

Heavy Metals in Marine Algae of the Kuwait Coast

A.-H. Buo-Olayan, M. N. V. Subrahmanyam

Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969,
Safat, 13060 Kuwait, State of Kuwait

Received: 25 October 1995/Accepted: 10 May 1996

Marine algae are considered as important primary producers in the coastal region. Several marine algal species are being considered as raw material for various economically important products and this has resulted in their increasing demand. Marine algal species also have been suggested to be the indicators of pollution (Bryan and Hummerstone 1973; Melhus et al. 1978). Keeping in view the importance of marine algal species for direct or indirect human and cattle consumption, it is necessary to monitor the bioaccumulation of certain elements in these species.

Large quantities of seaweed are washed ashore along the Kuwait coast. Their wide distribution and abundance in this area could very well be used in assessing their bioaccumulating potential and contamination by heavy metals. The first published list of the marine algal flora of Kuwait was by Newton (1955 a). This was followed by another list of algae from Bahrain by the same author (Newton 1955b). Jones (1986) published a field guide of the sea shores of Kuwait and Arabian Gulf in which he listed the common species of algae. Al-Hasan & Jones (1989) reported the marine algal flora of the coasts of Kuwait, based on collections made over a period of three years. Phillips (1977) has advocated the use of macroalgae as indicator organisms for depicting the metal levels in a given milieu. Several investigators subsequently have shown that the use of marine algae as an indicator of heavy metals gives at least a qualitative picture of heavy metals contamination in the area of study (Bryan 1969; Fuge & James 1974; Haug et al. 1974; Shiber & Washburn 1978 ; Munda 1978 ; Sivalingham 1980 ; Kureishy 1991) covering a wide variety of macroalgae representing different geographical areas.

Information on the distribution of trace metals in coastal waters is essential to assess their accumulation levels in organisms and their possible transfer to the food chain (Subrahmanyam & Ananthalakshmikumari 1990). The build up of metal concentrations in coastal areas may affect the growth and development of algae, leading to a decrease in the productivity of the region (Davies 1978).

Correspondence to: A.-H. Buo-Olayan

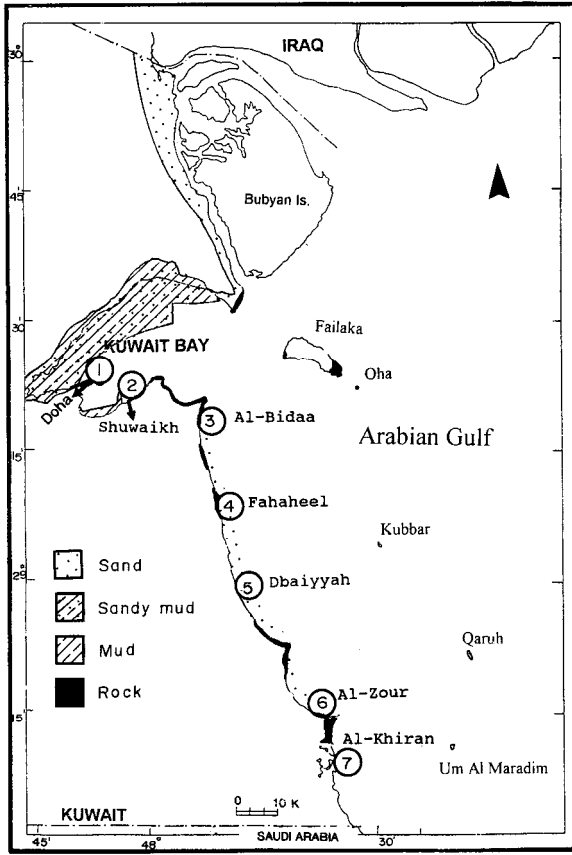


Figure 1. Sampling stations along the Kuwait coast.

Data on the concentrations of trace metals in Kuwait waters are meager. Anderline et al. (1982) and Bou-Olayan & Al-Sarawi (1993) have reported the high concentrations of metals in sediments and waters of the Kuwait coast. However, no report is available concerning algae. The present study was aimed at establishing the concentration levels of trace metals in marine algae of the Kuwait coast.

MATERIALS AND METHODS

A total of twenty-six algal samples was collected from seven different stations along the Kuwait coast (Fig.1). The algal species collected belonged to the Chlorophyta, Phaeophyta and Rhodophyta groups. Samples were washed with filtered seawater and finally with deionized water before drying at 65 °C. Coarse homogenization of each sample was done by crushing in a PVC pestle and mortar (particle size < 250 microns).

