

Heavy Metal Levels in Several Species of Marine Algae from the Red Sea of Saudi Arabia

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ABSTRACT. Thirteen species of marine algae of Chlorophycophyta, Phaeophycophyta and Rhodophycophyta of the Red Sea coast of Saudi Arabia have been analysed for the heavy metals: Ag, Al, As, Cd, Co, Hg, Mo, Ni, Pb, Ti, and V.

The heavy metal content of the thirteen species studied exhibited remarkable differences according to the species, but a certain range of concentration appeared likely to be restricted to each division.

The green species were characterized in having the highest proportions of Hg, Ni and Pb. In the brown species, largest amounts of Al, As, Ti and V were recorded. Most of metals in the red species were of moderate levels.

Halimeda opuntia was found to have considerably higher levels of six of eleven metals investigated indicating that this species, rather than other species, is potentially a better source of these metals. This plant could, therefore, be used to monitor metal levels in water.

The levels of Ag and Cd in all species were lower than those of other metals investigated. High levels of Al and Hg were notable in the thirteen species.

Introduction

Over the years, the algae, have been used by man in the preparation of certain foods and beverages. The seaweeds provide a very good supplement for well balanced diets, because of their high mineral contents. Also, seaweeds can provide excellent sources for the manufacture of agar, algin, laminarin, mannitol and protein^[1-5].

Although many investigations have been carried out on the occurrence and dis-

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tribution of the algal species of the Red Sea coast of Saudi Arabia^[6-11], very little is known about their chemical composition^[12]. In order to fill this gap in knowledge, the attention was focused on the study of the chemical composition of several species of these marine algae.

Inorganic constituents of marine algae, including heavy metals, have received attention of many authors^[13-18]. In recent years, there have been many reports of the use of organisms to assess the impact of environmental contamination of heavy metals^[19]. The most successful have been those which involve the analysis of terrestrial plant to monitor airborne pollution^[20-22]. The ability of aquatic plants to take up heavy metals from water, producing an internal concentration greater than in their surroundings has been shown for many species^[19]. It is clear from the literature that, in general, the higher the level of metal in water, the higher the level in the algae or bryophyta^[23]. Thus, analysis of heavy metal composition of aquatic plants gives a better indication of the fraction of the metals in the environment which is likely to affect the aquatic ecosystem than most types of direct chemical analysis^[24].

In the present work, the authors have looked the quantity and the variability of eleven heavy metals in the thirteen species of marine algae collected from the Red Sea coast of Saudi Arabia. This study may throw some light on the chemical nature of local marine algae and introduce some information for further taxonomic studies and environmental contamination of heavy metals.

Material and Methods

Samples of marine algae were collected from the Red Sea coast of Saudi Arabia at Shuaba, about 25 km south of Jeddah, during the period of August to December 1985. These specimens represent the most common species in the three major divisions (Chlorophycophyta, Phaeophycophyta and Rhodophycophyta) which occur in this area. Algal taxa were identified according to Nasr^[25], Zinova^[26] and Aleem^[9].

The samples were thoroughly washed with running water and rinsed three times in distilled water. The samples of each species were spread on string nets and allowed to dry in air. Air-dried samples were ground and stored in stoppered bottles at room temperature.

The algal samples were analysed for their Ag, Al, As, Cd, Co, Hg, Mo, Ni, Pb, Ti and V contents. Air-dried ground algal material was then treated with 20 ml A.R. HNO₃ and digested with the aid of heat until a clear digest resulted. After digestion, the flasks were treated with 0.01 M HCl. At the same time, a control and standard flasks were similarly treated^[27]. The metal concentration was then determined using Varian A.A.-1475 series atomic absorption spectrophotometer. The mean values of replicate determinations are presented in Table 1.

Heavy Metal Levels in Several Species

TABLE 1. Concentration of heavy metals (ppm) in several marine algae.

