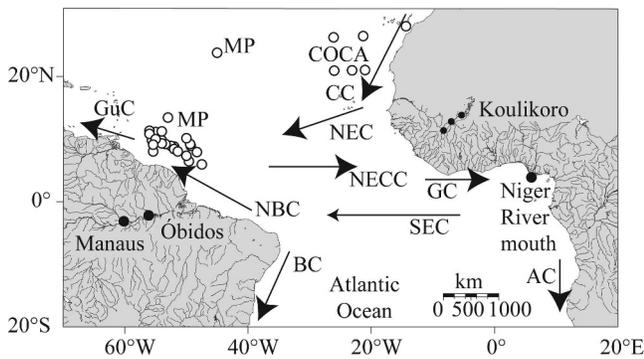


Fig. 1. Map of the tropical and subtropical Atlantic Ocean, with schematic representation of the main surface currents (arrows). Open circles correspond to the sampling sites of TS2006, COCA (eastern Atlantic) and MP (western Atlantic). Black circles correspond to the Niger River mouth, Niger River sampling area (Koulikoro) of Picouet (1999), and Amazon River sampling area (Óbidos) of Seyler and Boaventura (2003). CC is the Canary Current, NEC is the North Equatorial Current, NECC is the North Equatorial Counter Current, GC is the Guinea Current, SEC is the South Equatorial Current, AC is the Angola Current, BC is the Brazil Current, NBC is the North Brazil Current, and GuC is the Guiana Current. Map source: Online Map Creation, www.aquarius.ifm-geomar.de.

*Riverine Fe:Al and Mn:Al as proxies for tracing metal sources to Trichodesmium sp. in the Atlantic Ocean*—The riverine end members (Fe:Al and Mn:Al molar ratios) used in TS2006 were determined on samples collected from upstream of the river mouth. TS2006 used the metal molar ratios as in Caetano and Vale (2003), but did not consider the behavior of dissolved metal species in estuarine areas. The riverine metal concentrations (and ratios) used for comparison to *Trichodesmium sp.* samples in TS2006 were measured in areas very distant from the river mouth. For the Amazon River, the Manaus station (Aucour *et al.* 2003) and the Óbidos station (Seyler and Boaventura 2003) are about 1200 and 800 km upstream of the river outflow, respectively. For the Niger River, the stations are located in the upper river basin (Koulikoro region), about 1000 km upstream of the river outflow (Picouet 1999).

It is well established scientifically that processes operating in estuaries strongly modify both the dissolved and the particulate loads in river water. As a result, the amounts and element ratios of transported material entering an estuary can be very different from those that are effectively exported to the ocean. Sholkovitz (1978) showed, in an experiment for prediction of metal reactivity in estuarine mixing, that a large fraction (~80%) of river dissolved Fe is lost to the particulate phase because of flocculation in low salinity areas. A recent similar riverine water–seawater mixing study on the Amazon river showed that 88% of the riverine dissolved Fe flocculated at salinity 18 (Bergquist and Boyle 2006).

Kremling (1983) and Statham and Burton (1986) observed a very sharp decrease in dissolved Mn concentration on transition from coastal to open ocean waters. Aguilar-Islas and Bruland (2006) recently showed that the

