Pak. J. Sci. Ind. Res. 2005 **48**(3) 195-201

Variations of Heavy Metals in Green Seaweeds from Karachi Coast of Pakistan

Rashida Qari*[a] and Sardar Alam Siddiqui[b]

[a]Centre of Excellence in Marine Biology, University of Karachi-75270, Pakistan

[b]Department of Chemistry, University of Karachi-75270, Pakistan

(received December 20, 2003; revised January 7, 2005; accepted January 18, 2005)

Abstract. The main purpose of this study was to quantify heavy metals (Mg, Fe, Mn, Cu, Ni, Zn, Cr, Pb, Co, Cd) in different species of green seaweeds from the coastal areas of Karachi, Pakistan, to determine the seasonal and annual variability in the concentrations of these metals, and to assess the interralationship of their concentration in the green seaweeds. Metal concentrations in the green seaweeds showed significant variations. The accumulation of metals by green seaweed was the highest at Buleji coast, while the species of *Caulerpa* contained the highest concentrations of different metals as compared with other green seaweeds. Interannual variations were also noted in the accumulation of metal concentrations in the seaweeds. The study shows that the seaweeds, although exposed to metal pollutants, were still within the safe limits and can be commercially utilized.

Keywords: heavy metals, green seaweeds, metal pollution, Karachi coast

Introduction

The Karachi coast in Pakistan has a large number of green algal species, many of which occur in great abundance (Qari, 2002; Qari and Qasim ,1988). Algae are the primary producers, which possess a great ability to accumulate heavy metals (Zingde *et al.,* 1976). The metals that enter the marine environment are known to be taken up and accumulated by marine algae and animals (Seeliger and Edwards, 1977; Bradfield *et al.,* 1976; Boyden, 1975; Horne, 1969). Seaweeds selectively adsorb trace elements (Mn, Cd, Co, Cr, Cu, Fe, Ni, Pb, Zn) from the seawater, which are accumulated in their thalli. The accumulated elements vary from species to species. Seaweeds generally contain Mg and Fe in large quantities, up to 15-25% of their dry weight (Qasim, 1980). The inorganic contents appear to be very high when compared with 5-6% in hay and nearly 4% in cereals (Rizvi *et al.,* 2000; Dawes, 1974; Boney, 1969). Basson and Abbas (1992) reported the elemental composition (Mg, Fe, Cd, Cr, Co, Mn, Ni) of four green algae from the Bahrain coastline (Arabian Gulf). The trace metal distribution in green seaweeds of the Indian Ocean has also been well documented by Rao (1992), Agadi *et al.* (1978), and Zingde *et al.* (1976). Along the Indian coastline, Parekh *et al.* (1977) reported the Mg content in green seaweeds at Saurashtra coast, and Rajendran *et al.* (1993) studied metal concentrations (Mn, Fe, Cu, Zn) in *Chaetomorpha antennina* and *Enteromorpha compressa* from Tamil Nadu. Ho (1990) assessed suitability of *Ulva lactuca* as a bioindicator of trace metals and reported the levels of Mn, Fe, Ni, Cu, Zn, Cd and Pb in *Ulva lactuca* from the Island of Hong Kong. Ho (1987) reported levels of seven metals in five intertidal green algae, besides other groups, in the Hong Kong waters. Wong *et al.* (1979) investigated metal contents of the two marine green algae found on the iron ore tailings of Hong Kong Island. Shiber and Washburn (1978) studied Pb in *Ulva lactuca* from Ras Beirut, Lebanon, and Shiber (1980) also studied the seasonal variation of trace metals (Pb, Cd, Cu, Ni, Fe, Zn, Cr) in *Halimeda tuna* and *Ulva lactuca* from Ras Beirut, Lebanon.

The present study was undertaken to gather information to serve as the baseline values of heavy metals in green seaweeds found along the coast of Karachi, Pakistan. The main purpose of this study was to quantify heavy metals (Mg, Fe, Mn, Cu, Ni, Zn, Cr, Pb, Co, Cd) in the green seaweeds present at Buleji, Paradise Point and Nathia Gali of Karachi coast, to determine the seasonal and annual variability in the concentrations of these metals, and to assess the interrelationship of concentrations of heavy metals in the seaweeds at the three different sites along the coast of Karachi.

Materials and Methods

The seaweeds were sampled randomly from the exposed shores of Buleji, Paradise Point, and Nathia Gali at low tide (Fig. 1). A total of forty species of algae were collected from the three locations, Buleji (16), Paradise Point (10), and Nathia Gali (14) over the period of three years (January, 1989 to December, 1991). Buleji is a triangular rocky platform of a wave beaten shore with slightly uneven profile and protruding out

*Author for correspondence; E-mail: rqari2002@yahoo.com

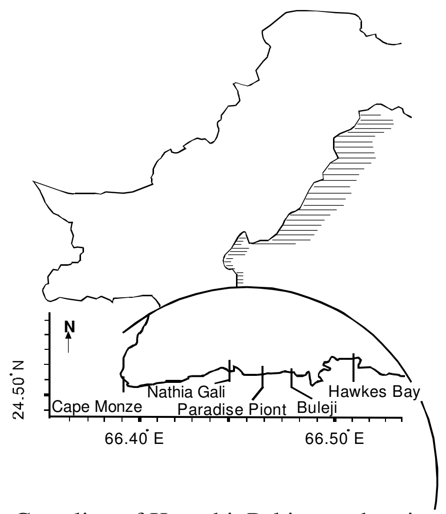

Fig. 1. Coastline of Karachi, Pakistan, showing the green seaweed collection sites, namely, Buleji, Paradise Point and Nathia Gali.

