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Trace Metals in Macroalgae from the Qatari Coastal Water

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ABSTRACT. Trace metals, Fe, Mn, Zn, Cu, Ni, Cr, Cd and Hg were measured in ten species of macroalgae from the Qatari coastal water. Concentrations in the various species indicate a nonpolluted environment, however, high iron and cadmium concentrations were observed in some species. Variations of the metal concentrations in the different species are apparently related to the specific accumulation capacity of each particular species, however, intraspecies variations may be appreciable. Iron was by far the dominant metal in all the species examined and it seems that it may influence the accumulation of the other metals. High concentration factors were observed by Zn, Cd, Cu and Hg emphasizing the role that macroalgae may play in the biogeochemical cycling of trace metals in the marine environment.

Introduction

In the aquatic environment, living organisms are constantly active in both sediments and water compartments. This biological activity results in the transformation of the chemical static equilibria of the abiotic constituents into a biologic steady state (Forstner and Wittmann 1981). In this context trace metals are of particular interest. Some of them are essential but can be toxic above a given concentration level, and others are highly toxic even at very low concentrations.

In the case of autotrophic organisms, trace metals are incorporated directly from the water into the organism, and the algal population may constitute a temporary sink for a large part of trace metals. In this way, marine macroalgae may play an important role in buffering trace metals concentration (Higgins & Mackey 1987a) and interfere in their speciation and cycling through detrital decomposition in coastal waters (Higgins & Mackey 1987b).

Marine macroalgae have been proposed as bioindicators (Phillips 1977). These organisms meet almost all the requirements for this purpose; sessile, have long life span and their metal content has been shown to be directly related to the metal concentration in the surrounding environment (Bryan 1971). Several authors have reported high trace metal concentrations in macroalgae from polluted coastal waters; concentration factors of several orders of magnitude have been frequently observed for several trace metals (Preston *et al.*, 1972; Bryan & Hummerstone 1973; Stenner & Nickless 1975; Foster 1976, Lande 1977; Foster *et al.*, 1978; Sivalingam 1980; Burdon-Jones *et al.*, 1982).

Generally, published data on the presence of trace metals in the aquatic environment of the Arabian Gulf are scarce (Anderlini *et al.*, 1982; Burns *et al.*, 1982; Fowler *et al.*, 1984). Trace metal levels in marine macroalgae from the area were first reported in 1990 but still are very limited (Heiba *et al.*, 1990; Kureishy 1991).

This work was envisaged to add new information on the presence of Fe, Mn, Zn, Cu, Ni, Cr, Cd and Hg in some of the most abundant macroalgae along the Qatari coastal area and to examine the possible interrelations that may exist between these metals.

Area of Study

The Qatari peninsula (Fig. 1) lies on the mid-western coast line of the Arabian Gulf. It extends in a north-east direction which gives different physicochemical characteristics to the eastern and western coastal areas (Emara *et al.*, 1989). Most of the population inhabits the eastern coast, consequently the urban and industrial (petrochemical, steel, fertilizers and desalination and thermal energy plants) impact may be more pronounced in this part of the peninsula.

Material and Methods

Healthy samples representing ten algal species were collected from four stations in the intertidal and subtidal area on the eastern and western coasts of the Qatari peninsula (Fig. 1 and Table 1). Samples were placed in acid washed plastic bags before transportation, in ice boxes, to the laboratory within 5-6 hr from collection. In the laboratory, samples were thoroughly washed with filtered seawater, collected from the site of sampling, to remove all adherent foreign particles including epifauna and epiphytes then rinsed in Milli-Q water to remove adhering salts. Washed samples were air dried under a laminar flow air stream (Class 100), then oven dried at 70°C for 24 hr. Samples were powdered in agate mortar after being cut into small pieces using plastic tweezers. Extreme care was taken during sample manipulation to avoid possible sources of contamination.

