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Influence of *Trichodesmium* red tides on trace metal cycling at a coastal station in the Great Barrier Reef lagoon

Great Barrier Reef lagoon
Trace metal cycling
Trichodesmium blooms
Metal-ion dissolution

Grande Barrière de Corail
Cycles de métaux-trace
Floraisons de *Trichodesmium*
Dissolution ion-métal

G. B. Jones [a], C. Burdon-Jones [a], F. G. Thomas [b]
[a] Department of marine Biology,
[b] Department of Chemistry,
James Cook University of North Queensland, Townsville, Queensland 4811, Australia.

ABSTRACT

Investigations carried out at a coastal station in the Great Barrier Reef lagoon (GBRL) at Townsville, Australia have shown that the cycling of several trace metals (Fe, Mn, Zn, Cu, Ni, Cd, and Pb) was significantly influenced by the presence of *Trichodesmium,* a blue-green alga, which throughout the year, frequently forms red tide densities along much of the Queensland coral coast. Whilst decomposition of large masses of *Trichodesmium* significantly affected metal concentrations, metal speciation changes also occurred, and took place during the presence of senescent *Trichodesmium* and high concentrations of humic material (10 mg/l).

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RÉSUMÉ

Influence des marées rouges de *Trichodesmium* sur le cycle des métaux-trace dans une station côtière lagunaire de la Grande Barrière de Corail.

Des études ont été effectuées sur le lagon de la Grande Barrière de Corail à Townsville, Australie. Elles ont montré que les cycles de métaux-trace (Fe, Mn, Zn, Cu, Ni, Cd et Pb) sont influencés significativement par la présence de *Trichodesmium,* une algue bleu-verte qui, toute l'année, provoque des marées rouges le long de la côte récifale du Queensland. En même temps que de grandes densités de *Trichodesmium* sont affectées par les concentrations en métaux, on observe également des changements de spéciation métallique qui se déroulent en présence de populations de *Trichodesmium* sénescentes et de concentrations en matériel humique élevées (10 mg/l).

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INTRODUCTION

The Great Barrier Reef is widely recognised as one of the most important features of Australia's coastal heritage. It is the world's largest single lagoonal environment with a unique assemblage of living corals, associated organisms, mangroves, estuarine lagoons, salt pans and tropical rain forest, and is a source of fascination and pleasure for many people. This complex and diverse lagoonal ecosystem is particularly vulnerable to any further intensification by human activities and this is true of similar lagoonal environments throughout the tropical world as under-developed countries rush to exploit their marine and coastal resources. Despite its size few oceanographic studies have been made on the Great Barrier Reef lagoon (GBRL ; see Revelante, Gilmartin, 1982), and this is particularly true of chemical studies. As man's influence on his environment becomes more apparent in the heavily industrialised parts of the world it is vital that more understanding of the natural processes affecting pristine environments is obtained if we are to protect these unique regions. One important area of research concerns that of the trace metals. Such substances are introduced into our environment by various routes and although many are necessary for the growth of organisms

some can be deleterious at low concentrations ($< 1\ \mu g/l$), and more importantly at low ion activities (Sunda, Guillard, 1976 ; Anderson, Morel, 1978 ; Jackson, Morgan, 1978).
During 1976-1979 trace metal investigations (Fe, Mn, Zn, Cu, Ni, Cd, Pb) were carried out on coastal and estuarine waters of the GBRL at Townsville in an attempt to understand the natural processes affecting their temporal and spatial distribution. Whilst high river runoff significantly affected results, it was always short-lived due to the variable and intermittent rainfall experienced during the monsoonal months (December-April). During the long dry winter months however red tide densities of *Trichodesmium* blooms significantly affected trace metal concentrations (Jones, 1981). Consequently during May 1978-April 1979 a detailed investigation of the effects of *Trichodesmium* blooms on trace metal concentrations in lagoon waters and their effect on suspension feeding organisms (oysters) was made. This communication reports the water studies.

STUDY AREA

The study was carried out at Townsville, Queensland on the tropical north-east coast of Australia within the central region of the Great Barrier Reef province (Fig. 1). The Great Barrier Reef lies approximately 65 km offshore at Townsville, but many fringing reefs are present in the GBRL, the region between the mainland and the Great Barrier Reef, where mean depths are close to 35 m (Pickard *et al.*, 1977).