in the open Arabian Sea, whereas the shore of Paradise Point is of three types, namely, rocky, boulders and sandy. The Nathia Gali beach starts with pale yellow coloured rocks at its front, the main boulder like forms are exposed to the surface, which slope steep towards the sea. All plants were carefully cleaned and dried at 70 °C to constant weight. Digestion of samples was carried out as described by Denton and Burdon-Jones (1986). One g of the sample (whole plant) was digested with 4 ml conc HNO_3 and 2 ml conc $HClO_4$ in a 50 ml beaker at 80 °C on a hotplate. After digestion and evaporation of acids, metal salts were redissolved in metal-free deionized water. In the digested samples of seaweeds, concentrations of Mg, Fe, Mn, Cu, Ni, Zn, Cr, Pb, Co and Cd were determined by atomic absorption spectrophotometer (Varian AA-20).

Results and Discussion

For the seasonal and annual variations in heavy metals, the seaweeds studied were members of the Family Chlorophyceae (green algae). A total of seventeen species of seaweeds, belonging to nine genera, were collected from the three sites, Buleji (16), Paradise Point (10), and Nathia Gali (14), between the period of January 1989 to December 1991. Concentrations of ten metals, namely, Mg, Fe, Mn, Cu, Ni, Zn, Cr, Pb, Co, Cd were determined in each species. The values of each reported metal are the mean of three separate replicate observations, expressed as µg/g, except Mg as mg/g dry weight.

The data presented in Tables 1, 2, 3 show the mean concentrations of the ten metals in all the species of seaweeds that were collected from Buleji, Paradise Point and Nathia Gali, respectively, whereas the summary showing variability and confidence intervals of metals in the green seaweeds at Buleji, Paradise Point and Nathia Gali are presented in Tables 4, 5, 6, respectively. The data reveal high variability in the concentrations of the metals studied in the seaweeds along the Karachi coast, within and between seaweed species, sampling sites and the collection time. The accumulation of metals by seaweed species was high at Buleji coast. The mean concentrations of Mg (5.5 mg/g), Cu (0.104 µg/g), Zn (0.2 µg/g), Cr (0.097 µg/g) and Co (0.03 µg/g) were high at Buleji, as compared with Paradise Point and Nathia Gali (Tables 4-6). At Paradise Point, the accumulation of Mn (0.192 µg/g) and Pb (0.097 µg/g), and at Nathia Gali of Fe (2.56 µg/g), Ni (0.046 µg/g) and Cd (0.014 µg/g) were high as compared with the Buleji coast. The metal distribution pattern in decreasing order was Mg > Fe > Mn > Cu > Zn > Cr > Pb > Ni > Cd > Co. The concentrations of metals were found to vary from 0.047-15.03 mg/g for Mg, 0.005-14 µg/g for Fe, 0.013-1.7 µg/g for Mn, 0.004-1.2 µg/g for Cu, 0.004-0.21 µg/g for Ni, 0.004-0.54 µg/g for Zn, 0.005-0.46 µg/g for Cr, 0.01-0.28 µg/g for Pb, 0.003-0.047 µg/g for Co and 0.001-0.12 µg/g for Cd at the three sites studied.

The Mg and Fe concentrations in green seaweed were high in pre- and post-monsoon and low during the monsoon period. The concentration of Mg and Fe increased from January to April and decreased till August and then increased again. The concentrations of Cu were approximately the same throughout the year except in June when their concentration was high. Cobalt concentration also showed similar pattern, which remained the same throughout the year, except in April and May when the concentrations were higher.

Interannual variations were also noted: Mg and Fe were high during the year 1991 and low during 1990; Mn concentration increased from 1989 to1991; Cu, Ni, Zn, Cr, and Cd concentrations were low during the year 1989 and 1991 but high during 1990. Only small variations were noated in the concentration of Zn and Cr during the three years of study; and Pb and Co concentrations were high during the year 1989, as compared with 1990 and 1991.

Metal concentrations in green seaweeds also showed variation between different sites along the Karachi coast: Mg, Cu, Cr, Pb were high at the Buleji coast; Co was the only one that was high at the Paradise Point; whereas Fe, Mn, Ni, Zn, Cd were high at the Nathia Gali coast. The completely randomized design with nested treatments analysis of variance (ANOVA) model were used to test the significant differences of heavy metals in seaweeds between sites (Buleji, Paradise Point and Nathia Gali), years and months. These results showed that there were highly significant variations (F-statistics) between sites and months, respectively, for Mg (F =

Table 1. Annual mean (± standard deviation of the mean) and the range of heavy metals concentration in green seaweeds from the Buleji coast, Karachi, Pakistan (µg/g, except for Mg in mg/g)