A dried algal sample of 0.125 g was weighed in a 50-ml Fisher brand disposable sterile centrifuge tube and wet ashed with 10% Aristar HNO₃, 1 % Aristar HCl and 1% Aristar HF acids for 48 hr. The sample was then diluted to 50 ml with deionized water and digested in an automatic microwave digestion system (Spectre-Prep-CEM). The digested sample solutions were analyzed by Perkin Elmer 5100 atomic absorption spectrophotometer. Flameless HGA-600 graphite furnace techniques equipped with deuterium background correction was used for the determination of Pb , Ni and V , while air-acetylene techniques were used for Cu , Cr , Fe ,Mn and Zn .Blanks were treated similarly.

The accuracy of the method was verified (10-replicates) using standard reference materials; oyster tissue (SRM-1566a) from the National Bureau of Standards. Recoveries were above 90% for the trace metals measured (Table 1). The reported results are the mean values of duplicate determinations and are expressed as µg/g dry weight (Table 2). Two-way analysis of variance (ANOVA) was used to determine the variations in 7 trace metals in the algal species and groups examined.

Table 1 Recovery values of heavy metal concentrations measured in certified reference material (oyster tissue; SRM - 1566a)

Metal	Certified values (µg/g)	Present study (µg/g)	Recovery (%)
Cu	66.3	65.1	98.6
Fe	539	516	91.6
Mn	12.3	12.41	95.7
Ni	2.25	2.21	100.5
Pb	0.371	0.362	98.2
V	4.68	4.56	97.4
Zn	830	823	99.1

RESULTS AND DISCUSSION

Analysis of 7 trace metals Cu, Fe , Mn , Ni , Pb , V and Zn in 26 marine algal species collected from different locations of the Kuwait coast (Table 2) are discussed below.

Station I (Doha): Five marine algal species were collected, of these three belonged to Chlorophyta and two to Phaeophyta. The concentration of Fe was the highest, followed by Zn , Cu, Mn , Ni, Pb,and V. At this station the

Table 2 . Trace metal concentrations in marine algae of the Kuwait coast ($\mu\text{g/g}$ dry weight).

Station	Species No.	Species	Cu	Fe	Mn	Ni	Pb	V	Z	n
I- Doha	1	<i>Enteromorpha intestinalis</i>	120	2065	055	07.9	02.2	05.5	425	
	2	<i>Ulva lactuca</i>	445	0595	020	02.9	00.7	06.0	130	
	3	<i>Cladophora loelothrix</i>	045	2910	075	07.0	03.2	06.0	200	
	4	<i>Padina boryana</i>	405	3500	190	13.3	01.8	06.2	515	
	5	<i>Colpomenia sps</i>	180	2060	045	09.5	02.7	05.5	185	
II- Shuwaikh	1	<i>Enteromorpha intestinalis</i>	105	2955	071	08.5	08.5	07.1	375	
	2	<i>Ulva lactuca</i>	250	1770	045	07.2	02.4	04.1	115	
	3	<i>Cladophoropsis sps</i>	150	2535	075	09.4	07.7	06.0	110	
III-Al-Bidda	1	<i>Enteromorpha flexuosa</i>	060	2725	063	06.5	09.1	10.0	201	
	2	<i>Ulva lactuca</i>	085	4810	075	12.8	04.5	11.1	275	
	3	<i>Padina gymnospora</i>	465	2500	135	7.25	02.8	07.1	510	
	4	<i>Colpomenia sinuosa</i>	145	3445	085	12.5	03.6	11.2	120	
	5	<i>Sargassum binderi</i>	150	0405	010	03.1	01.5	02.5	120	
IV- Fahaheel	1	<i>Padina tetrastromatica</i>	175	3000	145	09.1	02.2	03.2	406	
	2	<i>Sargassum binderi</i>	025	0595	010	00.1	00.1	01.5	015	
	3	<i>Sargassum angustifolium</i>	085	0751	030	03.5	07.1	04.5	375	
	4	<i>Sargassum asperifolium</i>	105	0340	025	01.2	02.3	02.5	550	
	5	<i>Spiridia filamentosa</i>	100	0435	015	02.2	02.1	03.0	090	
V- Dbaiyyah	1	<i>Padina boryana</i>	240	1055	050	03.0	00.7	03.1	285	
	2	<i>Sargassum binderi</i>	265	0125	005	01.1	00.5	02.5	170	
	3	<i>Sargassum asperifolium</i>	020	1750	055	10.2	06.6	04.2	150	
VI- Al-zour	1	<i>Sargassum binderi</i>	002	0310	022	01.7	01.4	01.0	125	
	2	<i>Padina boryana</i>	415	1290	080	01.7	02.1	01.9	192	
VII- Al-Khiran	1	<i>Padina boryana</i>	515	1885	120	07.9	02.0	04.5	610	
	2	<i>Colpomenia sinuosa</i>	003	1465	040	03.1	14.9	05.2	175	
	3	<i>Sargassum asperifolium</i>	105	0340	025	01.2	0.23	02.5	550	

Phaeophyta showed a tendency to concentrate trace metals in larger quantity than the Chlorophyta.

