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## Biogeochemical Cycling of Metals in Freshwater Algae from Manaus and Carajás, Brazil

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Abstract Freshwater algae were analyzed in different riverine environments in Manaus and Carajás, Brazil. Filamentous algae from both locations were characterized by enhanced levels of a wide array of heavy metals. A comparison of the two main rivers in the Manaus area indicated that the algal samples from the solute-rich waters of the Rio Solimões consistently contained higher metal concentrations than in the solute-deficient waters of the Rio Negro. A similar relationship also existed between algal samples collected from forested regions relative to adjacent deforested regions in the Carajás area.

In the Rio Negro, diatoms were shown to be the most prolific eucaryotic micro-organisms found in the study area. These siliceous algae were found adhering to a variety of submerged solid substrates, including wood, rocks, and leaves. The abundance of these unicellular micro-organisms suggested that the dissolved silicon levels of the Rio Negro were influenced by biological activity.

#### Introduction

Many of the chemical processes occurring within the hydrosphere have been shown to be biologically mediated. Organisms are continuously undergoing chemical exchanges with their aqueous environment, involving the uptake and excretion of various elements. Although all forms of life possess some characteristics that make them biogeochemically important, much of the focus today is being directed toward the role of micro-organisms in the cycling of elements.

The significance of micro-organisms, such as bacteria and algae, arises from their ability to live in a variety of habitats, many of which are devoid of higher organisms. Micro-organisms have been isolated from hostile environments such as hypersaline waters (Steinhorn and Gat, 1983), low pH-hydrothermal waters (Mann, Fyfe, and Kerrich, 1987), and acid mine effluents (Mann and Fyfe, 1988).

Within the hydrosphere, most elements are found in extremely low concentrations. Micro-organisms, however, possess the ability to accumulate and concentrate several of these elements from solution. Experimental work by Beveridge and Murray (1976, 1980) and Beveridge and Koval (1981) demonstrated the complexation of over thirty metals by bacteria. Metal concentrations have also been documented in both freshwater and marine algae. Mann and Fyfe (1988) and Mann et al. (1989a) have shown the contribution of both unicellular and filamentous green algae to the uptake and immobilization of many dissolved metals in freshwater systems. In their study of mine-tailing ponds in Elliot Lake (1988), Timmins (1988), and Sudbury (1989a) filamentous algae were shown to concentrate almost all metals by over  $10^2$  times their natural aqueous abundance with Fe, Co, and Zr up to  $10^6$ . Even elements with exceedingly low dissolved concentrations in rivers, such as uranium (global river average for U, 0.6 ppb) were shown to be concentrated over  $10^3$  times by unicellular algae (Mann and Fyfe, 1988).

Similar concentrations for a variety of metals were shown to occur in the marine environment. Both essential elements (to plant life) and nonessential elements were shown to be enriched by algae relative to sea water (Trudinger, Swaine, and Skyring, 1979).

Biologically mediated processes can also have profound effects on the precipitation of mineral phases. Through the process of biomineralization, micro-organisms are able to form mineralized deposits from several of the elements taken out of solution. Algae have been shown to extensively precipitate silica (diatoms) and calcium carbonate (coccolithophores), with lesser amounts of iron oxides (Mann and Fyfe, 1988; Mann et al., 1989b) and uranium oxide (Mann and Fyfe, 1985).

To supplement the information already published on the biogeochemical cycling of elements by algae, this paper presents the results of an examination on the presence of both filamentous and unicellular algae in two different natural riverine environments: the Manaus area, in the state of Amazonia (Fig. 1a), and the Carajás mining area, in the state of Para (Fig. 1b).

The city of Manaus is built at the confluence of the Rio Solimões and the Rio Negro in central Amazonia, 1600 km from the Atlantic coast. The tributaries of the Amazon have been categorized according to their appearance (Sioli, 1950). White-water rivers such as the Rio Solimões are rich in suspended sediments and dissolved solutes. In contrast, blackwater rivers such as the Rio Negro are characterized by low sediment yields and their "tea-colored" (Hedges et al., 1986) acidic waters, rich in dissolved humic material (Ertel et al., 1986). The inundated floodplain forest between the two Amazon tributaries is partly influenced by both rivers.

The Carajás Range is located approximately 550 km south of Belem in the state of Para. The area is almost completely covered by an equatorial rainforest, broken only by clearings of sparse vegetation. The enormous iron ore potential has resulted in some clearing within Carajás to create the "Iron Ore Project." Outside the Carajás area agricultural and/or livestock practices over the past decade have resulted in widespread clearing of the rainforests. Most of the Carajás area is served by the Itacaiunas River, which flows into the Tocantins River at Marabá. The main tributary of the Itacaiunas River, the Paraoapebas River, marks the eastern boundary of the Carajás area and also the abrupt transition from a forested to deforested landscape.