Name of species	Mg	Fe	Mn	Cu	Ni	Zn	Cr	Pb	Co	Cd
Bryopsis harveyana	8.58±0.98	6.365±2.79	0.408±0.025	0.039±0.004	0.02±0.001	0.024±0.02	0.216±0.139	0.113±0.046	0.04±0.001	0.011±0.003
Caulerpa manorensis±	3.891±1.01	1.886±1.15	0.199±0.089	0.024±0.017	0.026±0.015	0.036±0.009	0.062±0.033	0.055±0.039	0.056±0.024	0.011±0.001
C. peltata	3.32±0.67	1.88±0.56	0.202±0.21	0.01±0.103	0.074±0.00.	02±0.005	0.022±0.003	0.046±0.002	0.017±0.001	0.04±0.000
C. racemosa	5.475±1.97	1.568±0.79	0.174±0.04	0.046±0.026	0.031±0.013	0.049±0.036	0.15±0.111	0.115±0.074	0.046±0.038	0.014±0.01
C. scalpelliformis	0.07±0.03	0.914±0.18	0.109±0.014	1.022±0.095	0.014±0.007	0.119±0.012	0.014±0.005	0.02±0.001	0.012±0.005	0.006±0.003
C. sertularioides	2.3±0.9	1.06±0.04	0.61±0.2	0.02±0.007	0.015±0.0	0.06±0.02	0.02±0.001	0.026±0.003	0.011±0.002	0.004±0.001
C. taxifolia	9.18±2.63	2.177±0.723	0.235±0.115	0.105±0.068	0.098±0.082	0.157±0.152	0.026±0.03	0.059±0.028	0.026±0.019	0.006±0.001
Chaetomorpha antennina	6.93±2.98	0.939±0.124	0.041±0.006	0.105±0.01	0.04±0.004	0.042±0.01	0.037±0.009	0.116±0.022	0.024±0.017	0.011±0.001
Codium iyengarii	8.269±3.35	1.12±0.77	0.105±0.048	0.025±0.016	0.035±0.014	0.028±0.02	0.058±0.103	0.064±0.039	0.025±0.015	0.023±0.018
C. shameelii	3.3±1.85	2.4±0.21	0.022±0.003	0.011±0.001	0.04±0.0	0.05±0.006	0.04±0.000	0.13±0.04	0.012±0.001	0.007±0.001
Ulva anandii	2.43±0.12	2.33±0.22	0.04±0.002	0.11±0.021	0.04±0.0	0.04±0.002	0.21±0.01	0.04±0.002	0.02±0.001	0.04±0.003
U. fasciata	4.688±1.37	1.978±1.51	0.162±0.17	0.072±0.041	0.038±0.022	0.075±0.071	0.04±0.035	0.062±0.027	0.010±0.006	0.008±0.006
U. lactuca	*2.565*±0.44	3.79±0.59	0.053±0.011	0.04±0.004	0.042±0.004	0.021±0.003	0.013±0.003	0.096±0.025	0.03±0.012	0.022±0.007
Valoniopsis pachynema	7.023±3.85	6.183±3.54	0.305±0.42	0.018±0.015	0.045±0.022	0.065±0.029	0.049±0.023	0.074±0.032	0.039±0.017	0.015±0.008

Table 2. Annual mean (± standard deviation of the mean) and the range of heavy metals concentration in green seaweeds from the Paradise Point coast, Karachi, Pakistan (µg/g, except for Mg in mg/g)

Name of species	Mg	Fe	Mn	Cu	Ni	Zn	Cr	Pb	Co	Cd
Bryopsis harveyana	3.77±1.751.	639±0.84	0.134±0.0463	0.054±0.023	0.042±0.007	0.039±0.004	0.033±0.009	0.164±0.09	0.511±0.584	0.01±0.001
Caulerpa manorensis	1.715±0.73	4.315±0.34	0.032±0.012	0.14±0.099	0.006±0.001	0.011±0.001	0.11±0.0	0.043±0.00	40.018±0.04	0.01±0.0
C. racemosa	4.105±0.1	0.02±0.00	0.04±0.006	0.081±0.022	0.2±0.015	0.022±0.003	0.03±0.00	0.04±0.0	0.016±0.006	0.006±0.001
C. scalpelliformis	1.49±1.23	1.229±0.56	0.092±0.107	0.045±0.041	0.032±0.01	0.026±0.027	0.0360.017	0.055±0.013	0.01±0.002	0.004±0.002
Chaetomorpha antennina	3.127±2.6	3.127±0.74	40.057±0.029	0.019±0.009	0.025±0.008	0.081±0.058	0.069±0.052	0.085±0.031	0.018±0.009	0.015±0.007
Codium iyengarii	2.142±0.92	2.142±0.82	0.085±0.074	0.041±0.027	0.02±0.011	0.033±0.019	0.018±0.015	0.083±0.058	0.016±0.009	0.009±0.008
C. shameelii	2.934±2.11	2.939±0.84	40.166±0.148	0.022±0.013	0.042±0.017	0.042±0.033	0.02±0.007	0.085±0.058	0.012±0.003	0.012±0.06
Enteromorpha compressa	1.095±0.2	1.095±0.6	0.113±0.069	0.047±0.05	0.052±0.026	0.03±0.005	0.053±0.017	0.053±0.032	0.01±0.003	0.008±0.025
Ulva fasciata	4.077±1.74	1.355±1.32	0.544±0.485	0.043±0.034	0.021±0.009	0.04±0.016	0.041±0.028	0.046±0.017	0.014±0.008	0.008±0.007