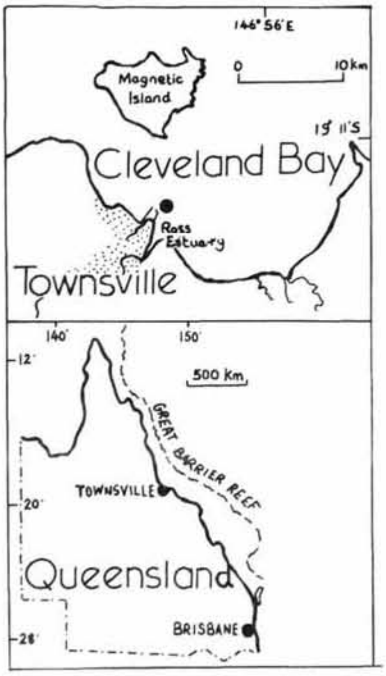

Figure 1
Study region showing sampling station.

In a shallow lagoon environment the wind is a particularly important parameter that can significantly affect lateral water movements. Across the Queensland continental shelf the SE trade winds (2-4 m/sec.) prevail for much of the year (May-November). During the monsoon season (December-April) tropical depressions and cyclones bring heavy rainfall. The majority (70 %) of the annual rainfall (1.2 m) falls during this season. The long dry season experiences only 0.06 m of rain (Meteorological Office, Garbutt).
The climatic conditions define two main seasons (Revelante, Gilmartin, 1982). A season of high precipitation associated with the northwesterly monsoon (December-April), characterized by high temperatures, low salinities, low densities some degree of increased vertical stability, and a season of low to no precipitation associated with the S.E. trade winds, characterized by low temperatures, high salinities, high densities and a vertically well mixed water column. Calm periods (nil sea conditions) occur predominantly during this time and are often accompanied by prolific *Trichodesmium* blooms (Jones, 1981 ; Revelante, Gilmartin, 1982).
Trichodesmium, a filamentous blue-green alga inhabits the nutrient-depleted waters of tropical and sub-tropical seas (Dugdale *et al.*, 1961). Spectacular blooms of this plankton occur in the surface waters of the GBRL throughout the year (Jones, 1981 ; Revelante, Gilmartin, 1982), as well as in the Arabian Sea (Qasim, 1970 ; Devassy *et al.*, 1978). In Townsville's coastal waters *Trichodesmium erythraeum* (Ehr. ex Gomont) Geitler is the dominant species but *T. thiebautii* (Gomont ex Gomont) is also present (Revelante, Gilmartin, 1982). During red tide blooms filaments are aggregated by the wind to form dense oily slicks, which accumulate in vast concentrations at the air/sea interface. This is due to the presence of gas vacuoles which can occupy up to 70 % of the cell volume (Fogg, pers. comm.), and the circulation processes acting in these waters.
From August to November, prior to the summer monsoons these surface slicks are borne landward by the prevailing winds where these malodorous aggregations decompose in shallow bays and estuaries along the tropical east Queensland coast. On occasions blooms can stretch along a major portion of the Queensland coast, extending from the shoreline to the outer barrier, occupying up to 51,000 km^2 of sea surface (Wood, 1965). In August and September 1976 a bloom stretched across the entire GBRL in front of Townsville lasting approximately 2 months (Revelante, Gilmartin, 1982) and significantly affected the coastal and estuarine lagoon waters sampled during the study (unpublished data).

MATERIALS AND METHODS

Surface seawater samples were collected from the eastern harbour breakwater (Fig. 1) in 4.5 l acid-cleaned (seawater-aged) polyethylene containers which have been rinsed thoroughly with seawater before filling. Samples were filtered through acid-cleaned 0.45 μ millipore membranes supported on 250 ml polycarbonate sterifil holders. All filtration equipment and membranes were rinsed with 10 % triply distilled HNO_3 and double distilled water (DDW) before use. During filtration the cleaned membranes were rinsed with 250 ml of seawater prior to final filtration. All filtration, sample preparation and analysis procedures were carried out in an air-conditioned room, each procedure being isolated from other procedures. Dust was overcome as a contaminant by protecting sampling containers, filtration and analysis apparatus with acid-cleaned plastic sheet. Material left on the filter membranes consisted of settled sediments, detritus, faecal and plant material, cell debris etc. and was termed suspended material. Measurements of suspended material (mg/l) were made by weighing to a constant weight the oven dried (65 °C) membranes before and after filtration.
Particulate metals (Fe, Mn, Zn, Cu, Ni) were determined by digesting the suspended material on the membranes with 10 ml triply distilled nitric acid. On evaporation to dryness the residue was dissolved in 2 ml concentrated $HNO_3 - HClO_4$ (1 : 1) and the solution evaporated to dryness. The dry white residue was dissolved in 5 ml 2M HNO_3 and the five metals determined by atomic absorption spectrophotometry (AAS) using a Varian Techtron AA5 spectrophotometer equipped with a hydrogen continuum lamp for background correction.
Salinity was determined with an inductively-coupled salinometer (" Autolab " Industries — Sydney, model 601-Mk IIIB).
Sea surface temperatures were measured with a mercury-in-glass thermometer accurate to ± 0.1 °C.
Humic acids were determined according to the method of

