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Levels of Some Trace Metals in Macroalgae from the Red Sea in Egypt.

مستوى بعض العناصر الشحيحة في طحالب من البحر الأحمر في مصر

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Abstract: The concentrations of iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), chromium (Cr), nickel (Ni) and cobalt (Co) in ten macroalgae species from the Red Sea coastal water varied widely and also the trend of abundance of each metal also differed from one group to another. Concentration factors varied among species for iron (Fe) copper (Cu) manganese (Mn), but with iron (Fe) showing generally high concentration factors. Highly significant ($P<0.05$) relationships were found between manganese (Mn) and nickel (Ni), and, zinc (Zn) & copper (Cu). Moreover, moderate correlations were observed between manganese (Mn) and iron (Fe) and chromium (Cr), indicating that manganese (Mn) is the most accumulated metal in the macro algae of the Red Sea. In spite of the level of trace metals in the macro algae, dominance is moderate relative to other sea areas subjected to intensive pollution. That is, the results indicated a non-polluted environment.

Key Words: trace metals, macroalgae, seaweeds, Red Sea.

المستخلص: أظهرت نتائج قياس تركيز كل من عناصر الحديد (Fe)، الزنك (Zn)، المنجنيز (Mn)، النحاس (Cu)، الكروم(Cr)، النيكل (Ni)، والكوبلت (Co)، في عشرة عينات منتشرة ومتواجدة فى طحالب قد تم جمعها من المياه الضحلة في البحر الأحمر، تبايناً كبيراً في جميع العناصر، وعلى اختلاف تواجدها في مجاميع الطحالب. كما كانت معدلات، التركيز مختلفة ومتباينة أيضاً، خاصة بالنسبة لعناصر الحديد (Fe)، والنحاس (Cu)، والمنجنيز (Mn) إلا أن عنصر الحديد (Fe) كان هو الأعلى تركيزا في جميع الطحالب. وكانت علاقات الترابط بين هذه العناصر مختلفة أيضا، إذ كانت ذات قيم عالية الترابط بين عنصر المنجنيز (Mn)، مع عناصر الحديد (Fe)، والزنك (Zn)، والنحاس(Cu)، وذات قيم متوسطة الترابط، بين عنصر المنجنيز(Mn) ،مع عنصري الحديد (Fe) ، والكروم(Cr) ، مما يؤكد أن عنصر المنجنيز (Mn)، هو أكثر العناصر تراكماً في طحالب البحر الأحمر. وعلي الرغم من تواجد العناصر الشحيحة ذات القيم المتوسطة في طحالب البحر الأحمر المتواجدة في مناطق أخرى، واقعة تحت تأثير التلوث المائي، إلا أن نتائج هذه الدراسة توضح أن بيئة البحر الأحمر مازالت صالحة ولا تعاني من تأثير التلوث البحري.

كلمات مدخلية: البحر الأحمر، طحالب، عناصر معدنية، تركيز، ترابط، تلوث بحري.

Introduction

In the marine environment, levels of trace metals among seaweeds are usually low with the exception of some coastal areas exposed to high local pollution. Therefore, macroalgae as well as seaweeds were used as bioindicators of trace metals (Phillips, 1977; Sivalingam, 1980; El-Sayed and Dorgham, 1994). Seaweeds may be the principal primary producers of the littoral zone (Blinks, 1955), more so than phytoplankton with regard to environmental contamination. However, seaweeds are often involved in food chains leading to man, since they are harvested commercially for food, feed and fertilizer (Davy de Virville and Feldmann, 1964).

Iron (Fe), copper (Cu), manganese (Mn), cobalt (Co) and zinc (Zn) are necessary for marine life, but mercury, lead and nickel are dangerous. Some trace metals are essential for cell metabolism, whereas others are more or less toxic. In some marine coastal areas, enrichment by zinc, lead and cadmium was higher when closer to industrial regions. Anthropogenic inputs showed also that high levels of (Zn), (Cd) and (Pb) in water bodies (Johnson, 1987) threaten the health of aquatic and terrestrial organisms, man included (Nriagu, 1980). In addition, nutrients from industrial discharges (Kautsky, 1982) have also been associ-ated with excessive growth of Enteromorpha.

The Egyptian Red Sea coastal water has been exposed to urbanization, recreational development and industrial installations during the last two decades. Available samples of macroalgae were found specifically at six sites in the Gulf of Aqaba and north Red Sea (Fig. 1). The Egyptian Red Sea coastal waters, especially Hurghada, have been subjected to extensive studies (Beltagy, 1975 & 1982). Recently, Abdel-Moati (1994) found that Hurghada suffered from oil and domestic sewage pollution. According to Mahmoud (1998), the presence of anionic detergents in Hurghada indicates that the area began to suffer from the effects of sewage discharged from the hotels and other buildings located along the coastal areas of the Red Sea.