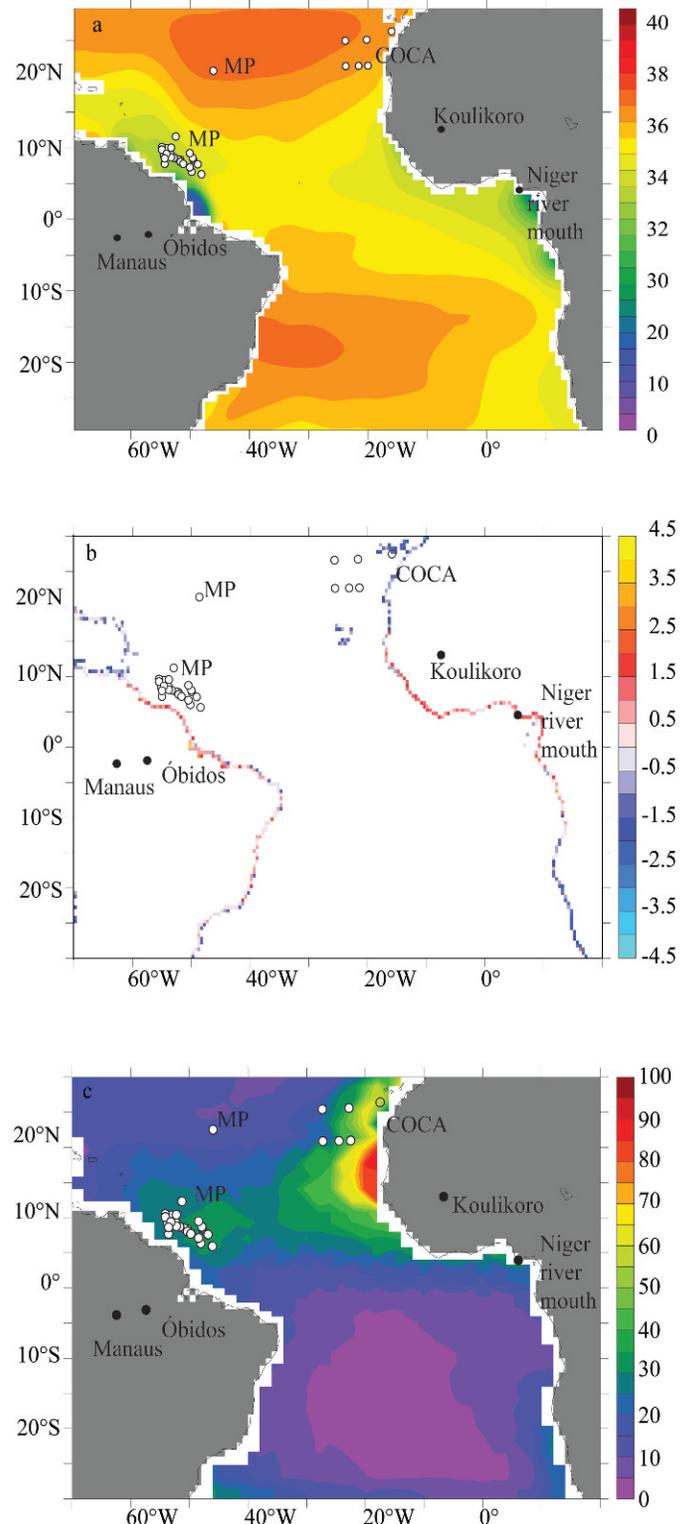


Fig. 2. (a) Mean surface salinity fields for the tropical and subtropical Atlantic Ocean, from the World Ocean Atlas 2005 (Antonov *et al.* 2006). (b) Annual river water runoff to the tropical and subtropical Atlantic Ocean in km<sup>3</sup> yr<sup>-1</sup> on a logarithmic scale (Korzoun *et al.* 1977; Ludwig and Probst 1998; Doell and Lehner 2002). (c) Mean Fe deposition on the ocean surface from dust in μmol Fe m<sup>-2</sup> yr<sup>-1</sup>, derived from dust deposition maps from Tegen and Fung (1995) and considering that dust contains 3.5% of Fe. Not all the deposited Fe is readily available for the phytoplankton.

processes controlling Mn concentrations in the Columbia River plume area include tidal amplitude, photodissolution of Mn oxide coatings in estuarine suspended matter, and resuspension of sediments from intertidal mudflats. Thus, the contribution of dissolved riverine Mn to open ocean waters is uncertain. Atmospheric deposition and advection of Mn from reducing shelf sediments (eastern boundary areas) can also be important sources of Mn to the surface open ocean (Chester 1990).