Mantoura and Riley (1975). In this study this material was defined as those organic substances which are removed by the XAD-2 resin at pH 2, and eluted from the resin with 0.2M NaOH. Clearly, other organic substances may be removed from solution under these conditions. Results reported for humic acids may therefore be an overestimate, especially during *Trichodesmium* blooms, as some of the material eluted from the resin may not be polyphenolic compounds.

Trichodesmium counts were made with a Leitz microscope (mag × 100) on 100 ml preserved samples (Lugol's iodine). *Trichodesmium* was collected from the air/sea interface and intertidal locations using net tows (20 µ mesh) with no metallic parts. Samples were stored in acid-cleaned plastic bags and frozen (− 20 °C) prior to metal analysis by AAS. The acid digestion technique was the same as that described above.

Extraction of *Trichodesmium* cell contents was carried out by shaking approximately 100 g (wet weight) of this alga with 2 l of filtered seawater. The seawater turned a wine red colour and slowly turned pink under natural light. This pink solution was immediately protected from light and frozen for subsequent experiments.

The analysis of dissolved metals is summarized in flow chart form in Figure 2. Dissolved Fe, Mn, Zn, Cu, Ni were determined by first concentrating the sample by passing 2 l of the filtrate through a 6 cm × 0.8 cm diameter column of Chelex-100 ion-exchange resin in the ammonium form (Riley, Taylor, 1968). The metals were eluted from the column with 100 ml 2M HNO_3 and measured by AAS using a Varian Techtron AA5 spectrophotometer equipped with a hydrogen continuum lamp for background correction.

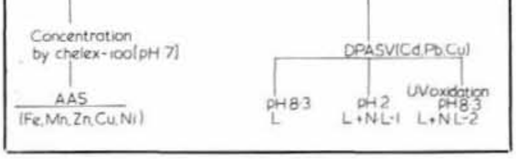

Figure 2

Flow-chart of the fractionation procedure for dissolved trace metal analysis (L = labile DPASV) ; N.L-1 = non-labile, released at pH2 ; N.L-2 = non-labile, released by photo-oxidation).

Dissolved forms of Cd, Pb, and Cu were determined by differential pulse anodic stripping voltametry (DPASV). Samples (25 ml) were analysed with a Princeton Applied Research (PAR) 174A Polarographic Analyser at pH 8.3, pH 1.9 (triply distilled HNO_3), and at pH 8.3 after photooxidation with ultra-violet (UV) light (Fig. 2). Measurements were made in the differential pulse mode at 25° ± 0.5 °C using a glassy carbon electrode set at − 1.0 V relative to the saturated calomel reference electrode. Deposition time was ten minutes, scan rate 5 mV sec.$^{-1}$, Hg^{2+} concentration 4×10^{-2} M, modulation amplitude 25 mV. The method of standard additions was used throughout and all other experimental conditions were closely similar to those recently reported (Batley, Florence, 1976 ; Duinker, Kramer, 1977 ; Blutstein, Smith, 1978).

Organic material in the filtrate was photo-oxidized with two 35W germicidal lamps (Oliphant, G24T15N) placed 2 cm from 50 ml samples contained in acid-washed quartz flasks. Samples analysed by DPASV were stored at 25° ± 0.5 °C. Results of storage tests (Table 1) showed no significant changes in metal concentration over 1 month from collection. It is assumed from this that metal speciation changes did not occur.

In this study Cd, Pb and Cu species analysed at natural pH by DPASV are called labile (electroactive) metal species (Fig. 2). The difference in Cd, Pb and Cu concentrations between UV photo-oxidized samples and unacidified samples is an estimate of the " organo-metallic " fraction. This is probably an underestimate of the soluble " organo-metallic " species, as soluble (labile) " organo-metallic " species, present in unacidified samples may also be reduced at the GCE under the experimental conditions already outlined. With the present speciation scheme these labile " organo-metallic " species cannot be estimated. Clearly, the addition of acid (pH 2) will release metal ions adsorbed onto inorganic and organic colloids as well as metal ions which are organically complexed. The difference in Cd, Pb, and Cu concentrations between acidified samples (pH 2) and UV photo-oxidized samples therefore reflects, to a fairly close degree, the amount of these metals " bound " to inorganic colloids (e.g. Fe, Mn, Al-hydroxides).