The aim of this work was to determine the trace metal contents (Fe, Zn, Mn, Cu, Ni, Cr and Co) in the dominating algal species in comparison with other studies. It may also help for the assessment of the predicted possible increase of trace metals in the marine algae as a tracer for pollution in the coastal waters of the Red Sea.

Materials and Methods

Macroalgal species, according to their availability, were collected from 6 sites selected in the Gulf of Aqaba and Northern Red Sea during April 2000 (Fig. 1).

Samples were placed in acid-washed plastic bags before being transported in ice boxes to the laboratory. Samples were identified according to the literature, washed initially with tap water to remove adherent foreign particles and then repeatedly in double distilled water to remove salt. Sub-samples taken from each of the samples were air-dried, and 5g of each subsample (wet weight) placed in 30ml tightly-capped PTFE cups with an $HClO_4$: NHO_3 acid mixture (1:5; v/v Merck Suprapur). These sub-samples were then put in an oven at 100-110°C until a completely colourless solution was obtained. Two reagent blanks were carried out in the same way. The filtered extracts were adjusted to 25 ml with diluted HNO_3 (Bernhard, 1976). Trace metals Fe, Zn, Cu, Mn, Cr, Ni and Co were analyzed using a flame Atomic Absorption Spectrophotometer (Berkin Elmer 2380) equipped with D_2 background correction.

Discussion and Results

The concentrations of Fe, Zn, Mn, Cu, Cr, Ni and Co, were expressed in mg g^{-1} wet weight in the macroalgae species of the green, brown and red groups collected from the six sites along the Red Sea coast appeared varying widely as shown in Table (1).

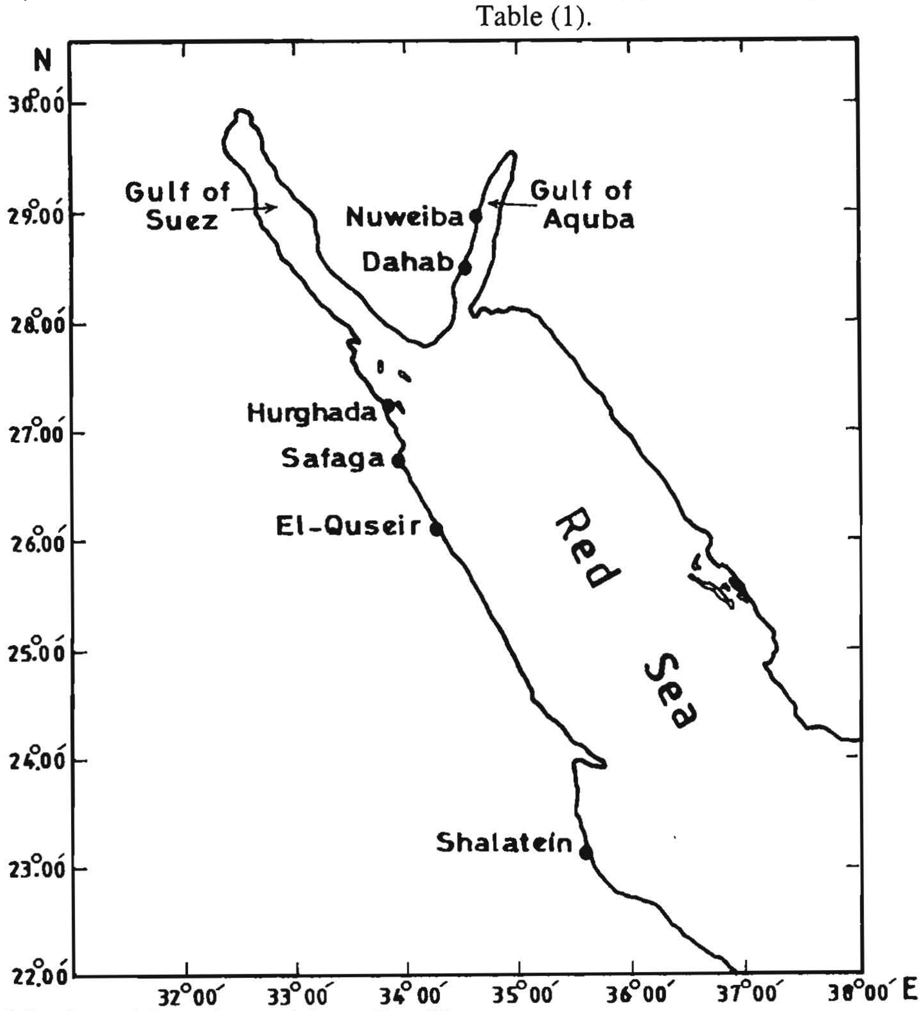

Fig. (1): Area of Study and Locations of Sampling Sites.