Accurately weighed subsamples were mineralized in 30 ml tightly capped PTFE cups using 5 ml of 3/1 (v/v) $HNO_3/HClO_4$ acid mixture (Merck Suprapur) in an oven at 100-110°C. Digestion was continued until complete dissolution of the organic material. Further 3 ml of the acid mixture were added when revealed necessary. Two

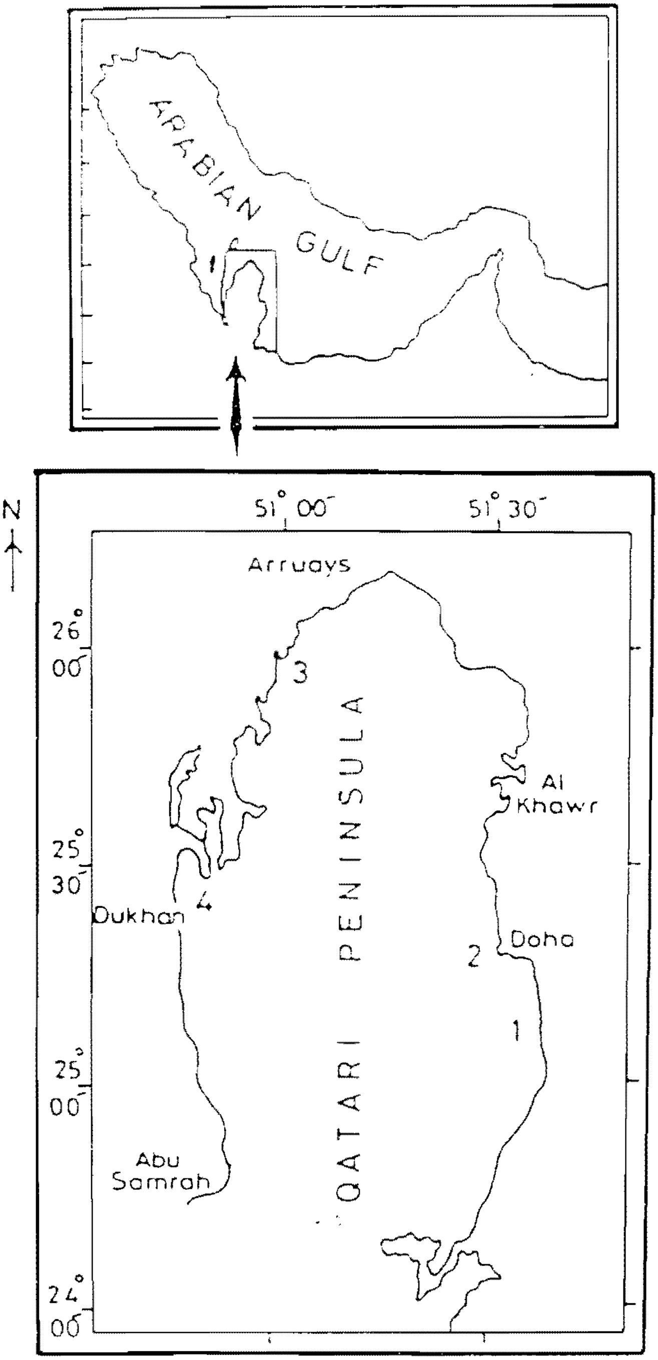


FIG. 1. Area of study and location of sampling sites.

TABLE 1. Locations and dates of sampling of the different algal species.

Species	Group	St. no.	Date
Sargassum binderi	brown	3	Mar. 88
S. boveanum	brown	2	Feb. 88
S. denticulatum	brown	2	Mar. 88
Hormophysa triquetra	brown	4	Apr. 88
Polysiphonia crassicollis	red	4	Mar. 88
P. kampsaxii	red	4	Mar. 88
Laurencia papillosa	red	1	Mar. 88
Amphiroa fragilissima	red	1	Mar. 88
Digenia simplex	red	3	Mar. 88
Cladophora sericoides	green	1	Mar. 88

procedural blanks were carried out in the same way. After complete digestion, sample solution was adjusted to a fixed volume and trace metals, excepting Hg, were analyzed using flame atomic absorption spectrophotometer (Berkin Elmer 2380 equipped with D_2 background correction). Standard addition technique was used for concentration evaluation and to test for any possible loss during mineralization. Hg was analyzed using the cold vapor technique. To test for the precision of our analysis, five replicates of one of the samples were processed as described above. The estimated precession was as follows (expressed as relative standard deviation): 5% for Cu, Mn and Hg; from 6 to 10% for Zn, Pb, Fe, Cr and Ni.