Table 3. Annual mean (± standard deviation of the mean) and the range of heavy metals concentration in green seaweeds from the Nathia Gali coast, Karachi, Pakistan (µg/g, except for Mg in mg/g)

Name of species	Mg	Fe	Mn	Cu	Ni	Zn	Cr	Pb	Co	Cd
Bryopsis harveyana	0.432±0.029	4.275±1.51	0.34±0.079	0.085±0.028	0.115±0.015	0.042±0.03	0.053±0.008	0.11±0.024	0.016±0.004	0.016±0.003
Caulerpa manorensis	0.82±0.005	2.78±0.61	0.05±0.001	0.11±0.003	0.13±0.002	0.04±0.0	0.033±0.002	0.04±0.002	0.031±0.00	0.021±0.006
C. peltata	3.639±2.78	4.056±1.84	0.078±0.041	0.063±0.005	0.137±0.015	0.076±0.035	0.026±0.007	0.047±0.008	0.034±0.017	0.01±0.002
C. racemosa	7.034±0.822	3.863±1.75	0.125±0.037	0.032±0.015	0.05±0.026	0.036±0.016	0.052±0.003	0.053±0.024	0.021±0.01	0.011±0.002
C. scalpelliformis	4.235±1.73	2.408±1.57	0.427±0.11	0.071±-0.011	0.033±0.011	0.088±0.041	0.027±0.01	0.083±0.037	0.018±0.004	0.025±0.003
C. taxifolia	8.43±0.56	1.9±0.004	0.23±0.003	0.18±0.002	0.025±0.003	0.054±0.004	0.01±0.00	0.061±0.002	0.01±0.007	0.006±0.002
Codium iyengarii	4.129±2.3	1.993±1.29	0.133±0.073	0.027±0.023	0.025±0.011	0.022±0.012	0.025±0.021	0.053±0.026	0.016±0.009	0.007±0.004
C. shameelii	1.754±0.91	1.88±0.51	0.188±0.05	0.023±0.017	0.0202±-0.009	0.018±0.008	0.035±0.014	0.04±0.038	0.016±0.112	0.006±0.003
Enteromorpha compressa	1.253±0.166	0.212±0.065	0.229±0.095	0.013±0.007	0.052±0.025	0.074±0.008	0.039±0.005	0.04±0.055	0.023±0.005	0.012±0.002
Halimeda tuna	5.311±2.58	2.8±0.72	0.127±0.048	0.046±0.03	0.025±0.018	0.066±0.042	0.038±0.003	0.054±0.063	0.02±0.006	0.017±0.002
Udotea indica	4.586±0.7	2.22±0.32	0.102±0.015	0.02±0.00	0.04±0.0108	0.023±0.005	0.031±0.001	0.133±0.028	0.011±0.00	0.012±0.001
Ulva fasciata	3.228±1.14	2.474±0.57	0.093±0.036	0.022±0.002	0.018±0.002	0.024±0.01	0.017±0.004	0.13±0.052	0.01±0.01	0.011±0.002
U. lactuca	2.625±0.11	2±0.0	0.11±0.00	0.02±0.00	0.013±0.002	0.02±0.0	0.02±0.00	0.12±0.004	0.011±0.003	0.011±0.00
Valoniopsis pachynema	1.084±0.11	6.238±2.81	0.7±0.25	0.048±0.017	0.042±0.007	0.118±0.052	0.036±0.029	0.042±0.00	0.021±0.00	0.011±0.005

63.47 and F = 2.01), Fe (F = 37.83 and F = 5.55), Mn (F = 4.29 and F = 3.91), Cu (F = 24.69 and F = 3.74), Ni (F = 8.57 and F = 5.97), and Cd (F = 19.15 and F = 7.28). Significant variations were found in-between months only for Co (F = 2.59). No particular correlation was found in-between metals studied in the seaweeds, except Zn and Cr (r^2 = 0.987) and Pb and Co (r^2 = 0.769) that showed positive significant correlation.

Among the metals studied, Mg, an essential element for nitrogen metabolism in algae, was found in high concentrations (0.047-15.03 mg/g) in all the species of seaweeds studied, in comperison with the other metals, whereas Co and Cd were found in very low concentrations than the other metals, which also showed less variation. It is commentable that only small variations in the Co and Cd levels were found among species, site and the collection time, indicating that probably no major source of these metals occurred in the Karachi coastal water.