Table 1: Trace Metal Concentrations in the Different Species of Macroalgae,

($\mu g\ g^{-1}$ wet weight) Collected from the Coasts of Red Sea.

Sample type	Species	Collection Site	Co	Cr	Cu	Fe	Mn	Ni	Zn
(1)	**Green algae**	Safaga	0.28	1.5	4.6	97	6.2	4.5	26
1.1	Enteromorpha compressa	El-Quseir	0.12	0.5	5.6	30	1.6	2.1	13
1.2	Gayralia oxypresa	Shalatein	0.22	2.5	3.0	46	2.1	2.7	15
1.3	Codium borsa								
	Mean + S.D		0.21+ 0.07	1.5+ 0.82	4.4+ 1.07	57.7+ 28.57	3.3+ 2.06	3.1+ 1.02	18.0+ 5.72
(2)	**Red algae**		0.15	9.6	17.4	65	10.9	22.4	32
2.1	Ceramium ciliatum	Dahab	0.70	8.3	6.2	22	3.1	5.2	13
2.2	Laurencia obtusa	Dahab	0.30	4.0	1.3	77	-	3.9	6
2.3	Laurencia papillosa	Hurghada	0.10	0.3	1.3	3	0.6	1.0	13
2.4	Alsidium corallium	Dahab							
	Mean + S.D		0.31+ 0.24	5.55+ 3.67	6.55+ 6.58	41.75+ 30.31	4.8+ 4.39	8.13+ 8.38	16.0+ 9.67
(3)	**Brown algae**		0.24	0.5	2.0	26	1.5	2.6	13
3.1	Sargassum vulgare	Nuweiba	0.35	1.4	5.4	153	-	5.0	9
3.2	Sargassum acinarium	Hurghada	0.62	1.8	7.1	30	7.5	15.5	20
3.3	Padina pavonica	Dahab							
	Mean + S.D		0.40+ 0.16	1.2+ 1.23	4.8+ 2.12	69.67+ 58.95	4.5+ 3.0	7.7+ 5.60	14.0+ 4.55

The results of iron revealed higher values and more pronounced variation from 3 to 153 $\mu g\ g^{-1}$ wet weight in Alsidium corallium and Sargassum vulgaris, respectively. Iron is an essential element, necessary in the biosynthesis of chlorophyll. The order of abundance of trace metals in green alga studied was

Fe > Zn > Cu > Mn > Ni > Cr > Co,

while among brown algae studied it was

Fe > Zn > Ni > Cu > Mn > Cr > Co.

In red algae studied it was

Fe > Zn > Ni > Cu > Cr > Mn > Co.

Although the metal contents of macroalgae species are subjected to a wide range of variation, the trend of abundance of each metal also differed from one group to another. According to (Gutnecht 1965), the concentration of zinc in brown seaweed (Fucus vesiculosus) changed with that in the sea water. This was confirmed experimentally for zinc, copper and lead in another species of brown algae (Laminaria digitata) by (Bryan 1969 & 1971).

In the ten species of macroalgae studied, higher means of

Ni ($8.13\pm8.38\ \mu g\ g^{-1}$), Mn ($4.87\pm4.39\ \mu g\ g^{-1}$), Cu ($6.55\pm6.58\ \mu g\ g^{-1}$) and Cr ($5.55\pm3.67\ \mu g\ g^{-1}$)

were found in the red algae than in the green and brown group, and the highest values were recorded in red algae (Ceramium ciliatum) from Dahab. This species has cilia and nodules which may collect suspended sediment particles continuously and thus it is provided with an opportunity for scavenging metals from sediment as reported by (Luoma *et al.* 1982) in Fucus vesiculosus and by (Rajendran *et al.* 1993) in Centroceras clavulatum. On the other hand, (Munda 1982) studied the effect of different pollutants on benthic marine algae in the populations of red algae which has disappeared from polluted sites and replaced by patches of green algae (genera Cladophora), (Enteromorpha, Blidingia) and (Ulva rigida). In addition, in some polluted sites, distant from the outfalls, Mytilus shells have replaced algal settlements.

Unfortunately, comparative data pertaining to the trace metals content of seaweeds from the Red Sea were not available. However, a comparison of the present data was made with that reported by (El-Sayed and Dorgham 1994) of different groups of red, green and brown algae from the Qatar coastal water in the Arabian Gulf, expressed in mmol kg^{-1} dry weight. The ranges were from:

3223-35651 Fe, 86-897 Mn, 83-338 Zn,
20-172 Cu, 12-219 Cr, 10-152 Ni,
1.5-8.2 Cd and 11.0-45.9 Hg.

Our results for all metals were higher except for Fe which was in agreement. Another comparison was made with algae collected from the Covelong and Mahabalipuram areas in the Indian Sea the ranges are expressed in

mg g-1 dry weight and range from 32-43 (Cu), 213-754 (Fe), 38-84 (Zn) and 42-176 (Mn),

suggesting that the bio-concentration of metals is prone to temporal changes due to the discharge of considerable quantities of domestic and industrial wastes. These levels of trace metals showed higher values than those of our results.