Results and Discussion

Trace metals concentrations in the different algal species are presented in Table 2. The results show a great interspecies variations. Degree of accumulation varies between the different metals with the essential metals like iron, manganese and zinc having the highest concentrations (Table 2). Metals can be ranked according to their average concentrations in the following decreasing order: Fe $>>$ Mn $>$ Zn $>$ Ni $>$ Cr $>$ Cu $>$ Cd $\gg$ Hg. This order probably reflects the concentration of these metals in the water. Bryan (1969) stated that trace metals concentrations in the macroalgae are directly related to their concentrations in the surrounding water. Available data on dissolved trace metal concentrations (Fowler *et al.*, 1984) show that Zn, Cu, Cd and Hg in the Gulf water could be arranged, according to their relative concentrations, in the same mentioned order (Table 3). Reported trace metal concentrations in some algal species from the area (Heiba *et al.*, 1990; Kureishy 1991) are comparable to our results but iron in some of our samples is relatively higher. The particularly high iron values in our results belong to species never examined before. Comparison with trace metals results for other species from relatively nonpolluted coastal areas (Manley 1981; Rosell & Srivastava 1984; Higgins & Mackey 1987a&b) indicates that Cu and Zn lie in the ranges reported for these metals; Fe, Mn and Cd show exceptionally high values but still lower than values reported from polluted areas (Bryan and Hummerstone 1973; Morris and Bale 1975; Burdon-Jones *et al.*, 1982).

TABLE 2. Trace metals concentrations in different algal species (μmol kg^{-1} except Hg nmol kg^{-1}, dry weight).

Species	Fe	Mn	Zn	Cu	Cr	Ni	Cd	Hg
S. binderi	1325	86	95	36	12	10	1.6	359
S. boveanum	3330	264	207	31	15	31	7.9	249
S. denticulatum	25444	785	338	83	138	152	1.6	120
H. triquetra	3223	107	106	20	15	75	4.8	179
P. crassicollis	33968	659	174	74	206	129	4.6	459
P. kampsaxii	35651	897	332	153	219	148	1.5	110
L. papillosa	14056	388	338	68	79	109	8.2	244
A. fragilissima	32231	708	280	172	185	133	3.0	110
D. simplex	5032	286	176	41	31	30	3.2	110
C. sericoides	14969	406	83	39	90	90	6.4	294

TABLE 3. Trace metal concentrations in the Arabian Gulf coastal waters (Cu, Zn and Cd in nmol l^{-1} and Hg in pmol l^{-1}).

	Cu	Zn	Cd	Hg
Average	5.50	6.02	0.18	78
S.D.	4.99	4.41	0.04	29

Calculated from Fowler *et al.* (1984), Cu and Zn at pH 4-4.5; Cd and Hg at pH 1.5.

The low trace metal concentrations in the various species examined might reflect an environment not significantly impacted by trace metal contamination as has been stated by Fowler *et al.* (1984), and our data may serve as reference for future monitoring programs.

The various human activities concentrated along the eastern coast may result in relatively higher trace metals level in organisms from this region. Our results do not allow any comparison since no identical species were examined from the two regions. However, comparison with previous work (Kureishy 1991) shows that most of the metals in *S. binderi* and *H. triquetra* are higher in samples from the eastern coast. This comparison should be taken with care because it showed also that identical species from the same region may show appreciable differences.

Interspecies concentration differences must be regarded as depending on the specific bioaccumulation capacity of the individual species (Preston *et al.*, 1972; Foster 1976; Lande 1977). The brown alga *S. denticulatum* and the red algae *P. crassicollis, P. kampsaxii, L. papillosa* and *A. fragilissima* showed the highest accumulation for most of the metals examined (Table 2 and Fig. 2). It appears that red algae have average concentration two to three times higher than the brown algae for all the metals except Cd and Hg (Table 4). On account of their distribution and their trace metals biomagnification ability, these species may be proposed as bioindicators.