The highest concentration of different metals found in the different algal species, at the different sites, are presented in Table 7. These observations indicate the extent of pollution at a particular site and preferential accumulation of a particular metal by different seaweed species. The species of *Caulerpa* contained high concentrations of different metals as compared with other green seaweed species. *Caulerpa taxifolia* had the highest concentration of Mg, Ni and Zn with the mean value of 9.18±2.63 mg/g, 0.098±0.082 µg/g and 0.157±0.152 µg/g, respectively, at the Buleji coast (Table 1), and Mg and Cu with the mean value of 8.43±0.56 mg/g and 0.18±0.002 µg/g, respectively, at the Nathia Gali coast (Table 2). *Caulerpa sertularioides* showed high concentration of Mn with the mean value of 0.61±0.2 µg/g at Buleji (Table 1). *Caulerpa scalpelliformis* contained high concentration of Cu with the mean value of 1.022±0.095 µg/g at Buleji and Cd with the mean value of 0.025±0.003 µg/g at Nathia Gali (Tables 1, 3, respectively). *Caulerpa manorensis* showed high concentration of Co with the mean value of 0.056±0.024 µg/g at Buleji and Cu, Fe and Cr with the mean value of 0.14±0.099 µg /g, 4.315±0.34 µg/g and 0.11±0.0 µg/g, respectively, at Paradise Point (Tables 1, 2, respectively). *Caulerpa peltata* showed high concentration of Cd with the mean value of 0.04±0.00 µg/g at Buleji, and Ni and Co with the mean value of 0.137±0.015 µg/g and 0.034±0.017 µg/g, respectively, at Nathia Gali (Tables 1, 3, respectively). *Caulerpa racemosa* showed high concentration of Ni with the mean value of 0.2±0.015 µg/g at Paradise Point (Table 2). In *Bryopsis harveyana,* the concentration of Fe and Cr were high with the mean value of 6.365±2.79 µg/g and 0.216±0.139 µg/g at Buleji coast, Co with the mean value of 0.511±0.584 µg/g at Paradise Point, and Cr with the mean value of 0.053±0.00 µg/g at Nathia Gali (Tables 1, 2, 3). *Enteromorpha compressa* and *Udotea indica* had the highest concentra-

Table 4. Variability and confidence intervals (Ci) of metals in green seaweeds for the Buleji coast, Karachi, Pakistan (µg/g, except for Mg in mg/g)

Metal	Mean	Sd	Se (mean)	Ci (95%)
Mg	5.500	1.164	0.194	(5.106, 5.893)
Fe	2.023	0.927	0.154	(1.709, 2.337)
Mn	0.154	0.042	0.007	(0.140, 0.168)
Cu	0.104	0.087	0.015	(0.074, 0.133)
Ni	0.040	0.010	0.002	(0.036, 0.043)
Zn	0.200	0.851	0.142	(-0.088,0.488)
Cr	0.097	0.244	0.041	(0.014, 0.179)
Pb	0.079	0.019	0.003	(0.072, 0.085)
Co	0.030	0.016	0.003	(0.024, 0.035)
Cd	0.013	0.006	0.001	(0.011, 0.015)

Sd: standard deviation; Se: standard error

Table 5. Variability and confidence intervals (Ci) of metals in green seaweeds for the Paradise Point coast, Karachi, Pakistan (µg/g except for Mg in mg/g)

Metal	Mean	Sd	Se (mean)	Ci (95%)
Mg	3.044	0.677	0.118	(2.804, 3.284)
Fe	1.366	0.169	0.029	(1.306, 1.425)
Mn	0.192	0.098	0.017	(0.157, 0.227)
Cu	0.037	0.014	0.002	(0.032, 0.041)
Ni	0.032	0.007	0.001	(0.029, 0.034)
Zn	0.037	0.011	0.002	(0.033, 0.041)
Cr	0.036	0.010	0.002	(0.032, 0.039)
Pb	0.097	0.155	0.027	(0.042, 0.152)
Co	0.024	0.038	0.007	(0.010, 0.037)
Cd	0.009	0.003	0.001	(0.008, 0.010)

Sd: standard deviation; Se: standard error

Table 6. Variability and confidence intervals (Ci) of metals in green seaweeds for the Nathia Gali coast Karachi, Pakistan (µg/g, except for Mg in mg/g)

Metal	Mean	Sd	Se (mean)	Ci (95 %)
Mg	3.448	1.179	0.197	(3.049, 3.847)
Fe	2.567	0.585	0.098	(2.368, 2.764)
Mn	0.177	0.070	0.012	(0.153, 0.200)
Cu	0.039	0.015	0.002	(0.033, 0.043)
Ni	0.046	0.021	0.003	(0.039, 0.053)
Zn	0.057	0.029	0.005	(0.046, 0.066)
Cr	0.041	0.020	0.003	(0.034, 0.047)
pb	0.076	0.020	0.003	(0.068, 0.082)
Co	0.019	0.004	0.001	(0.017, 0.020)
Cd	0.014	0.005	0.001	(0.012, 0.015)

Sd: standard deviation; Se: standard error tions of Pb (0.133±0.025 µg/g) at Buleji, and (0.133±0.028 µg/g) at Nathia Gali (Tables 1, 3, respectively). The highest concentration of Mn with the mean value of 0.544±0.48 µg/g were found in *Ulva fasciata* at Paradise Point (Table 2). *Valoniopsis pachynema* showed the high concentrations of Mg, Pb and Cd with the mean value of 8.72±1.34 µg/g, 0.22±0.003 µg/g and 0.052±0.004 µg/g, respectively, at Paradise Point, whereas Mn, Fe and Zn with the mean value of 0.7±0.25 µg/g, 6.238±2.81 µg/g and 0.118±0.052 µg/g, respectively, at Nathia Gali (Tables 2, 3). *Chaetomorpha antennina* showed the high concentrations of Zn with the mean value of 0.081±0.058 µg/g at Paradise Point (Table 2).