#### Methods

In the Manaus area, water and algal samples were collected upstream of Manaus on the Rio Negro (and some of its tributaries) and on the Rio Solimões. Submerged wood samples coated by a gelatinous algal film were collected from site M8, and several submerged leaves and rocks, also covered by algae, were taken from sites M6 and M7, respectively (Fig. 1a). In the Carajás area, water and algal samples were collected randomly from a variety of streams. Some of the streams drained forested areas, while others drained areas having undergone almost-complete deforestation (Fig. 1b).



(a)



Figure 1. Location of sample sites in: (a) Manaus and (b) Carajás.

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Approximately 1 L samples of water (midstream from all sites) were collected for multielement analysis. The water samples were placed in two 500 mL Nalgene bottles and then acidified on site with 5 mL analytical grade  $HNO_3$ . Large populations of filamentous algae were gathered from below the water surface by hand using surgical gloves to avoid contamination. The algae were washed in the natural river water to remove loose detritus, placed in polyethylene bags, and drained of excess water. Samples of wood, leaves, and rocks were gathered from below the water surface by hand, again, using surgical gloves, dried in the sun, and placed in polyethylene bags.

In the laboratory, sections of wood were cut away from the outer surface for observation by scanning electron microscopy (SEM). Random samples of leaves and rocks, selected from the sealed polyethylene specimen bags, were also selected for similar observation as above. In preparation for analysis, samples were mounted on a specimen stub with conductive carbon paint and sputtered with gold for 3 minutes. Samples were examined with an SEM model 1S1 DS 130, coupled with a Tracor Northern EDX Analyzer, model TN 5500.

Prior to analysis, the algal samples were placed in 500 mL Nalgene bottles, half filled with deionized water, and then submerged in a Crest ultrasonic bath for 30 minutes (on "heavy cleaning" setting) to remove excess sediment particles. Algal samples were then weighed wet and digested in pure nitric acid at elevated pressures in a Teflon pressure vessel. Concurrently, a percent moisture was determined so that all data could be reported relative to dry weight. After digestion, the samples were diluted to appropriate volumes. Multielement analyses of the algae were performed on the aqueous digestates by inductively coupled plasma emission spectroscopy-mass spectroscopy: an ICP-MS Model PQ1 by VG Elemental Ltd. was used.

Prior to multielement analysis, the water samples were filtered through a 0.2  $\mu$ m Nuclepore membrane (Costar Corp.) to remove suspended sediments. The samples were then analyzed by ICP-MS.

#### Results

#### Manaus Area

Filamentous algae growing in waters from the Rio Negro (Table 1) and the Rio Solimões (Table 2) were characterized by high concentrations of a wide array of heavy metals. A comparison of the two rivers indicated that the metal concentrations in the algae of the Rio Solimões were consistently higher than in the algae from the waters of the Rio Negro.

Using a plot of concentration factors (concentration in algae/concentration in water), the algae are characterized by enrichments of between  $10^2$  to  $10^7$  for the metals studied (Fig. 2). Exceptionally high concentration factors (> $10^6$ ) are indicated for Ti and Zr, with Ti values exceeding  $6.6 \times 10^6$  times. Low concentration factors (< $10^3$ ) are indicated for Hg. Figure 2 also displays a difference in concentration factors between the two main rivers. Concentration factors for the metals analyzed are typically higher in the algae from the Rio Solimões than in the algae from the Rio Negro.