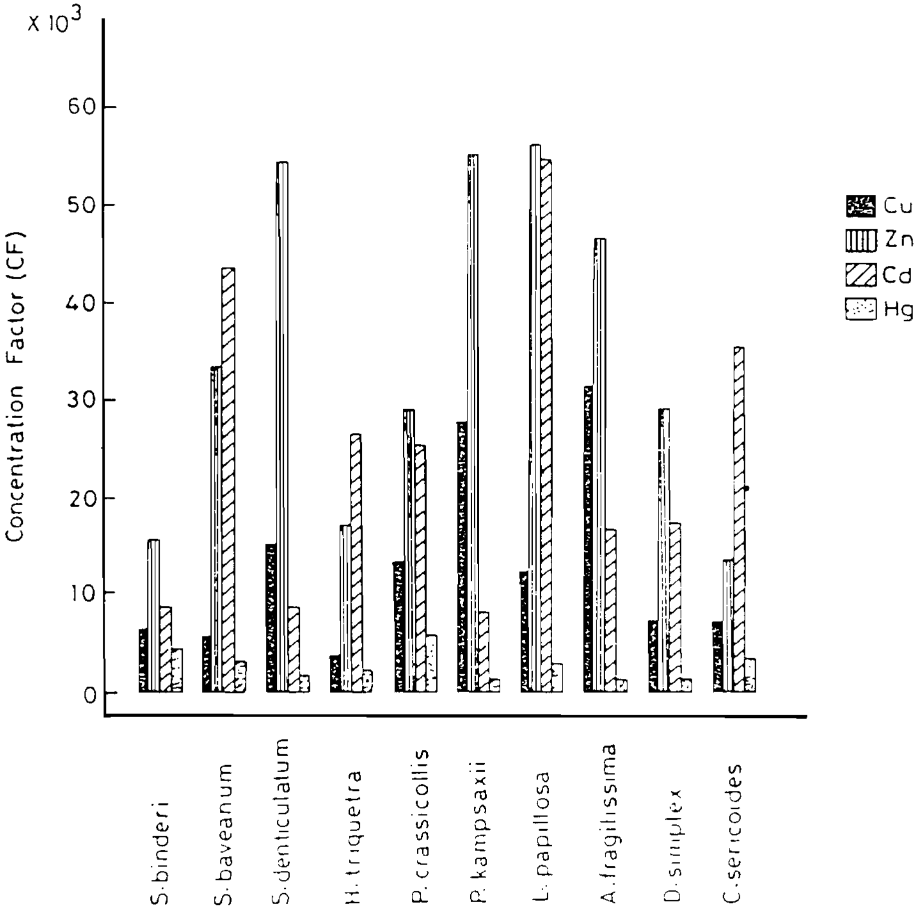


FIG. 2. Trace metal concentration factors (CF) in the different algal species.

TABLE 4. Average trace metals concentrations in different groups of algae, n number of samples, ( ) S.D. (all results in μmol kg⁻¹ except Hg in nmol kg⁻¹).

	Fe	Mn	Zn	Cu	Ni	Cr	Cd	Hg
Brown algae	8326	309	182	42	66	44	3.9	224
n = 4	(11442)	(326)	(109)	(28)	(63)	(57)	(3)	(100)
Red algae	24173	386	360	101	109	144	4.1	205
n = 5	(13788)	(248)	(81)	(57)	(48)	(85)	(2.6)	(150)
Green algae n = 1	14969	406	82	39	90	90	6.4	294