The Mg concentrations in the present study were the same in *Bryopsis harveyana*, *Caulerpa racemosa*, *C. scalpelliformis, Udotea indica, Ulva fasciata* and *U. lactuca,* when compared with the concentrations of the same species of Saurashtra coast (Parekh *et al.,* 1977). In *Caulerpa peltata, Codium iyengarii, Enteromorpha compressa* and *Ulva fasciata* the concentrations of Mn, Cu, Ni, Zn, Fe, Pb and Co obtained in the present study were lower when compared with the study done in Goa coast, India (Agadi *et al.,* 1978). The values obtained in the present study for Cu and Zn were also low, and for Mg, Pb and Fe were similar to *U. lactuca* when compared with the previous study done in Ras Beirut, Lebanon (Shiber and Washburn, 1978). The values for metals Cu, Ni, Zn, Fe, Cr, Pb and Cd were low as compared with the previous study conducted for the species *Halimeda tuna*, collected from different sites of Beirut, Lebanon (Shiber, 1980). However, the concentrations for metals, Cu, Ni, Zn, Pb and Cd, observed in the current investigation were lower than the values found in Great Barrier Reef, Australia for the *Caulerpa racemosa*, *C. taxifolia* and *Udotea* species (Denton and Burdon-Jones, 1986). The concentrations for Fe, Mn, Cu, Ni, Zn, Cr, Pb and Cd were also low in *C. antennina* and *Enteromorpha* when compared with the work of Wong *et al.* (1979) and Ho (1990; 1987), carried out at Hong Kong for the same species. The concentrations obtained in the present study for Mn, Cu, Zn and Fe content were very low when compared with the previous study done in the Gulf of Manner, Bay of Bengal, for the species *C. antennina*, *Enteromorpha* and *U. lactuca* (Ganesan *et al.,* 1991). The concentrations obtained for Mn, Cu, Zn, Fe, Cr, Pb, Co and Cd were also lower in the present study as compared with the local species of *Chaetomorpha* in the Black Sea (Guven *et al.,* 1992). The concentrations for Mn, Cu, Zn and Fe were low when compared with the study conducted in Tamil Nadu coast of India (Rajendran *et al.,*1993) for the same species of *Chaetomorpha,* and *Enteromorpha*. The present results for *Ulva fasciata* for Cu, Zn, Cr, Pb, Co and Cd were lower than the previous results reported by Drude de Lacerda *et al.* (1985), who studied the same species in different creeks of Brazil. The present results for metals Mn, Cu, Ni, Zn, Pb, Fe, Cr, Co and Cd in *Caulerpa, Enteromorpha, Ulva fasciata* and *Valoniopsis pachynema* gave low values when compared with the previous study done in Batu Ferringhi, Malaysia (Sivalingam, 1978), Izmir, Turkey (Turkan *et al.,* 1989), and Northern Chile (Vasquez and Guerra, 1996). Rao (1992) reported high concentrations of Mg, Cr, Mn, Fe, Cu, Ni, Co, Zn, Cd and Pb for total marine algae from the Indian coast as compared with the present study. A trend in concentration of metals Mg > Fe > Mn, Zn > Cu was found in most of the species of the seaweeds in the present study, which was also observed along the East and West Coast of India (Rajendran *et al.,* 1993).

The concentrations of Mg and Fe metals observed in the present study for *C. racemosa, C. scalpelliformis, C. taxifolia, Codium iyengarii* and *U. lactuca* were almost the same when compared with a previous study conducted at the Karachi

Table 7. List of species that accumulated highest concentrations of different heavy metals at the three different study sites along Karachi coast, Pakistan

	Buleji	Paradise Point	Nathia Gali
Mg	*Caulerpa taxifolia*	*Valoniopsis pachynema*	*Caulerpa taxifolia*
Fe	*Bryopsis harveyana*	*Caulerpa manorensis*	*Valoniopsis pachynema*
Mn	*Caulerpa sertularioides*	*Ulva fasciata*	*Valoniopsis pachynema*
Cu	*Caulerpa scalpelliformis*	*Caulerpa manorensis*	*Caulerpa taxifolia*
Ni	*Caulerpa taxifolia*	*Caulerpa racemosa*	*Caulerpa peltata*
Zn	*Caulerpa taxifolia*	*Chaetomorpha antennina*	*Valoniopsis pachynema*
Cr	*Bryopsis harveyana*	*Caulerpa manorensis*	*Bryopsis harveyana*
Pb	*Enteromorpha compressa*	*Valoniopsis pachynema*	*Udotea indica*
Co	*Caulerpa manorensis*	*Bryopsis harveyana*	*Caulerpa peltata*
Cd	*Caulerpa peltata* and *Ulva fasciata*	*Valoniopsis pachynema*	*Caulerpa scalpelliformis*

coast (Qasim ,1980). In the present work, Fe, Cd, Cr, Co, Mn and Ni concentrations were low as compared with the local species of *Chaetomorpha*, *Enteromorpha* and *Ulva lactuca* at the Bahrain coastal area, Arabian Gulf (Basson and Abbas, 1992). The present values of Mg, Zn, Pb, Fe, Cd, Co, Cr and Cu were also low in *C. racemosa, C. scalpelliformis, C. taxifolia* and *U. lactuca* when compared with the results obtained by Rizvi *et al.* (2000) on the same species of Karachi coast.