Element Algal species	Ag	Al	As	Cd	Co	Hg	Mo	Ni	Pb	Ti	V
Chlorophycophyta											
<i>Enteromorpha clathrata</i> (Roth) J. Ag.	0.044	55.9	6.48	0.11	0.437	11.62	0.150	1.04	2.44	4.73	0.90
<i>Halimeda opuntia</i> (L.) Lamour	0.119	67.3	5.87	0.14	0.490	14.34	0.900	0.64	2.52	6.34	0.54
<i>Caulerpa racemosa</i> (Forsk.) J. Ag.	0.025	25.3	5.42	0.10	0.344	10.62	0.270	0.87	1.83	0.81	0.65
<i>Chaetomorpha linum</i> (Muller) Kutzing	0.011	12.7	4.84	0.06	0.141	2.74	0.150	3.86	0.58	0.30	00.00
<i>Cladophora heteronema</i> (C. Ag.) Kutzing	0.025	79.9	5.33	0.10	0.311	7.84	0.120	0.53	1.77	3.01	0.43
Phaeophycophyta											
<i>Padina boryana</i> Thivy	0.040	152.6	4.96	0.11	0.274	7.61	0.270	1.10	1.65	6.67	2.96
<i>Turbinaria triquetra</i> (J. Ag.) Ag.	0.016	36.9	7.79	0.06	0.210	4.65	0.380	0.55	0.89	2.15	0.16
<i>Sargassum subrepandum</i> (Forsk.) C. Ag.	0.017	10.8	6.19	0.07	0.259	5.92	0.000	0.52	0.45	1.06	0.11
<i>Cystoseira myrica</i> (S.G. Gmelin) C. Ag.	0.025	60.7	6.67	0.07	0.291	7.33	0.320	0.49	1.66	6.51	0.99
Rhodophycophyta											
<i>Acanthophora najadiformis</i> (Delile) Papenfuss.	0.025	58.7	4.88	0.07	0.197	5.35	0.156	1.70	1.19	1.52	1.06
<i>Digenea simplex</i> (Wulfen) C. Ag.	0.025	24.7	5.94	0.07	0.361	8.68	0.540	0.65	1.65	2.27	1.37
<i>Laurencia obtusa</i> (Hudson) Lamour.	0.016	11.2	4.80	0.08	0.247	5.43	0.000	0.47	1.19	0.22	0.32
<i>Hypnea musciformis</i> (Wulfen) Lamour.	0.025	77.9	5.30	0.09	0.247	7.52	0.040	1.04	0.55	10.23	0.32

Results

Silver

It can be seen from Table 1, that the values of silver content of the thirteen algal species were found between 0.011 and 0.119 ppm. The majority of these values fall between 0.016 and 0.025 ppm. The results further show that the value of silver reached its maximum in *Halimeda opuntia* and its minimum in *Chaetomorpha linum*.

In general, the relatively narrow range of variation of silver content, in the present work, differs from that of Estabrook *et al.*^[28] where values ranging between 0 and 25.7 ppm have been recorded in *Cladophora* spp.

Aluminium

Concentrations of this metal in the thirteen algae (Table 1) were higher than any of the other elements investigated and showed considerable variation from one species to another. In general, the highest concentration of this element was found in *Padina boryana* followed by *Cladophora heteronema* and *Hypnea musciformis*. *Chaetomorpha linum*, *Laurencia obtusa* and *Sargassum subrepandum* were characterized in having very low amounts of aluminium. Considering the values of this element found in the three algal divisions, it seems that the brown algae had the highest concentration of aluminium (Table 2).

TABLE 2. The mean levels of heavy metals (ppm) in the algal divisions.

Element \ Algal division	Ag	Al	As	Cd	Co	Hg	Mo	Ni	Pb	Ti	V
Chlorophycophyta	0.045	48.220	5.588	0.102	0.345	9.432	0.318	1.388	1.828	3.038	0.504
Phaeophycophyta	0.025	65.240	6.403	0.078	0.259	6.378	0.243	0.665	1.163	4.098	1.080
Rhodophycophyta	0.023	43.125	5.230	0.088	0.263	6.745	0.184	0.965	1.145	3.560	0.768

Arsenic

Concentrations of this metal were found to vary with species (Table 1). However, in general, the brown species showed relatively large amounts of arsenic. Similar results were found by Young and Langille^[13] for several Canadian marine species. But, on the other hand, our data for the brown algae were considerably lower than those observed in brown algae by Young and Langille^[13] who found that the level of arsenic in brown algae ranges between 38 and 50 ppm.