Station II (Shuwaikh): Three species of Chlorophyta were analyzed from this station for the trace metal concentrations. A high concentration was observed in case of Fe, which was followed by Zn, Cu, Mn, Ni, Pb and V .

Station III (Al-Bidaa): Five marine algal species were collected from this area, two of which were Chlorophyta and three Phaeophyta. The concentration of Fe was highest in all the algal species followed by Zn, Cu, Mn, Ni, V and Pb. At this station Chlorophyta had higher concentrations of Fe, Pb , and V, while the Phaeophyta accumulated more Cu, Mn, Ni and Zn.

Station IV (Fahaheel): Five species were collected from this station, four of which were Phaeophyta and one Rhodophyta . Maximum concentration was found to be of Fe, followed by Zn,Cu, Mn, Ni, Pb and V. Species belonging to Phaeophyta were observed with the highest concentrations of all these metals.

Station V (Dbaiyyah): Three species of Phaeophyta were analyzed from this station and Fe was present at the highest followed by Cu, Zn, Mn, Ni, V and Pb.

Station VI (A-Zour): In two species of Phaeophyta from this station, Fe was found in the highest concentration followed by Zn, Cu, Mn, Ni, Pb, and V .

Station VII (Al-Khiran): In three species of Phaeophyta, Fe concentrations were the highest followed by Zn, Cu, Mn, Ni, Pb and V.

Analysis of variance 'ANOVA' showed that for all the stations there was no statistical evidence to reject the null hypothesis (i.e., there is no variation in species / metals with respect to concentration of metals/algal species) at the 1% level of significance (Table 3). On the other hand, there was a significant variation in the concentration of metals, with respect to algal species at all the stations, except Al-Zour. The variation in metals was particularly highly significant at stations Shuwaikh, Doha and Al-Bidaa (Table 2), and the same was true for the Kuwait coast as a whole. It was observed also that the concentrations of trace metals did not vary with algal groups Chlorophyta, Phaeophyta and Rhodophyta. ANOVA for all stations of the Kuwait coast also showed no variation in the concentrations of elements with respect to algal groups.

The present results showed wide variation in the concentrations of all seven

trace metals analyzed in the twenty-six algal species. The accumulation of trace metals is stated to be unregulated in marine waters and the accumulation of metals in marine algae and seaweed is probably by the non-metabolic absorption or an ion-exchange process (Gutknecht 1965), and are retained by organisms by strong chemical bonds (Goldberg 1957).

The highest concentration of Cu (445 µg/g) was observed in *Ulva lactuca*, whereas the highest concentrations of Mn (190 µg/g) and Ni (13.25 µg/g) were observed in *Padina bolyana* from Doha (Table 3). Except for the Doha power station, there was no prominent means of causing water contamination and therefore the high metal concentration could not be explained. The extracellular polyanions like alginates have been shown to act as ion-exchange material (Myklested 1969). The maximum concentrations of Fe and Mn may have been due to the inflow of drainage along with other contaminants of the Kuwait coast.

Table 3. Area-wise variation in species and trace metals.

Station	Number of species collected	Number of metals analyzed	Variation in species	Variation in metals
I- Doha	5	7	**F= 1.0	*F=18.18
II- Shuwaikh	3	7	**F= 1.2	*F=42.66
III- Al-Bidaa	5	7	**F= 1.1	*F=13.90
IV- Fahaheel	5	7	**F= 1.07	*F= 3.75
V - Dbaiyyah	3	7	**F= 1.01	*F= 3.79
VI- Al-Zour	1	7	**F= 1.00	**F= 2.04
VII-Al-Khiran	3	7	**F= 1.03	*F= 5.50

* significant ** non significant

The concentrations of Zn and Pb were greater in the large multicellular algae *Padina boryana* and *Colpomenia sinuosa*, respectively, collected from Al-Khiran . This may possibly be attributed to a sewage outfall located in the area.

The present results revealed that the concentrations of trace metals in marine algae of the Kuwait coast are on the higher side as compared to the earlier report on Qatar coast (Kureishy 1991) in the Arabian Gulf region. The reasons for high concentrations may be due to ph, high temperature (Bryan 1976), salinity and other metal-binding nutrients in seawater (Sivalingham 1978). This may also be due to high water movement (Provasoli 1963) and recycling of the mineral elements after the decomposition of organisms in the seawater.