In general, higher metal concentrations were found in the pre- and post-monsoon seasons, which was also true for seaweed biomass. However, some species of seaweeds were not collected during the summer monsoon period (Qari, 2002). Different metals showed high concentrations and a variable distribution in seaweed species. The causes for the variations seem to lie in the variation of metal concentrations in the seawater due to the direct discharge of industrial and domestic wastes, along the coast, by Layari River input and the river-borne trace metals, and higher terrestrial inputs caused by increased summer rainfall with a consequent increase in suspended particles with adsorbed metals (Qari and Siddiqui, 2004; Rizvi *et al.,* 1988). It is estimated that about 37,000 tonnes of industrial waste is being dumped through the two main rivers, viz., Layari and Malir, into the coastal environment of Karachi every year (Saleem *et al*., 1999). The influx of the discharged effluents increases most of the pollutants because these effluents are mostly in the form of total dissolved solids (131,000 metric tonnes), organic matter (16,000 metric tonnes), fixed nitrogen (800 tonnes) and phosphates (900 tonnes) (Beg *et al*., 1975). High iron concentrations were encountered in all the seaweeds, as compared with other trace metals, except Mg. The high iron concentration is probably due to several factors, which include the established need of iron for the normal growth of marine plants, the ability of most algal species to biomagnify iron from the surrounding environment, and the contamination from industrial and other operations (Qari and Siddiqui, 2004; Eisler, 1981). Next to Fe, seaweeds bioaccumulated Mn the most, which is because seaweeds are better representatives of Mn in seawater than other organisms. High concentrations of Zn were found, since algae are known to readily concentrate Zn from the seawater (Qari and Siddiqui, 2004). Marine algae show a marked ability to accumulate copper from seawater and level of 200-300 mg/g have been recorded in species from different polluted areas of the world (Ho, 1988; Denton and Burdon-Jones, 1986; Bryan and Hummerstone, 1973). High concentrations of Cu and other metals in the coastal areas are believed to be elevated due to the discharge of considerable quantities of untreated and partially treated domestic and industrial wastes, the discharge of industrial coolant waters, and the harbour activities, such as dredging and cargo handling, the dumping of ship waste and other coastal activities (Qari and Siddiqui, 2004).

Conclusion

The results of present study clearly indicate that regular monitoring of the flora of coastal areas is required, and though trace metals are present yet they are considerably low in their ranges. It may be attributed to their dilution in their saline water environment. The dispersal of these pollutants appears to be not towards the western side due to the circulation pattern, i.e., clockwise circulation, especially during the south-west monsoon, high energy along the coastal areas that disperse the pollutants, and the long shore currents that move from the west to the east. A consideration of the aspects reported in the present study may help to select the species as pollution indicators for further assessment of the environmental health of our coastal areas.

Acknowledgement

The authors are grateful to Dr. Naureen Aziz Qureshi, Assistant Professor, Centre of Excellence in Marine Biology, University of Karachi, Karachi, Pakistan, for help in data analysis and Mr. M. Jawed for composing the manuscript.

References

Agadi, V. V., Bhosle, N.B., Untawale, A.G. 1978. Metal concentration in some seaweeds of Goa (India). *Bot. Mar.* **21:** 247-250.

Basson, P.W., Abbas, J.A. 1992. Elemental composition of some marine algae from the Bahrain coastline (Arabian Gulf). *Indian J. Mar. Sci.* **21:** 59-61.

Beg, M.A.A., Mahmood, S.N., Yousufzai, A.H.K. 1975. Industrial effluents, their nature and disposal in Karachi region. Part 1. Survey of the polluted Layari River. *Proc. Pakistan Acad. Sci.* **12:** 125-131.

Boney, A.D. 1969. *A Biology of Marine Algae,* pp. 1-216, Hutchinson Educational Ltd., London, UK.

Boyden, C. 1975. Distribution of some trace metals in Poole Harbour, Dorset. *Mar. Pollut. Bull.* **6:** 180-187.

Bradfield, R., Kingsbury, R., Rees, C. 1976. An assessment of the pollution of Cornish coastal waters. *Mar. Pollut. Bull.* **7:** 187-193.

Bryan, G.W., Hummerstone, L.G. 1973. Brown seaweeds as an indicator of heavy metals in estuaries in South-West England. *J. Mar. Biol. Ass.* **53:** 705-720.

Dawes, C.J. 1974. *Marine Algae of the West Coast of Florida,* pp. 1-201, University of Miami Press, Coral Gables, Florida, USA.

Denton, G.R.W., Burdon-Jones, S. 1986. Trace metals in algae from the Great Barrier Reef. *Mar. Pollut. Bull.* **17:** 98-107.

Drude de Lacerda, L., Teixeira, V. L., Davee Guimaraes, J. R.D. 1985. Seasonal variation of heavy metals in seaweeds from Conceicao de Jacarei (R.J.), Brazil. *Bot. Mar.* **28:** 339-343.