Dissolved Al behavior in the coastal zone is difficult to establish because of (1) the variability of geochemical characteristics in estuaries and (2) its reactive nature. According to Maring and Duce (1987), about 50% of the gross dissolved riverine Al flux is retained in the estuarine zone. On the other hand, Upadhyay and Sengupta (1995) showed that at the Mandovi estuary in India, removal of dissolved Al onto riverine sediments occurs during the initial stages of estuarine mixing but with little or no net permanent loss, because resuspended sediments release sorbed Al back into solution.

Therefore, an analysis such as the one presented by TS2006 might have been possible and justifiable had the authors taken their source trace metal ratios at the estuarine and plume areas rather than far upstream from the river mouth. Riverine dissolved metal ratios subjected to estuarine processing are thus not good proxies for tracing metal sources to particulate material in the coastal and open ocean.

*Aerosol Fe: Al and Mn: Al as proxies for tracing metal sources to Trichodesmium sp. in the Atlantic Ocean*—Although atmospheric aerosols may supply considerable amounts of nutrients and trace metals to the surface ocean, the solubility of these elements in seawater is variable. For example, aerosol Fe solubility depends on a number of factors such as suspended particle concentration, chemical-photochemical atmospheric processing, or aerosol source (Jickells and Spokes 2001; Bonnet and Guieu 2004). Baker *et al.* (2006) found that the solubility for Fe, Al, and Mn in Saharan aerosol samples varied from 1.4% to 4.1% for Fe, 1.9% to 5.5% for Al, and 55% to 64% for Mn. After dissolution of the deposited aerosol in seawater, the ratios of metals available to the phytoplankton are different from those reported for bulk aerosol. Therefore, phytoplankton metal concentrations are unlikely to reflect the metal ratios from bulk aerosol.

*Normalization of metal ratios to Al*—The normalization of metal ratios to Al for biogenic material, as done in TS2006, is problematic because Al is present almost exclusively in the lithogenic fraction of the particulate material collected. Typically, Al is used to estimate and subtract the lithogenic component from particulate samples in order to estimate the biogenic component; thus, comparison of metal to Al ratios in pure biogenic material is not commonly performed. An example of this approach is found in recent work from the FeCycle experiment (Frew *et al.* 2006), wherein particulate Al was used in concert with a lithogenic Fe:Al ratio to estimate biogenic particulate Fe.

Presently we could find neither data on the biogenic Al composition of *Trichodesmium* nor any published work outlining why *Trichodesmium* would bioaccumulate Al to a higher internal concentration than Fe, which is a required element. In the absence of a clear biological requirement for Al, it would be logical to conclude that the particulate Al is lithogenic material associated with the phytoplankton material collected and that the metal:Al ratios presented in TS2006 reflect a mixture of lithogenic and biogenic particles, or abiotic adsorption of Al to the surface of *Trichodesmium* colonies. In contrast, the cellular internalization of Fe is carried out by high-affinity transport systems, as further discussed in section “Regulation of internal metal concentration by *Trichodesm* sp.” Given that Al and Fe ions measured in *Trichodesmium* are most likely acquired by passive and active mechanisms, respectively, there is no reason to assume that the Fe:Al ratio of the dissolved source will be retained in the organism.

Aerosol deposition was reported to fuel new production during the same COCA2 cruise (Duarte *et al.* 2006), which contradicts the suggestion in TS2006 that the Niger River controlled the metal composition of *Trichodesmium* at this location. In our opinion there is ample evidence that it is not valid to interpret trace metal ratios in marine particulate matter (in the case of TS2006, *Trichodesmium* samples) without making a correction for entrained lithogenic material or cell surface adsorption.

*Tracing multiple sources for natural samples*—In TS2006 there appears to be an apparent misapplication of the method of Phillips and Gregg (2003), which uses stable isotope composition to trace multiple sources for natural samples, because many of the field data points, particularly in the COCA2 and MP08 samples, lie outside the polygon (or line, when using only 2 end members and a logarithmic scale) enclosed by the assumed compositions (dust or river). Thus, the data in TS2006 cannot be interpreted using only two end members via the approach of Phillips and Gregg (2003).