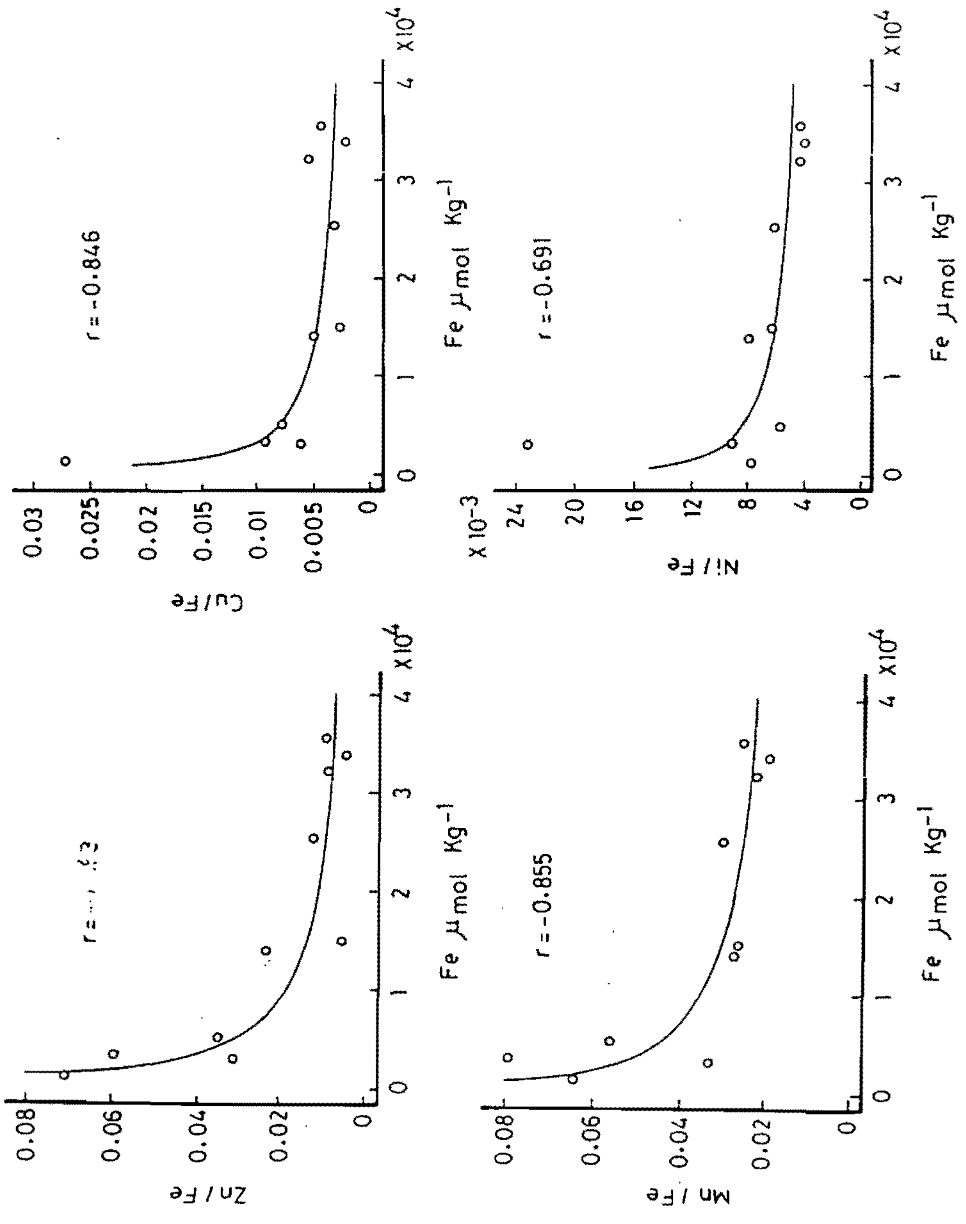
Using the data available on the concentration of trace metals in the water of the Gulf (Table 2), we calculated the concentration factors CF (CF equivalent to: concentration in algae/concentration in water) for Cu, Zn, Cd and Hg in the different species. It could be seen (Fig. 2), that Zn was the most bioaccumulated metal with CF ranging between 13 to 56 $\times 10^3$ and an average of 35 $\times 10^3$ while Hg showed the lowest CF with more uniform values (1.5 to 6 $\times 10^3$ averaging 2.9 $\times 10^3$. These extremely high concentration factors support the suggestion that marine macroalgae could be a principal partner in the recycling of trace metals in coastal waters beside their role as substantial metal buffers in the ecosystem (Higgins & Mackey 1987a). It should, however, be mentioned that these concentration factors may be overestimated and should be taken as order of magnitude permitting the comparison between the different species. Probably higher dissolved trace metals concentrations are expected in the intertidal zone than the values given for the open coastal waters and used for our calculations.

Correlation analysis reveals the presence of a good agreement between Fe, Cr, Cu, Ni and Mn; Zn is weakly correlated with these metals, while Cd and Hg do not show any particular relation with the other metals (Table 5). This pattern indicates that the first group of metals exists at almost regular proportions in the plant tissue, probably as a result of a controlled accumulation processes.

TABLE 5. Correlation matrix (significant level = 0.6319).