Table 1

Dissolved Cd, Pb, Cu (µg/l) in seawater collected from Cleveland Bay and stored at 25 °C.

Time interval (days)	Fraction	Dissolved metals (µg/l)		
		Cd	Pb	Cu
0	Unacidified (pH 8.3)	0.07	0.14	0.25
	Acidified (pH 2)	0.07	0.31	0.47
	Photo-oxidised (pH 8.3)	0.07	0.17	0.27
24	Unacidified (pH 8.3)	0.07	0.16	0.25
	Acidified (pH 2)	0.05	0.33	0.50
	Photo-oxidised (pH 8.3)	0.07	0.17	0.28
28	Unacidified (pH 8.3)	0.05	0.16	0.23
	Acidified (pH 2)	0.07	0.33	0.50
	Photo-oxidised (pH 8.3)	0.07	0.19	0.28

The analysis of unacidified samples presented some problems due to the presence of soluble sequesting substances reacting with added metal ions. Addition of metal ions may displace other metals from their complexes, or simply increase the concentration of labile and/or ionic metal already present (Duinker, Kramer, 1977). In order to determine the labile metal concentration correctly it is essential that any uncomplexed, non-labile (non-electroactive) ligands (colloids) are first reacted with added metal ions. This was particularly important during high freshwater runoff, and to some extent during *Trichodesmium* blooms (unpublished).

Method blanks were obtained by refiltering seawater subsamples through another acid-cleaned filtrer membrane and carrying sub-samples through the entire procedure. Using the ion-exchange-AAS method blanks were < 0.3 µg (Fe), < 0.17 µg (Mn), 0.21 µg (Zn), 0.04 µg (Cu), and < 0.11 µg (Ni). In the DPASV method blanks were < 0.2 ng (Cd and Pb) and < 0.9 ng (Cu). In the voltametric and AAS procedures reproducibility tests gave standard deviations of about ± 10 % for most metals.

RESULTS

Results of *Trichodesmium* counts, humic acids, suspended material, salinity, rainfall and temperature (Fig. 3) showed that *Trichodesmium* blooms of red tide proportions occurred from late August to mid-October when temperatures were low (23-27 °C), salinities were high (36 ‰), and rainfall was negligible (< 30 mm). Minor blooms of *Trichodesmium* also occurred at other times of the year but were of short duration. In addition to live *Trichodesmium,* the presence or absence of large masses of senescent filaments (see hatched bar in Fig. 3) was also assessed. High densities of this material often occurred after *Trichodesmium* blooms, particularly from October to January (Fig. 3) when

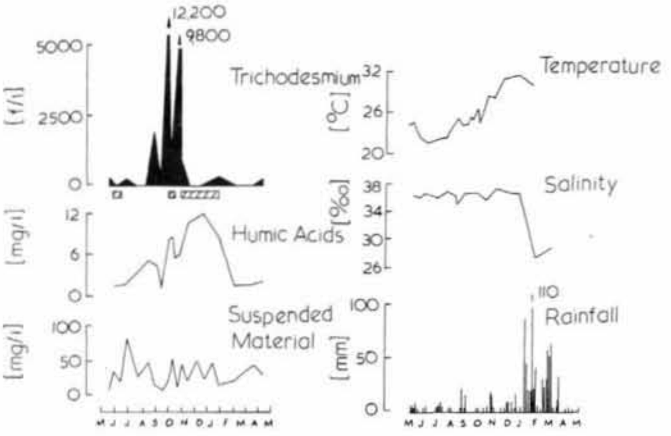

Figure 3

Trichodesmium *counts (f/l) humic acids (mg/l), suspended material (mg/l), salinity (‰), rainfall (mm) and temperature (°C) at the harbour breakwater from May 1978-April 1979 (hatched bar represents senescent* Trichodesmium).

suspended material was very variable, due to resuspension of material by wind and tide. Humic acid concentrations often peaked during such periods. Salinity and rainfall results, suggested that these humic substances were not land-derived (Fig. 3).

Metal analysis of *Trichodesmium* showed that highest concentrations of most trace metals, particularly iron, occurred in inshore *Trichodesmium* samples (Table 2). *Trichodesmium* collected from the sea surface at an upstream station (Ross River Bridge) in the Ross Estuary (Table 2). *Trichodesmium* collected from the sea surface at a more seaward station (Bundi Creek) on the same day showed no such exudate. It is suggested that the production of these iron-rich particles from senescent *Trichodesmium* filaments reflected the marked reduction in salinity between these two stations (36 to 22 ‰). These iron-rich particles displayed high UV absorbance (Jones, 1981).