Several analyses of arsenic in algae have been previously made. Thus, Jones^[29], analysed 11 species and observed a range from 5 ppm in *Chondrus* to 94 in *Laminaria*. William and Whetstone^[30] found a variation from 1-12 ppm. Adachi *et al.*^[31] observed that the arsenic content was 12.8 ppm in *Digenea simplex* but 182.6 ppm in *Hijikia fusiforme*.

Cadmium

Difference in cadmium concentration of all species examined, specially the brown and red, were not quite remarkable. The cadmium content of the green species was relatively high as compared with that of the other species. In the brown species, cadmium was consistently low (0.06-0.07 ppm) except for *Padina boryana*. The highest concentration of cadmium was found in *Halimeda opuntia* (Table 1).

Cobalt

The concentration of cobalt in all species was quite variable particularly in the green species (Table 1). *Halimeda opuntia* and *Enteromorpha clathrata* were charac-

terized by high amounts (0.490 and 0.437 ppm, respectively), while *Chaetomorpha linum* had smaller levels (0.141 ppm).

In general, the order of magnitude of cobalt in the 13 species examined corresponds with that of atlantic coast of Canada^[13]. But, the values obtained by Estabrook *et al.*^[28] in *Cladophora* spp. (1.1-2.6 ppm) are above the range of values reported here in *Cladophora heteronema* (0.311 ppm).

Mercury

The thirteen species studied exhibited high proportions of mercury. Its level in the green species was consistently higher than that of the others (Tables 1 & 2). The highest concentrations of mercury were found in *Halimeda opuntia*, while the lowest were in *Chaetomorpha linum*.

In this connection, it may be mentioned that the mercury content of the thirteen species examined was higher than that reported by Porzi and Bertazzoni^[32] for twelve species of algae taken from Mediterranean sites in Italy including *Enteromorpha linza*, *Cystoseira crinita* and *Sargassum* sp. in which mercury ranged between 1.25 and 3.30 ppm.

Molybdenum

Molybdenum content was generally low in all species as compared with other metals investigated (Tables 1 & 2). The highest levels of molybdenum were found in *Halimeda opuntia* (0.900 ppm). *Enteromorpha clathrata*, *Chaetomorpha linum* and *Acanthophora najadiformis* showed more or less comparable values (0.150-0.156 ppm). A similar result had been obtained with *Caulerpa racemosa* and *Padina boryana* (0.270 ppm). On the other hand, molybdenum was not detected in either *Sargassum subrepandum* or *Laurencia obtusa* (Table 1). Generally, the concentrations of molybdenum were more or less comparable in all algal divisions (Table 2). This conclusion is similar to that of Young and Langille^[13] who reported that molybdenum was approximately in equal amounts in all divisions (classes).

Nickel

Marked differences were observed between the amounts of nickel in the thirteen species studied. *Chaetomorpha linum* contained the maximum value of nickel (3.86 ppm), while *Laurencia obtusa* yielded the minimum one (0.47 ppm).

Again, the green species showed the highest nickel levels while the brown species had the lowest ones (Table 2).

Lead

Results showed that the green species were also rich in lead. Among the green studied, *Halimeda opuntia* and *Enteromorpha clathrata* were found to have the high-

est levels of lead (2.52 and 2.44 ppm, respectively). However, *Sargassum subrepandum*, *Hypnea musciformis* and *Chaetomorpha linum* were low in lead content.

Titanium

Marked differences were shown in the concentrations of this metal among the thirteen species studied. High concentrations of titanium were determined in *Hypnea musciformis*, *Padina boryana*, *Cystoseira myrica* and *Halimeda opuntia*. In contrast, *Laurencia obtusa* and *Chaetomorpha linum* were characterized by exceedingly low titanium levels (Table 1).

Generally, titanium concentrations were relatively high in the brown species (Table 2).

Vanadium

Padina boryana had the highest value of vanadium (2.96 ppm). Detectable amounts were also present in *Digenea simplex* and *Acanthophora najadiformis*. On the other hand, relatively low levels of vanadium were recorded in *Sargassum subrepandum* (0.11 ppm) and *Turbinaria triquetra* (0.16 ppm). In *Chaetomorpha linum*, however, vanadium was not detected (Table 1).