Finally, seaweeds Padina species in $\mu g\ g^{-1}$ wet weight by (Tariq *et al.* 1993), from the Arabian Sea facing pollution concentrations of some metals were

0.76 (Cd), 9.12 (Cr), 1.7 (Cu), 373 (Fe), 10 (Mn), 19 (Ni), 4.1 (Zn).

However, our results for Cr, Fe, Mn and Ni were lower, while Cu and Zn showed higher levels in the Padina in the present work.

(1) Concentration factors (CF):

The trace metal concentrations available in the water of Hurghada were 79.0, 27.0 and 2.9 $\mu g\ l^{-1}$ for Fe, Cu and Mn, respectively

(Beltagy, 1982). We calculated the concentration factors CF (CF equivalent to: concentration in algae/ concentration in water) for Fe, Cu and Mn in different algae species (Table 2).

The concentration factor showed a wide range of variations with a decreasing trend in concentration Mn > Fe > Cu. Manganese was the most bio-accumulated metal ranging between

1.138×10^3 and 1.678×10^3

in green algae and red algae respectively. Thus red algae were found to accumulate more Mn and Cu metals than green and brown algae (see, table 2).

Our results were in good agreement with those reported by (Rajindran *et al.* 1993) and (Aulio 1983) for the metals content in seaweeds from the Indian and Archipelago Sea respectively. Higher metal levels in ambient seawater lead to a greater bio-accumulation of these metals in algae (Patel *et al.*, 1980). The extent to which an organism regulates these metals is extremely important when the possibilities of pollution by these metals or their radio-nuclides are considered (Bryan, 1969).

From our findings, it seems that concentration factors, which might give an index or a guide for contamination of sea areas with trace metals, did not reveal an indication for contamination. The concentration factor levels mostly lies below 103 with few exceptions. According to (Bryan 1969), trace metal concentrations in the macro-algae are directly related to their concentration in the surrounding water. (Bryan and Hummerstone 1973), found, generally, concentration factors greater than 1000.

Table (2): Concentration Factor (CF) in Different Algal Species ($x10^3$), For (Fe, Cu, & Mn)

Sample No.	Algae species	Fe	Cu	Mn
(1)	Green algae			
1.1	Enteromorpha compressa	1.228	0.170	2.138
1.2	Gayralia oxypresa	0.380	0.207	0.552
1.3	Codium borsa	0.582	0.111	0.724
	Mean	0.730	0.163	1.138
(2)	**Red algae**			
2.1	Ceramium ciliatum	0.823	0.644	3.759
2.2	Laurencia obtusa	0.279	0.230	1.069
2.3	Laurencia papillosa	0.975	0.048	-
2.4	Alsidium corallium	0.038	0.048	0.207
	Mean	0.529	0.243	1.678
(3)	**Brown algae**			
3.1	Sargassum vulgare	0.329	0.074	0.517
3.2	Sargassum acinarium	1.937	0.200	-
3.3	Padina pavonica	0.380	0.263	2.586
	Mean	0.882	0.179	1.552

*Reference, Beltagy (1982)

(2) Correlation matrices (CM):

When correlation analysis was carried out between trace metal concentrations in the different sea-weeds, it revealed high signific-ance ($P<0.05$) between manganese and nickel, and, zinc & copper (0.9349, 0.9304 and 0.8698 respectively). Furthermore, there is moderate correlation between manganese and Fe and Cr (0.6080, 0.5912 respect-ively).

This result indicates that manga-nese is the most accumulated metal in the macroalgae of the Red Sea.

Table (3): Correlation Matrix (CM), (significant level = 0.5760).

Metals	Fe	Zn	Ni	Mn	Cu	Cr	Co
Fe	1						
Zn	0.0009	1					
Ni	0.0839	0.7287	1				
Mn	0.6080	0.9304	0.9349	1			
Cu	0.1354	0.7611	0.8955	0.8679	1		
Cr	0.0024	0.4031	0.6201	0.5912	0.7037	1	
Co	-0.0156	-0.1024	0.1886	0.1869	0.0304	0.3097	1

Conclusion

In conclusion, interspecific differ-ences found in the levels of Fe, Cu, Zn, Mn, Ni, Cr and Co studied in the ten species of seaweeds collected from different sites along the Egyptian Red Sea, are due to different discharges of domestic and industrial wastes, and local harbour activities. In spite of the level of trace metals in the macroalgae dominating in the different sites of the coastal waters of the Red Sea, they are moderate relative to other sea areas subjected to intensive pollution. It is important to follow the concentration of the different metals in the algae as an indicator of pollution.

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