	Fe	Mn	Zn	Cu	Cr	Ni	Cd	Hg
Hg	- 0.102	- 0.297	- 0.511	- 0.426	- 0.071	- 0.228	- 0.318	1.000
Cd	- 0.332	- 0.369	- 0.110	- 0.427	- 0.341	- 0.194	1.000	
Ni	0.900	0.887	0.660	0.718	0.878	1.000		
Cr	0.997	0.939	0.556	0.835	1.000			
Cu	0.842	0.831	0.689	1.000				
Zn	0.587	0.716	1.000					
Mn	0.950	1.000						
Fe	1.000							

Metal uptake of macroalgae depends on physiological and/or physicochemical factors. This process has been studied by several authors (Gutknecht 1963 & 1965; Skipness *et al.*, 1975; Eide *et al.*, 1980; Manley 1981) who showed that it can be considered as a two stage process. The first stage represents the transfer of metals from seawater to the apparent free space (AFS); this physicochemical process is rapid and reversible. During the second stage trace metals are transferred across the cell membrane by regulated and energy consuming process, the rate of which depends on the metal concentration in the AFS and time of exposure (Rice 1984; Higgins & Mackey 1987a). It has been shown by several authors (Manley 1981; Rosell & Srivastava 1984; Higgins & Mackey 1987a) that between 60 and 90% of Zn was associated with the free space in different algal species while more Cu and Fe was found as intracellular. The same result was also obtained with Cd in *Ecklonia radiata* (Higgins & Mackey 1987a) where about 90% of the metal was found associated with the free space.


Cu / Fe
0.03
0.025
0.02
0.015
0.01
0.005
0
r = -0.846
0
1
2
3
4
X10^4
Fe μmol Kg^-1
Ni / Fe
X 10^-3
24
20
16
12
8
4
0
r = -0.691
Zn / Fe
0.08
0.06
0.04
0.02
0
Mn / Fe
r = -0.855