The two-end-member approach of TS2006 would not be able to explain any data that do not lie exactly on the line between the two assumed end members. Other possible metal sources for phytoplankton, such as shelf pore water, sediments, or upwelling (Fitzwater *et al.* 2003; Aguilar-Islas and Bruland 2006; Bergquist and Boyle 2006), could have been considered here so that the data in TS2006 would have been enclosed within the polygon described by the end members. Additionally, the metal concentrations for *Trichodesmium* and aerosol reported in the TS2006 web appendix do not fit the Fe:Al and Mn:Al molar ratio values used to visualize the assumed end members (dust or river as sources for phytoplankton; fig. 3 in TS2006).

*Regulation of internal metal concentration by Trichodesmium sp.*—The method of Phillips and Gregg (2003) used by TS2006, although valid for estimating conservative mixing between measurable properties, is not justified for living microorganisms. Numerous organisms can regulate

their chemical composition and stoichiometry (Ho *et al.* 2003; Quigg *et al.* 2003; Finkel *et al.* 2006). Fortunately, many biochemical mechanisms have evolved in living organisms to allow complex reactions to take place against concentration gradients such that even simple cyanobacteria can actively internalize Fe from seawater containing picomolar amounts of dissolved Fe, while concurrently extruding toxic trace metals and other cations to the outside environment (Berman-Frank *et al.* 2007). One needs only to glance at the abundance and diversity of genes encoding Fe uptake systems that have been recovered from recently acquired metagenome sequences from the euphotic zones of oligotrophic oceans (Delong *et al.* 2006). These studies also revealed that microbial communities within the euphotic zone have a predominance of genes encoding for membrane proteins involved in active transport, permeases, and multidrug efflux proteins all contributing to the traffic of dissolved molecules in and out of microorganisms.

Equally important, the dominance of photosynthetic genes also gives the key to why and how active transport is possible in the euphotic zone: Sunlight energy when harvested by the photosynthetic apparatus can easily provide the energy to catalyze the chemical reactions.

Whether *Trichodesmium* homeostatically regulates its chemical composition remains to be determined experimentally. However, its genome, like that of other eubacteria, contains several genes that encode a putative component of Fe and Mn transport systems, and, in addition, it contains a gene of unknown function involved in Al resistance.

In conclusion, it is unlikely that northeast subtropical Atlantic *Trichodesmium* sp. colonies (COCA2) are influenced by Niger River metal inputs to the ocean. On the western tropical Atlantic, MP01 and MP08 average surface salinities were 36.18 and 34.35, respectively. Therefore, it is contradictory to argue that the mixed coastal and oceanic *Trichodesmium* sp. samples had higher Amazon River influence when compared to MP03 samples (average salinity 31.55). Finally, we urge a cautious interpretation of the potential metal sources for phytoplankton, because (1) estuary and plume processing alter riverine metal concentrations, (2) total aerosol metal content is not readily available for phytoplankton uptake, and (3) measured metals in *Trichodesmium* sp. are acquired by passive (Al) or active (Fe) mechanisms, and thus it is unlikely that the Fe:Al ratio of the dissolved source will be retained in the organism.

We agree with TS2006 that there is still much work to be done regarding the determination of sources of trace metals for phytoplankton as well as the nutritional requirements of *Trichodesmium* sp. The dataset presented in TS2006 is clearly an important step forward for this and is a valuable contribution to this work. However, based on the serious issues raised above, we can not agree with TS2006's application and subsequent interpretation of an end-member approach regarding the trace metal sources for *Trichodesmium* sp. in the tropical Atlantic. We would encourage future work in this field to consider the physical

processes involved and the other potential sources of metals we have outlined above in their assessment.

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