 Table 1

 Concentration of Metals in Water and Algae from the Rio Negro

Element	Water (ppb)	M5-90 (ppm)	M6-90 (ppm)	M8-90 (ppm)	M8-91 (ppm)	Average (ppm)	Conc. Factor*
Titanium	0.92	580.00	75.00	400.00	290.00	336.25	365,489
Vanadium	0.27	17.00	3.20	21.00	10.00	12.80	47,407
Chromium	0.31	11.00	0.83	5.70	21.00	9.63	31,073
Manganese	9.68	110.00	95.00	130.00	14.00	87.25	9,013
Iron	406.00	15000.00	4000.00	16000.00	2900.00	9475.00	23,337
Cobalt	0.08	2.80	1.00	2.20	1.90	1.98	24,688
Nickel	0.32	6.00	1.40	4.90	4.50	4.20	13,125
Copper	0.32	11.00	4.00	5.80	8.50	7.33	23,180
Zinc	11.54	74.00	21.00	73.00	27.00	48.75	4,224
Arsenic	0.06	0.90	0.35	2.10	0.64	1.00	16,625
Zirconium	0.03	17.00	1.80	7.20	7.30	8.33	260,156
Molybdenum	0.05	0.49	0.11	1.40	0.89	0.72	13,380
Silver	0.03	0.12	0.02	0.08	2.40	0.66	20,523
Cadmium	0.08	0.16	0.05	0.09	0.11	0.10	1,294
Tin	0.05	0.83	0.21	0.60	0.55	0.55	11,902
Mercury	0.21	0.08	0.04	0.17	0.06	0.09	410
Lead	0.12	16.00	2.10	9.90	3.00	7.75	66,810
Uranium	0.02	0.84	0.17	0.65	0.26	0.48	21,818

#### Carajás Area

Algal communities living in the waters of Carajás also contained high metal concentrations relative to their water source. A comparison of algal samples collected from pristine forested regions (Table 3) to regions deforested several years earlier (Table 4) indicated that metal concentrations were generally higher in the former environment. An exception to this pattern is sample site AZ4. The algal samples were collected from a stream draining an active manganese mining operation, which invariably supplied metal-rich sediment to the stream.

The concentration factors for the Carajás area ranged from  $10^2$  to  $10^7$  (Fig. 3). Zr and Ti are characterized by high concentration factors (>10<sup>6</sup>), while Zn, Hg, Pb, and Mo have low factors (<10<sup>3</sup>). In addition, Fig. 3 illustrates that, for a majority of metals analyzed, the concentration factors for algae were higher in streams draining forested sites.

#### Silica Precipitation

Scanning electron micrographs illustrate that the submerged wood, leaf, and rock samples served as solid substrates for siliceous epiphytic algae (Figs. 4a-f). The ubiquitous nature of the diatoms suggests that any available surface will serve as a solid interface for growth.

 Table 2

 Concentration of Metals in Water and Algae from the Rio Solimões

Element	Water (ppb)	M11-90 (ppm)	S4-91 (ppm)	S5-91 (ppm)	S6-91 (ppm)	Average (ppm)	Conc. Factor*
Titanium	0.89	2400.00	7500.00	3500.00	10000.00	5850.00	6,610,169
Vanadium	0.59	170.00	230.00	150.00	290.00	210.00	358,974
Chromium	0.31	71.00	250.00	86.00	160.00	141.75	457,258
Manganese	43.00	9300.00	17000.00	4500.00	2800.00	8400.00	195,349
Iron	985.00	110000.0	59000.00	44000.00	49000.00	65500.00	66,497
Cobalt	0.36	61.00	110.00	21.00	36.00	57.00	160,563
Nickel	0.71	49.00	120.00	40.00	59.00	67.00	94,366
Copper	2.40	74.00	190.00	49.00	66.00	94.75	39,479
Zinc	7.10	200.00	160.00	200.00	270.00	207.50	29,225
Arsenic	0.21	47.00	4.00	30.00	24.00	26.25	128,049
Zirconium	0.06	64.00	160.00	58.00	150.00	108.00	1,963,636
Molybdenum	0.06	4.20	2.00	1.60	2.30	2.53	42,083
Silver	0.03	0.76	3.80	16.00	3.50	6.02	200,500
Cadmium	0.12	3.60	0.55	2.20	2.10	2.11	17,604
Tin	0.03	4.30	2.10	3.00	6.00	3.85	128,333
Mercury	0.21	0.40	0.46	0.36	0.61	0.46	2,179
Lead	0.64	72.00	18.00	26.00	41.00	39.25	61,811
Uranium	0.07	6.10	4.10	2.90	5.50	4.65	66,429



TI Zr Cr V Ag Mn Co Sn As NI Fe U Pb Mo Cu Zn Cd Hg

Figure 2. Concentration factor plot for filamentous algae in the Rio Solimões and the Rio Negro, Manaus.