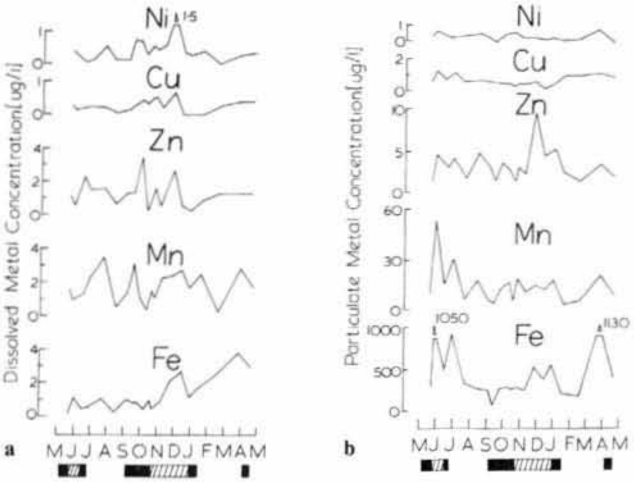

Figure 4

Dissolved (a) and particulate (b) metal (µg/l) variation at the harbour breakwater from May 1978-April 1979 (full and hatched bar represents live and senescent Trichodesmium, *respectively).*

The monthly variation in dissolved and particulate metals, determined by AAS, showed that the concentration of most metals peaked during the presence of senescent *Trichodesmium* filaments and high humic acid concentrations (Fig. 4 *a-b*). High UV absorbance and low molecular weight fluorescent compounds have been attributed to senescent *Trichodesmium* filaments (Traganza, 1969; Jones, 1981). Whilst it is recognized that low molecular weight fluorescent compounds do occur in coral reefs in this region (Gentien, 1981), it is suggested that during this study a major fraction of the " humic acids " detected during the presence of senescent *Trichodesmium* blooms inshore, was due to the decay of this organism. Consequently in the ensuing discussion correlations with humic acids reflect decomposition processes involving *Trichodesmium*.

Dissolved metal — *Trichodesmium* correlations (Fig. 5 *a*),

Table 2

Trace metal content (µg/g dry weight) of Trichodesmium *collected from inshore and offshore locations in GBRL.*

Location	Date collected	Fe	Mn	Zn	Cu	Ni	Cd	Pb
Offshore Magnetic Island (4 miles offshore)	29.8.78	123	6	14	3	11	< 0.26	N.A.
Magnetic Island (2 miles offshore)	29.8.78	61	9	7	3	4	< 0.11	N.A.
Inshore Magnetic Island (5) (Balding Bay)	15.11.78	120	5	4	4	30	< 0.10	< 0.10
Magnetic Island (Nelly Bay)	18.5.78	205	77	3	7	38	< 0.13	< 0.25
• Townsville (5) (Cape Pallerenda)	7.10.77	635	58	10	9	42	N.A.	N.A.
Ross Estuary (mouth)	21.5.78	264	58	4	4	18	< 0.05	N.A.
Ross Estuary (3) (upstream, Ross River Bridge)	21.10.78	4.96 %*	2,831	186	53	28	N.A.	N.A.

Numbers in parenthesis indicate number of replicates ; N.A. = Not available ; * = Expressed as a percentage ; • = intertidal collection.

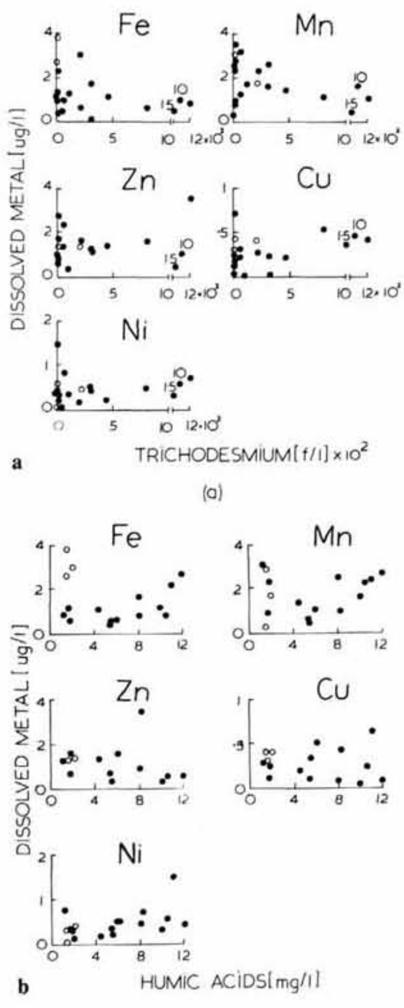

Figure 5

Correlation of dissolved metals (μg/l) with Trichodesmium *counts (f/l)-(a) and humic acids (mg/l)-(b).*