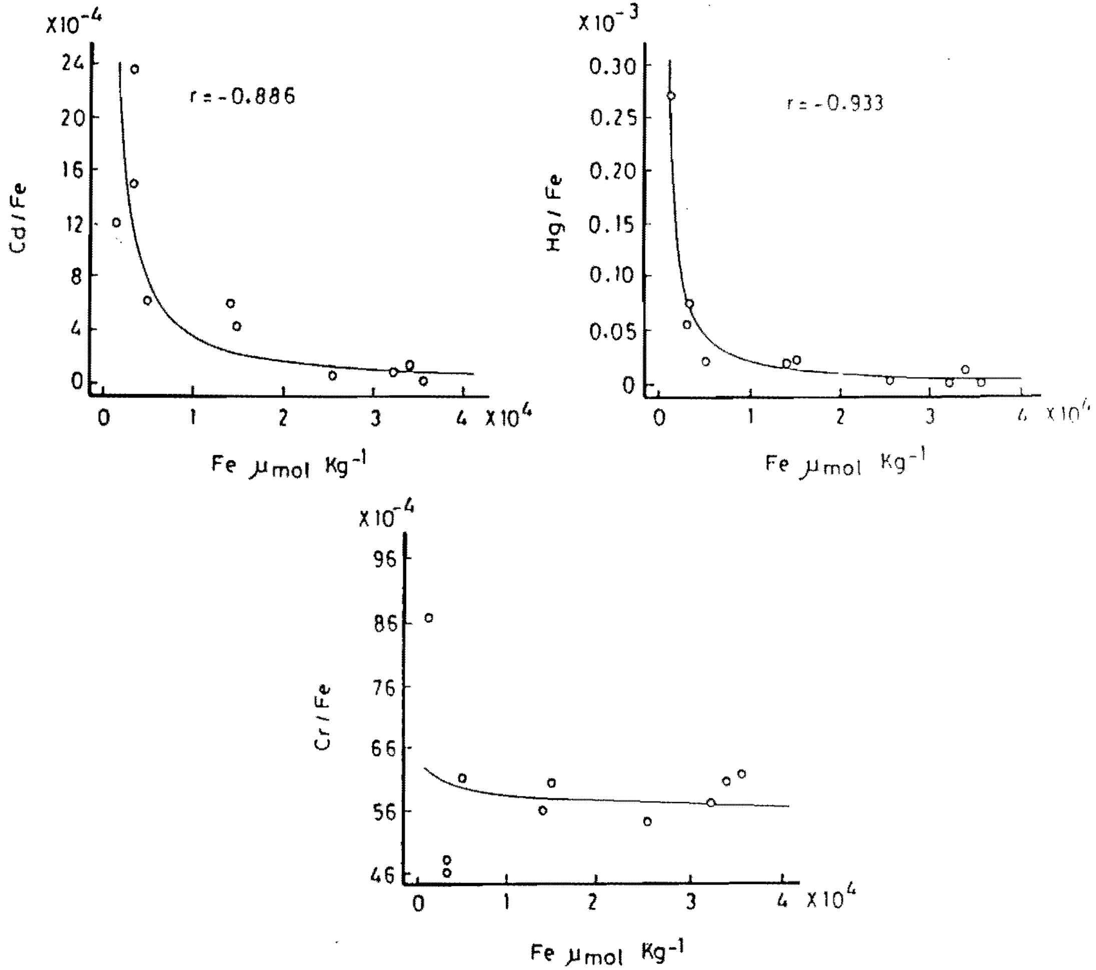


FIG. 3. Relationship between the metal/iron ratio and iron concentration in the different algal species.

The reversibility of the first stage in the metal transfer process do mean that metal concentration in the free space might vary with the variation of the physicochemical characteristics of the environment; these variations are expected to be appreciable in the intertidal zone where conditions are repeatedly changing. Therefore, metals in the AFS are more dynamic. On the contrary, intracellular composition is probably more stable since the transfer during the second stage is a relatively slow regulated process. It is expected that, in the species examined, perhaps, Fe, Mn, Cu, Ni and Cr are associated, mainly, as intracellular and Cd, Hg and Zn are dominantly present in the free space. Further work is needed to evaluate the contribution of the AFS to the total tissue associated metals particularly to determine the ability of the species studied to assess long-term integrated changes of trace metals in the water.

Iron is by far the dominant metal in all the species tested, it has an elevated tendency to form surface complexes (adsorption) and organic complexes, therefore it may conflict with the other metals for the complexing sites either on the external surface or in the free space. To test for this possibility we plotted the metal/iron ratio against iron concentration (Fig. 3). Below an iron concentration of about 7000 μmol kg^{-1}, the metal/iron ratio increases very rapidly; in almost all the cases the relation is best fitted by a multiplicative model. Chromium was the unique exception, its iron ratio was almost stable. This result shows that iron may influence the presence of the other metals, except chromium. This statement does not contradict with the assumption that iron is mainly present in the intracellular. According to Rice (1984) and Higgins and Mackey (1987a) concentration in the intracellular depends on the concentration in the AFS, therefore, iron in the AFS should exist at high levels relative to the other metals and may also control occupation of the free surface sites.

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العناصر الشحيحة في الطحالب البحرية العملاقة من المياه الساحلية القطرية

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المستخلص . تم قياس تركيزات ثمانية عناصر وهي (الحديد ، المنجنيز ، الزنك ، النحاس ، النيكل ، الكروم ، الكاديوم والزئبق) في عشرة أصناف من الطحالب العملاقة التي تنمو في المياه الساحلية القطرية . تدل التركيزات في الأصناف المختلفة على أن الوسط غير ملوث ، غير أن بعض الأنواع احتوت على تركيزات مرتفعة من الحديد والكاديوم . ويبدو أن الاختلافات في التركيزات بين الأنواع المختلفة إنما يرجع إلى قدرة كل نوع على تركيز العناصر الشحيحة ، غير أن الاختلافات داخل النوع الواحد قد تكون ملموسة وقد وجد أن الحديد هو أكثر العناصر تركيزًا في جميع الأنواع على الاطلاق ، ومن الممكن أن يؤثر على تركيز العناصر الأخرى .

وقد وجد أن معاملات تركيزات عناصر الزنك والكاديوم مرتفعة جدًّا حيث بلغت في بعض الأنواع أكثر من ٥×١٠^{٤} يليها النحاس وبلغت أقصى قيم معامل تركيزاته حوالي ٣×١٠^{٤} بينما كان أقلها الزئبق ولم يتعدى معامل تركيزه ١×١٠^{٣} وهذا يوضح الدور الذي يمكن أن تلعبه الطحالب العملاقة في الدورة البيوجيوكيميائية لبعض العناصر الشحيحة في الوسط البحري .