Element	Water (ppb)	K3-91 (ppm)	K8-90 (ppm)	K9-90 (ppm)	K11-90 (ppm)	Average (ppm)	Conc. Factor*
Titanium	2.33	12000.00	1200.00	600.00	910.00	3677.50	1,578,326
Vanadium	0.27	310.00	59.00	22.00	42.00	108.25	400,926
Chromium	14.18	240.00	55.00	7.60	44.00	86.65	6,111
Manganese	50.86	2400.00	2400.00	1800.00	6200.00	3200.00	62,918
lron	413.50	100000.0	51000.00	22000.00	45000.00	54500.00	131,802
Cobalt	0.60	140.00	28.00	22.00	180.00	92.50	154,167
Nickel	1.37	110.00	30.00	17.00	110.00	66.75	48,723
Соррег	3.82	370.00	74.00	65.00	730.00	309.75	81,086
Zinc	18.50	330.00	120.00	53.00	100.00	150.75	8,149
Arsenic	0.03	12.00	7.80	0.82	9.60	7.56	251,833
Zirconium	0.06	530.00	44.00	19.00	26.00	154.75	2,579,167
Molybdenum	5.75	5.30	0.93	0.55	2.00	2.20	382
Silver	0.07	2.50	0.06	0.04	0.23	0.71	10,114
Cadmium	0.07	0.77	0.28	0.12	0.48	0.41	5,893
Tin	0.07	4.50	1.40	5.60	0.85	3.09	44,107
Мегсигу	0.24	0.25	0.02	0.02	0.42	0.18	741
Lead	16.99	22.00	6.20	2.20	4.00	8.60	506
Uranium	0.05	14.00	2.10	1.20	2.80	5.03	100,500

 Table 3

 Concentration of Metals in Water and Algae from Forested Areas

Sections obtained from the outer surfaces of the submerged wood samples revealed morphologically distinct benthic diatom species. One section of wood is dominated by blocky-shaped (unidentified) diatoms (Figure 4*a*), while other sections show a virtual monoculture of the pennate-shaped Navicula sp. (Fig. 4*b*). Overlying many of the surface diatoms is a blanket of siliceous gel (Figs. 4c,d), indicated by the EDX spectrum in Fig. 5*b*.

Samples collected from the submerged leaves (Fig. 4e) and rocks (Fig. 4f) show different diatom species from that seen on the wood. Several diatoms species on the leaf surface overlie a sediment composed of Si, Al, Fe, Mg, K, and Ca (Fig. 5c) and are in turn covered by a thin veneer of siliceous gel. Diatoms (*Navicula* sp.) were also found on the outer surface of a submerged rock chemically composed of Fe and Al-silicates (laterite) (Fig. 5d).

Analyses of the water samples indicated that the dissolved silicon concentrations for the Rio Negro and its tributaries ranged from 1900  $\mu$ g/L (sites M8 and M9) to 2000  $\mu$ g/L (site M7) and 2100  $\mu$ g/L (site M6). These values are considerably lower than the world river average of 7000  $\mu$ /L (Bowen, 1979).

#### Discussion

Algal samples collected from different riverine environments in both the Manaus and Carajás areas indicated that metals were consistently removed from the waters by micro-organisms. The pattern that seems to arise is that algae effectively

 Table 4

 Concentration of Metals in Water and Algae from the Deforested Areas

Element	Water (ppb)	C1-90 (ppm)	K1-90 (ppm)	K15-91 (ppm)	Average (ppm)	Conc. Factor*	AZ4-91 (ppm)
Titanium	3.00	1500.00	1000.00	1200.00	1233.33	411,111	8800.00
Vanadium	0.50	55.00	59.00	97.00	70.33	141,801	340.00
Chromium	12.20	42.00	47.00	57.00	48.67	3,989	190.00
Manganese	403.67	3400.00	4300.00	3100.00	3600.00	8,918	89000.00
Iron	1596.67	47000.00	85000.00	26000.00	52666.67	32,985	230000.00
Cobalt	2.09	43.00	110.00	18.00	57.00	27,273	110.00
Nickel	2.11	28.00	22.00	46.00	32.00	15,166	80.00
Copper	8.73	18.00	180.00	44.00	80.67	9,240	140.00
Zinc	170.00	140.00	64.00	210.00	138.00	812	150.00
Arsenic	0.81	11.00	1.80	7.90	6.90	8,487	46.00
Zirconium	0.06	46.00	32.00	17.00	31.67	558,495	370.00
Molybdenum	0.17	0.82	6.80	1.20	2.94	17,711	16.00
Silver	0.07	0.10	0.36	0.25	0.24	3,381	1.50
Cadmium	0.15	0.42	0.27	3.20	1.30	8,475	1.40
Tin	0.08	2.20	2.40	1.70	2.10	27,632	5.40
Мегсигу	0.24	0.058	3 0.38	0.11	0.18	774	0.66
Lead	6.27	14.00	3.70	18.00	11.90	1,898	130.00
Uranium	0.37	3.30	4.00	1.70	3.00	8,174	4.30



Zr TI V As Co Fe U Cu Mn NI Sn Ag Zn Cr Cd Hg Pb Mo

Figure 3. Concentration factor plot for filamentous algae in forested and deforested areas, Carajás.