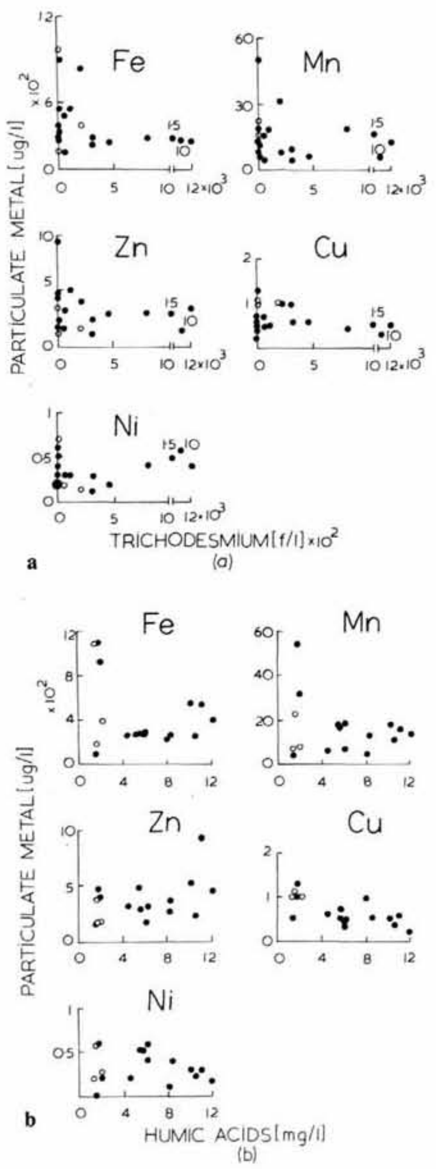

Figure 6

Correlation of particulate metals (μg/l) with Trichodesmium *counts (f/l)-(a) and humic acids (mg/l)-(b).*

indicative of uptake, and dissolved metal — humic acid correlations (Fig. 5 *b*), indicative of decomposition suggested a simple uptake-regeneration cycle for Fe, Mn, and Zn during and after *Trichodesmium* blooms. Correlation of particulate metals with *Trichodesmium* counts (Fig. 6 *a*) and humic acids (Fig. 6 *b*) also indicated a simple uptake-regeneration cycle for Fe, Mn and Zn. Dissolved Cu concentrations were high (≃ 0.5 μg/l) at high *Trichodesmium* counts (Fig. 5 *a*) and particulate fractions of Cu and Ni decreased during high humic acid concentrations (Fig. 6 *b*). In view of the fairly high concentrations of Cu and Ni in inshore *Trichodesmium* samples (Table 2) this seemed surprising.

To ascertain the effect of the cell contents of *Trichodes-*

Table 3

Variation of dissolved and particulate Fe, Mn, Zn, Cu and Ni concentrations (μg/l) in a control seawater sample when varying volumes of the Trichodesmium *leachate were added.*

Volume of *Trichodesmium* leachate (ml)	Dissolved metals (μg/l)					Particulate metals (μg/l)				
	Fe	Mn	Zn	Cu	Ni	Fe	Mn	Zn	Cu	Ni
1	3.6	0.24	2.7	0.27	< 0.26	68	14	0.68	N.D.	N.D.
2	9.2	1.8	4.2	30*	< 0.26	69	14	0.80	N.D.	N.D.
5	5.2	4.8	5.3	9*	< 0.26	60	14	0.91	N.D.	N.D.
10	N.A.	N.A.	N.A.	N.A.	N.A.	30	7	0.50	N.D.	N.D.
20	17	3.5	5.0	1.7	< 0.26	20	1.3	0.30	N.D.	N.D.
40	67	20	5.0	3.3	< 0.26	10	0.70	0.22	N.D.	N.D.
Control seawater	3.6	0.24	2.7	0.26	< 0.26	261	15	0.74	N.D.	N.D.
Leachate	5.0	< 0.50	< 0.10	< 0.10	< 0.26	N.A.	N.A.	N.A.	N.A.	N.A.

N.A. = Not available.
N.D. = Not detectable.
* = contamination suspected.