It is known that in minute quantities many trace metals are required for growth of marine algae (North et al. 1972). However, the results found here far exceed the values for other marine plants (Bowen 1966). The effect of trace metal pollution on marine algae along this coast was observed at Doha and Al-Khiran stations, perhaps due to the large quantities of domestic sewage, industrial waste and other types of pollutants that find their way into the nearby marine waters. The economically important multicellular brown algae are the most affected. Since marine algae are useful as primary producers in coastal waters (Mann 1973), their reduction due to pollution would pose a threat to the next link in the food chain.

Based on the present investigation, we can conclude, in general, that filamentous algae showed the ability to concentrate greater amounts of trace elements than foliaceous algae.

Acknowledgment. The authors wish to acknowledge the Research Management Unit of the Kuwait University for the Financial support under the Research Project No.SC-062.

REFERENCES

- Al-Hasan RH, Jones WE (1989) Marine algal flora and sea grasses of the coast of Kuwait. *J. of the University of Kuwait (Science)* 16:289-341
- Anderline VC, Mohammed OS, Zerba MA, Fowler SW, Mirimand P (1982) Trace metals in marine sediments of Kuwait. *Bull Environ Contam Toxicol* 28:75-80
- Bowen HJM (1966) Trace metals in biochemistry. Academic Press Inc. London 241
- Bryan GW (1969) The absorption of zinc and other metals by the brown seaweed *Laminaria digitata*. *J Mar Biol Assoc UK* 49: 225-243
- Bryan GW , Hummerstone LG (1973) Brown seaweeds as indicators of heavy metals in estuaries in south west England. *J Mar Biol Assoc UK* 53:705-720
- Bou-Olayan AH , Al-Sarawi M (1993) Inorganic and organic pollutant measurements at the Kuwait waterfront project. *Wat Air Soil Pollut* 69:301-308
- Davies AG (1978) Pollution studies with marine plankton II.Heavy metals. *Adv Mar Biol* 15: 381-508
- Fuge R, James KH (1974) Trace metal concentrations in *Fucus* from the Bristol Channel. *Mar Pollut Bull* 5: 9-12
- Goldberg ED (1957) Biochemistry of trace metals. *Geol Soc Amer Memoir* 67: 345-356

- Gutknecht J (1965) Uptake and retention of Cesium-137 and Zinc-65 by seaweeds. *Limnol Oceanogr* 10:58-66
- Haug A, Melson S, Omang S (1974) Estimation of heavy metal pollution in two Norwegian Fjords areas by analysis of the brown algae *Ascophyllum nodosum*. *Environ Pollut* 7: 179-192
- Jones DA (1986) A field guide to the sea shores of Kuwait and the inside Arabian Gulf. University of Kuwait. 192 pp
- Kureishy TWA (1991) Heavy metals in algae around the coast of Qatar. *Mar Pollut Bull* 22: 414-416
- Mann KH (1973) Seaweeds: Their productivity and strategy of growth. *Science* 182: 975-981
- Melhus A , Seip KL, Seip HM, Mykkested S (1978) A preliminary study of the use of benthic algae as biological indicators of heavy metal pollution in Sorfjorden, Norway. *Environ Pollut* 15: 101-107
- Mykkested S (1969) Ion-exchange properties of sulfated polysaccharides in brown algae. *Proc Int Seaw Symp* 6: 545-552
- Munda IM (1978) Trace metal concentrations in some Iceland seaweeds. *Bot Mar* 21: 261-262
- Newton LM (1955a) The marine algae of Kuwait. In: Dickson V (ed). *The Wild Flowers of Kuwait and Bahrain* , 100-102 . George Allen & Unwin, London
- Newton LM (1955b) The marine algae of Bahrain. In: Dickson V (ed). *The Wild Flowers of Kuwait and Bahrain*, 141-144. George Allen & Unwin, London
- North WJ, Stephens GC, North BB (1972) Marine algae and their relation to pollution problems. In: Ruivo M (ed) *Marine Pollution and Sea Life* FAO Publication, London
- Phillips DJH (1977) The use of biological indicator organisms to monitor trace metal pollution in marine and estuarine environments - a review. *Environ Pollut* 13:281-318.
- Provasoli L (1963) Growing marine seaweeds. *Proc Intl Seaw Symp* 4:9-17
- Sivalingam PM (1978) Bio-deposited trace metals and mineral content of some tropical marine algae. *Bot Mar* 21: 327-330
- Sivalingam PM (1980) Mercury concentration in tropical algal species of the island of Penang, Malasia. *Mar Pollut Bull* 11: 106-107
- Shiber J, Washburn E (1978) Lead mercury and certain nutrient element in *Ulva lactuca* (Linn) from Ras Beirut, Lebanon. *Hydrobiol* 61: 187-192
- Subrahmanyam MNV , Ananthalakshmikumari KVV (1990) Trace metals in water and phytoplankton of Visakhapatnam harbour area, east coast of India. *Indian J Mar Sci* 19:177-180