Eisler, R.L. 1981. *Trace Metal Concentration in Marine Organisms*, pp. 1-687, Pergamon Press, New York, USA.

Ganesan, M., Kannan, L., Rajendran, K., Govindasamy, C., Sampathkumar, P., Kannan, L . 1991. Trace metal distribution in seaweeds of the Gulf of Manner, Bay of Bengal. *Mar. Pollut. Bull.* **22:** 205-207.

Guven, K.C., Topcuoglu, S., Kut, D., Esen, N., Erenturk, N., Saygi, N., Cevher, E., Guvener, B., Ozturk, B. 1992. Metal uptake by Black Sea algae. *Bot. Mar.* **35:** 337-340.

Ho, Y.B. 1990. *Ulva lactuca* as bioindicator of metal contamination in intertidal waters in Hong Kong. *Hydrobiologia* **203:** 73-81.

Ho, Y.B. 1987. Metals in nineteen intertidal macroalgae in Hong Kong waters. *Mar. Pollut. Bull.* **18:** 564-466.

Horne, R.A. 1969. *Marine Chemistry,* pp. 1-568, John Wiley and Sons, Inc., NY, USA.

Qari, R. 2002. Studies of Biodeposited Trace Metals and Minerals in Marine Algae from Karachi Coast. *Ph.D. Thesis,* Centre of Excellence in Marine Biology, University of Karachi, Pakistan.

Qari, R., Qasim, R. 1988. Seasonal changes in the standing crops of intertidal seaweeds from the Karachi coast. In: *Proceedings Marine Science of the Arabian Sea,* M.F. Thompson, N.M. Tirmizi (eds.), pp. 449-456, American Institute of Biological Sciences, Washington D.C., USA.

Qari, R., Siddiqui, S.A. 2004. Heavy metal levels in coastal seawater of Paradise Point, Karachi. *J. Resources Ind. Environ. Geol.* **1:** 39-44.

Qasim, R. 1980. Chemical composition of seaweeds from Karachi coast. *Karachi Uni. J. Sci.* **8:** 135-139.

Parekh, R.G., Maru, L.V., Dave, M. J. 1977. Chemical composition of green seaweeds of Saurashtra coast. *Bot. Mar.* **20:** 359-362.

Rajendran, K., Sampathkumar, P., Govindasamy, C., Ganesan, M., Kannan, R., Kannan, L. 1993. Levels of trace metals (Mn, Fe, Cu and Zn) in some Indian seaweeds. *Mar. Pollut. Bull.* **26:** 283-285.

Rao, C.K. 1992. Elemental composition of Indian marine algae. A biogeochemical perspective. *Indian J. Mar. Sci.* **21:** 167-177.

Rizvi, M.A., Farooqui, S., Shameel, M. 2000. Bioactivity and elemental composition of certain seaweeds from Karachi coast. *Pakistan J. Mar. Biol.* **6:** 207-218.

Rizvi, S.H.N., Saleem, M., Baquer, J. 1988. Steel mill effluents: influence on the Bakran Creek environment. In: *Proceedings Marine Science of the Arabian Sea,* M.F. Thompson, N.M. Tirmizi (eds.), pp. 549-569, American Institute of Biological Sciences, Washington D.C., USA.

Saleem, M., Kazi ,G.M., Memon, M.Q. 1999. Heavy metal concentration in the fish and shellfish of Karachi harbour area. *Pakistan J. Mar. Biol.* **5:** 143-154.

Seeliger, U., Edwards, P. 1977. Correlation coefficients and concentration factors of copper and lead in seawater and benthic algae. *Mar. Pollut. Bull.* **8:** 16-19.

Shiber, J.G. 1980. Trace metals with seasonal considerations in coastal algae and molluscs from Beirut, Lebanon. *Hydrobiologia* **69:** 147-162.

Shiber, J.G., Washburn, E. 1978. Lead, mercury and certain nutrient elements in *Ulva lactuca* (Linnaeus) from Ras Beirut, Lebanon. *Hydrobiologia* **61:** 187-191.

Sivalingam, P.M. 1978. Biodeposited trace metal and minerals content studies of some tropical marine algae. *Bot. Mar.* **21:** 327-330.

Turkan, I., Ozturk, M., Sukatar, A. 1989. Heavy metal accumulation by the algae in the Bay of Izmir, Turkey. *Rev. Int. Oceanogr. Med. Tomes.* **93-94:** 771-76.

Vasquez, J.A., Guerra, N. 1996. The use of seaweeds as bioindicator of natural and anthropogenic contamination in northern Chile. *Hydrobiologia* **326/327:** 327-333.

Wong, M.H., Chan, K.Y., Kwan, S.H., Mo, C.F. 1979. Metal contents of the two marine algae found on iron ore tailings. *Mar. Pollut. Bull.* **10:** 56-59.

Zingde, M.D., Singbal, S.Y.S., Moraes, C.F., Reddy, C.V.G. 1976. Arsenic, copper, zinc and manganese in the marine flora and fauna of coastal and estuarine waters around G o a . *Indian J. Mar. Sci.* **5:** 212-217.