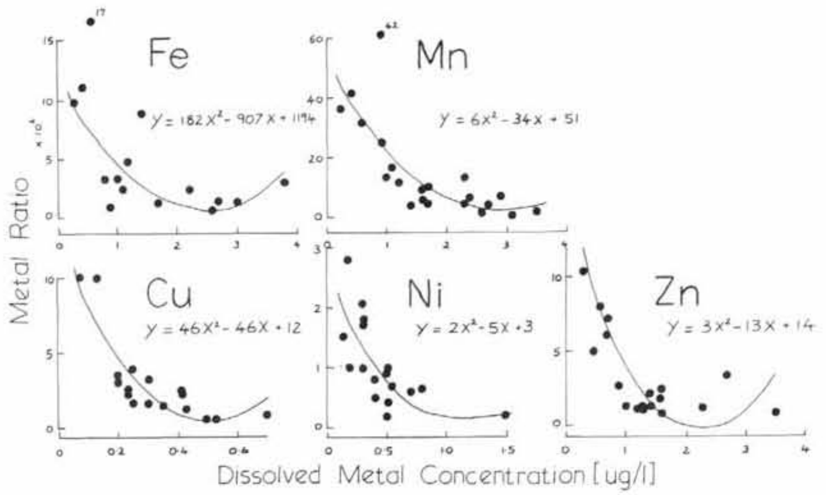

Figure 7

Metal ratio — dissolved metal correlations [metal ratio = particulate metal concentration (µg/l)/dissolved metal concentration (µg/l)].

mium on dissolved and particulate trace metals, varying volumes of the pink solution extracted from this alga, were added to aliquots (500 ml) of a control seawater sample of known dissolved and particulate metal concentration. The results (Table 3), after subtracting the metal content of the leachate, showed that substances extracted from *Trichodesmium* dissolved particulate Fe, Mn and Zn. No estimation of this dissolution process on particulate Cu and Ni could be made as these fractions were undetectable in the control seawater.

To test whether this dissolution process occurred at the harbour breakwater during *Trichodesmium* blooms the particulate to dissolved metal concentration ratios were calculated for Fe, Mn, Zn, Cu and Ni and plotted against their dissolved concentration (Fig. 7). Ratios of all metals decreased with increasing dissolved metal concentration. Such a situation not only suggested decomposition but also a dissolution mechanism whereby the decomposition products of *Trichodesmium* dissolved particulate metal fractions. Metal speciation studies at the harbour breakwater also substantiated this viewpoint.

Dissolved Cu concentrations (DPASV) in the three pretreated samples (Fig. 8 *a*) showed that throughout the majority of the investigation little difference was observed in the dissolved Cu concentrations in unacidified (pH 8.3) and U.V. irradiated samples. Dissolved Cu concentrations were often highest in acidified (pH 2) samples, except when senescent *Trichodesmium* filaments were present (i.e. October to January).

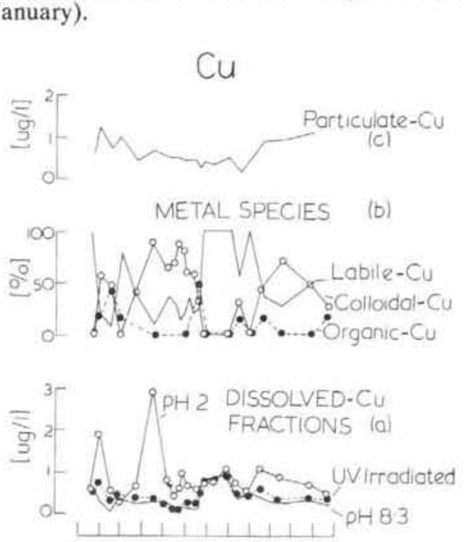

Figure 8

Copper speciation. a) Copper fractions (µg/l) ; b) copper species expressed as a percentage (%) of total soluble copper species ; c) particulate copper variation.

Metal speciation profiles (Fig. 8 *b*) showed that organic Cu fractions were only significant (> 10 %) in June and October. During the major bloom period (August to October) colloidal Cu was the dominant Cu fraction (> 60 %). From late October to late December however, this Cu fraction markedly decreased (< 30 %). During this period labile Cu species ranged from 50-100 % (mean 90 %) of the total soluble Cu species. Labile Cu concentrations ranged from 0.83 – 1.0 µg/l during this period, a 600 % increase compared to early October (0.13 µg/l). This marked increase in labile Cu concentrations occurred during high densities of senescent *Trichodesmium* filaments, and when humic acid concentrations were high (10 mg/l). During this period particulate Cu was also low (Fig. 8 *c*).

Correlation of labile metals (DPASV) with *Trichodesmium* counts (Fig. 9 *a*) and humic acids (Fig. 9 *b*) also showed that labile forms of Cd, Pb and Cu increased during the decomposition phase of *Trichodesmium*.