(a)



(b)



Figure 4. Scanning electron micrographs of: (a) diatoms on the outer wood surface, (b) different diatoms on the outer wood surface. Arrows indicate a patch of siliceous gel, (c) outer wood surface covered by a siliceous gel (arrows).



Figure 4. (Continued): (d) magnified view of the gel (arrows), (e) partial leaf structure. Arrows indicate diatoms, leaf structure, and siliceous gel, and (f) diatoms obtained on the laterite surface.



Figure 5. EDX spectral analysis of: (a) diatoms on the wood surface, (b) the siliceous gel, (c) sediment on the leaf surface, and (d) the lateritic chemical composition. Au peaks are from SEM preparation.

sequester and concentrate the metals available to them within their aqueous environment. Some metals are extracted from their surrounding environment to fulfill essential physiological functions (Table 5). These functions range from cell synthesis (O'Kelley, 1974) to the formation of skeletal and supporting tissues (Borowitzka, 1986; Sullivan and Volcani, 1981). The accumulation of many of these metals to levels far in excess of their needs may also be due to the way the organism allows metals to move passively through its permeable cell membrane. Several metals may be concentrated to enhanced levels as a consequence of the organism's attempt to obtain other physiologically required elements.

The extraction of other metals without known cellular functions largely reflects the strong complexing ability of the reactive organic components of the living cell.

Table F

Inorganic Elemer	its Required by One or More Algal Species
	Macronutrient Elements
	S, K, Ca, Mg, N, P
Micronutr	ient Elements Essential to All Algae
	Fe, Mn, Cu, Zn, Mo, Cl
Elen	nents Required by Some Algae
	Co, B, Si, Na, V, I
Source: O'Kelley (19	74).

For example, Kuyucak and Volesky (1989) have shown that the cellulosic materials of the cell wall play an important role in the biosorption of gold. The availability of these metals in solution, therefore, may lead to high metal accumulations by algae.

If we conclude that metal concentrations within the algal biomass are a direct reflection of availability, then it is not surprising that the concentration of metals in the filamentous algae of the Rio Solimões greatly exceeds those of the Rio Negro. The Rio Solimões is characterized by a high concentration of suspended sediments and dissolved solutes due to rapid and substantial drainage of the Andes Mountains (Stallard and Edmond, 1983). In recent volcanic areas the supply of fresh rock residues allows for a relatively fertile river system. In contrast, the Rio Negro drains the highly weathered Precambrian shield. In these stable cratonic regions, the lack of exposed rock and the intense chemical weathering over long periods of time result in the development of thick lateritic soils (Kronberg et al., 1979) with low weathering rates (Stallard and Edmond, 1983). The waters that drain these areas, therefore, are solute-deficient.

A similar relationship of metal concentration arises between algal samples obtained from forested and completely deforested regions. Tropical plant species have adapted over millions of years to the highly leached and weathered soils of the tropics by developing a closed system that effectively conserves and recycles needed nutrients (Jordan, 1985). Under these forested conditions the river system is continuously supplied with nutrients through the slow leaching from leaves, soils, and decaying organic matter. Removal of the vegetation through logging and slash-and-burn agricultural practices, however, disrupts the nutrient-conserving mechanisms. Initial losses will consist of those in the standing biomass (Salati and Vose, 1984) and those liberated as aerosols by the burning of the felled forest (Ewel et al., 1981). Over time, increased soil erosion causes the level of soil nutrients to fall below the level of an undisturbed forest (Jordan, 1985). Invariably, the nutrient input into the river system will be minimal. We believe that this situation is consistent with the data from these algal samples.

The role of micro-organisms in biogeochemical cycling extends beyond heavy metal extraction. Siliceous micro-organisms, such as diatoms, were shown to effectively sequester silicon from the surface waters of the Rio Negro, where the dissolved silicon levels were a maximum of 2100  $\mu$ g/L. While the low silicon levels are highly indicative of the Precambrian shield through which the river flows, the widespread occurrence of diatoms further suggests that these levels have been influenced by biological activity.

#### Conclusions

Analysis of both filamentous and unicellular algae indicated that these microorganisms played a very important role in the immobilization and concentration of dissolved metals. Their ability to scavenge metals has important environmental and economic implications. Algae can be of potential use in the retardation of heavy metal dispersion and also in the exploration of ore bodies.

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