Discussion

The survey has, in general terms, indicated that the amount of heavy metals in all taxa varied considerably according to species and showed somewhat characteristic relation to division. The results summarised in Table 2 indicated that the green species were characterized by having the highest proportions of mercury, nickel and lead, while the brown species had high levels of aluminium, arsenic, titanium and vanadium.

Compared with other elements, silver amounts in all species studied fall within a narrow range of values. It is apparent that levels of silver were relatively constant for most of the thirteen species. Despite the marked differences in the morphological and anatomical structure which exist between the green algae: *Caulerpa racemosa* and *Cladophora heteronema*, the red algae: *Acanthophora najadiformis*, *Digenea simplex*, and *Hypnea musciformis* and the brown alga: *Cystoseira myrica*, they had similar quantities of silver. Furthermore, the level of silver was more or less comparable in the two brown algal species: *Turbinaria triquetra* and *Sargassum subrepandum*. Also, cadmium was found in low levels.

In contrast, the algae examined were characterized by high level of aluminium and mercury. It is clear from the literature that metal accumulation by a plant gives a better indication of the fraction of the metals in environment^[19,24]. There appears to be linear relationship between the logarithm of the level of zinc in plant and the logarithm of the level in the water for *Lemanea fluviatilis*^[33]. Consequently, the levels found in these algae reflect the high concentrations of these metals in the water

of the Red Sea at this region.

Lead as well as arsenic in the thirteen species were consistently found in moderate amounts (Table 2). Normal range of lead in plants was 0.5-3.0 mg/kg^[34].

Alga like *Halimeda opuntia* which accumulates the heavy metals (Ag, Cd, Co, Hg, Mo & Pb) largely from the water may prove helpful in designing practical systems for the removal of heavy metals from industrial effluents by encouraging the growth of plants^[35-36].

In addition, the results indicated that high proportions of aluminium and vanadium were notable in *Padina boryana* and those of arsenic, nickel and titanium in *Turbinaria triquetra*, *Chaetomorpha linum* and *Hypnea musciformis*, respectively.

Using the plant to accumulate heavy metals to monitor the levels of heavy metals in water have been used in recent years^[19,24&37]. Therefore any one of the above organisms, specially *Halimeda opuntia*, may be useful as a monitoring organism.

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مستويات المعادن الثقيلة في أنواع عديدة من طحالب البحر الأحمر بالمملكة العربية السعودية

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يتناول هذا البحث دراسة وجود كل من الفضة والألومنيوم والكاديوم والكوبلت والموليبدنوم والنيكل والرصاص والتيتانيوم والزنثيق والزرنيخ والفاناديوم في ثلاثة عشر نوعاً من الطحالب البحرية التابعة للأقسام الخضراء والبنية والحمراء بمنطقة الشُعبية .

وقد تبين من نتائج هذا البحث أن كمية المعادن الثقيلة تتفاوت كثيراً تبعاً لنوع الطحلب ، وإن كان هناك ارتباط بين بعض التركيزات والأقسام الطحلبية عامة .

انفردت الأنواع الخضراء باحتوائها على أعلى التركيزات لكل من الزنثيق والنيكل والرصاص . كما لوحظ أن أعلى تركيزات الألومنيوم والزرنيخ والتيتانيوم والفاناديوم قد وجدت في الأنواع البنية . وقد احتوت الأنواع الحمراء بصفة عامة على كميات متوسطة لمعظم المعادن التي درست .

تميّز الطحلب الأخضر *Halimeda opuntia* باحتوائه على تركيزات عالية لستة من تلك المعادن . وبذلك يعتبر هذا الطحلب أفضل تلك الأنواع كمصدر لهذه المعادن . ومن هنا يمكن استخدامه ككاشف لها في المياه .

وقد دلت هذه الدراسة على أن أقل المعادن تركيزاً في الطحالب المدروسة هما الفضة والكاديوم ، في حين وجدت نسب عالية من الألومنيوم والزنثيق .

* العنوان الدائم : قسم النبات ، كلية العلوم ، جامعة المنصورة ، المنصورة ، جمهورية مصر العربية