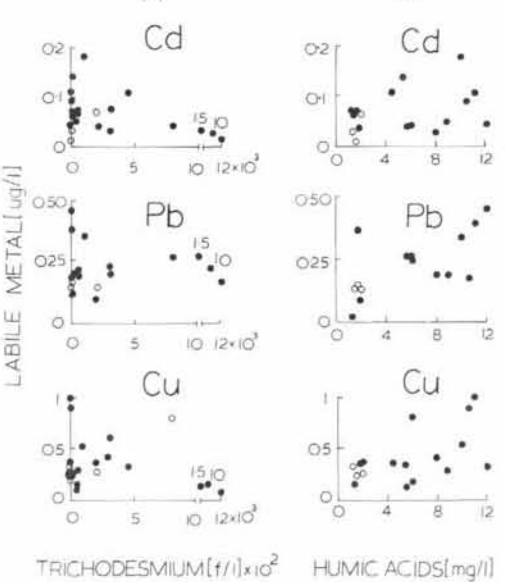

Figure 9

Correlation of labile metals (µg/l) with Trichodesmium *counts (f/l)-(a) and humic acids (mg/l)-(b).*

The marked increase in labile Cd, Pb and Cu occurred when the metal ratios of these elements decreased (i.e. at the expense of the colloidal metal fractions ; Fig. 10).

DISCUSSION AND CONCLUSION

The dramatic increases in dissolved and particulate metals at a coastal station in the GBRL during senescent *Tricho-*

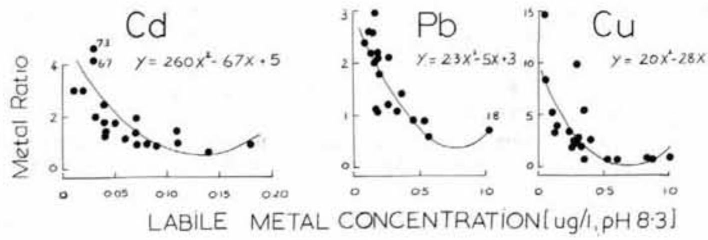

Figure 10

Metal ratio — labile metal correlations (metal ratio = metal concentration at pH 2/labile metal concentration at pH 8.3 after photo-oxidation).

desmium blooms reflects decomposition processes involving this alga. Whilst many of the changes can be ascribed solely to decomposition of this alga, laboratory studies and metal speciation analysis at this coastal site suggest that the increases in labile metals during the decomposition phase of *Trichodesmium* reflected a situation whereby many of the metals were not so efficiently scavenged from solution, either by incorporation into organisms which followed the blooms or by their adsorption onto particles. This could be due to several processes involving *Trichodesmium* :

Release of an iron-chelating compound from *Trichodesmium*

This is suggested by the iron-rich particles associated with *Trichodesmium* exudates (Table 2). Such substances could be hydroxamic acids, which are strong chelators of iron, and have been shown to be excreted from a blue-green alga in the Bay of Quinte, Canada (Murphy *et al.*, 1969). Regardless of the exact nature of the chemical compounds released from *Trichodesmium* one consequence of the release of an excess of a strong iron chelator inshore would be a decrease in colloidal iron. As many trace elements are " bound " to colloidal iron destabilisation of this material by iron chelation could result in increases in labile metal concentrations.

Dissolution involving surfactants

Parker *et al.* (1967) have shown that fatty acids (monocarboxylic acids) are important components of blue-green algae. In *Trichodesmium* collected from the Gulf of Mexico one half of the total fatty acid content was found to be ten-carbon acid n-decanoic acid. As fatty acids exhibit surface active properties they can be expected to concentrate at the particle/water interface. Thus a high surface concentration of these molecules would facilitate any reaction with metal ions adsorbed onto particulate material, i.e. it could assist a dissolution process whereby colloidally-bound metal ions are converted to labile metal ions. A build-up of surfactant material can occur after planktonic blooms (Žutić *et al.*, 1981) and can modify metal ion-particulate matter interactions (Davis, Leckie, 1978 ; Balistrieri *et al.*, 1981).

Dissolution involving pH changes

Metal ion-particulate matter interactions can also be modified by changes in pH (Davis, Leckie, 1978) which are related to CO_2 increases arising from organic decomposition (Balzer, Wefer, 1981). In tropical waters this can lead to significant changes in pH (Morse, Berner, 1972), which can cause pronounced increases in rates of dissolution of carbonates.

Clearly, in view of this present work, metal ion speciation experiments should be carried out with organic substances that are similar to the chemical composition and molecular size of surfactants and extracellular material associated with phytoplankton blooms. At present this organic material is uncharacterized.

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